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.

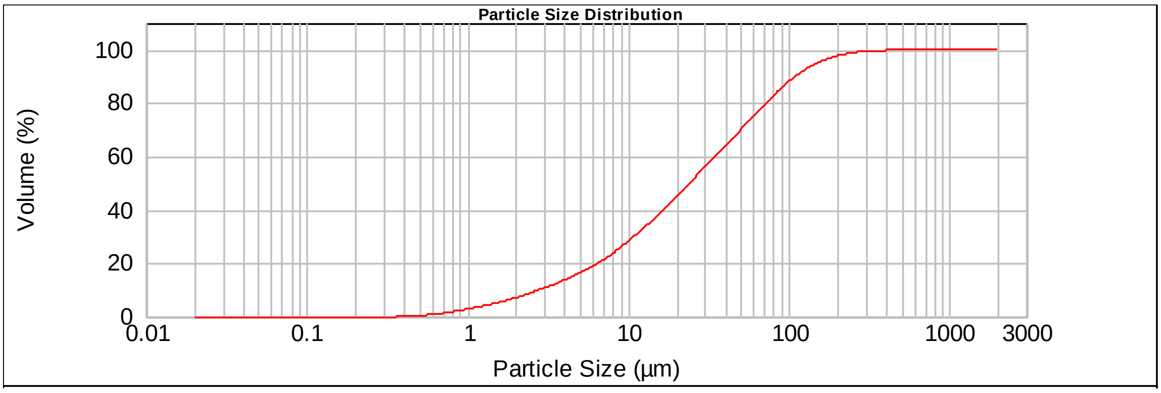


Figure 5.1.Typical particle size distribution of the Rosh Pinah composite used in this study.

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.

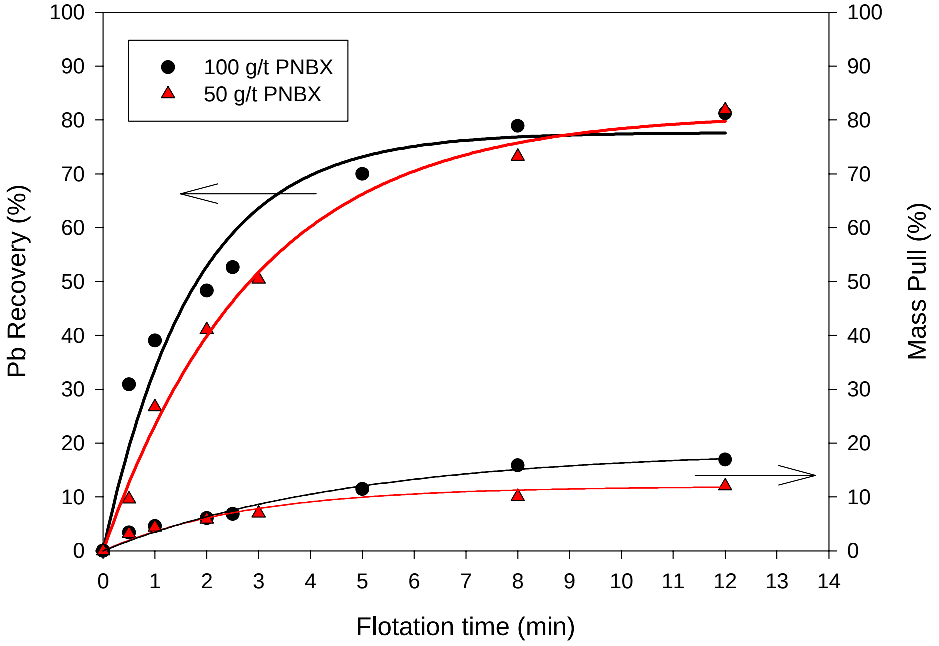


Figure 5.2. Flotation recovery of Pb and concentrate mass pull for two PNBX dosages at pH 8.5. Solid lines represent fitted curves.

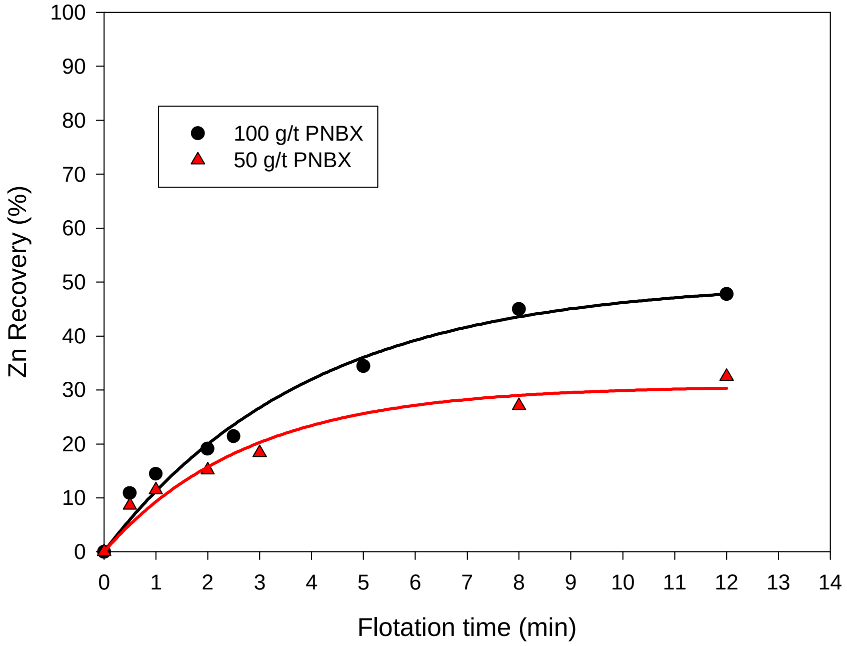


Figure 5.3. Flotation recovery of Zn in the lead rougher concentrate for two PNBX dosages at pH 8.5. Solid lines represent fitted curves.

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.

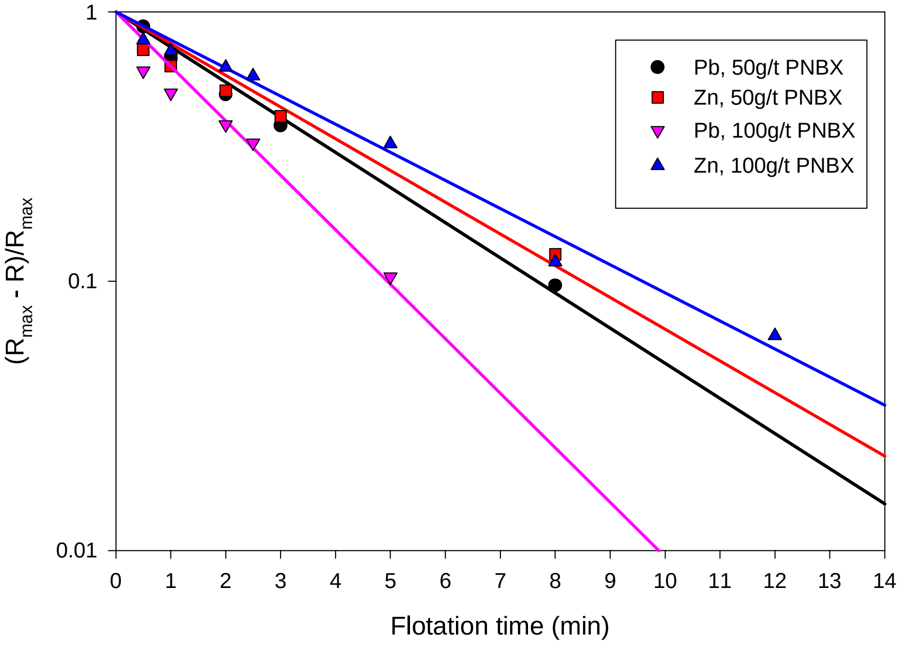


Figure 5.4. Rate of flotation of Pb and Zn in the lead rougher concentrate for two concentrations of PNBX at pH 8.5. Solid lines represent fitted curves.

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.

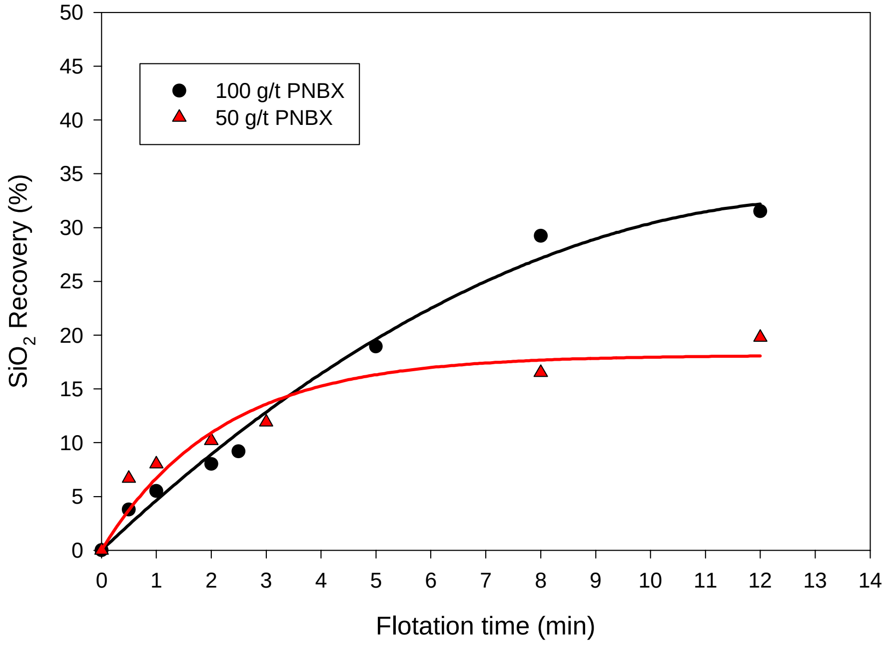


Figure 5.5. Flotation recovery of silica in the lead rougher concentrate for two PNBX dosages at pH 8.5. Solid lines represent fitted curves.

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.

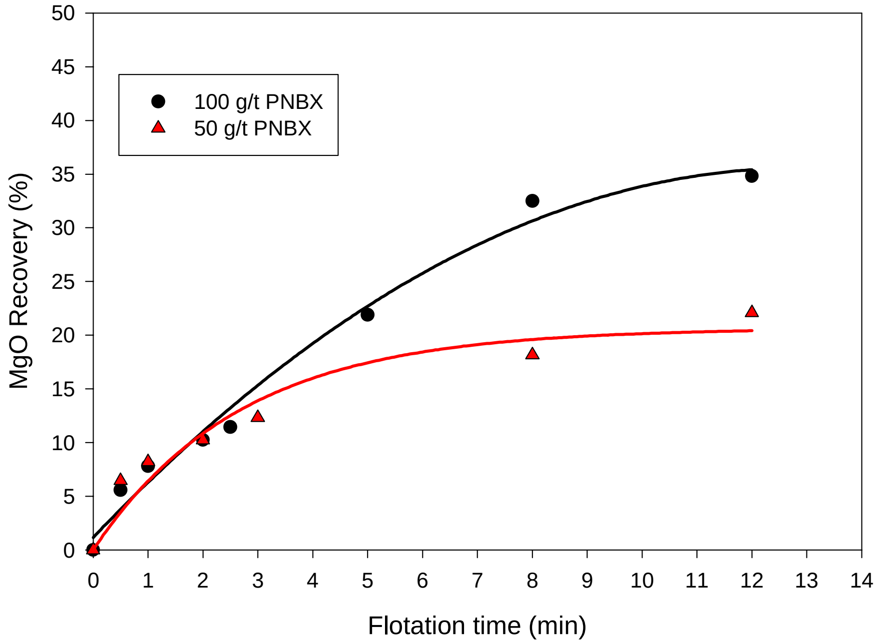


Figure 5.6. Flotation recovery of MgO in the lead rougher concentrate for two PNBX dosages at pH 8.5. Solid lines represent fitted curves.

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.

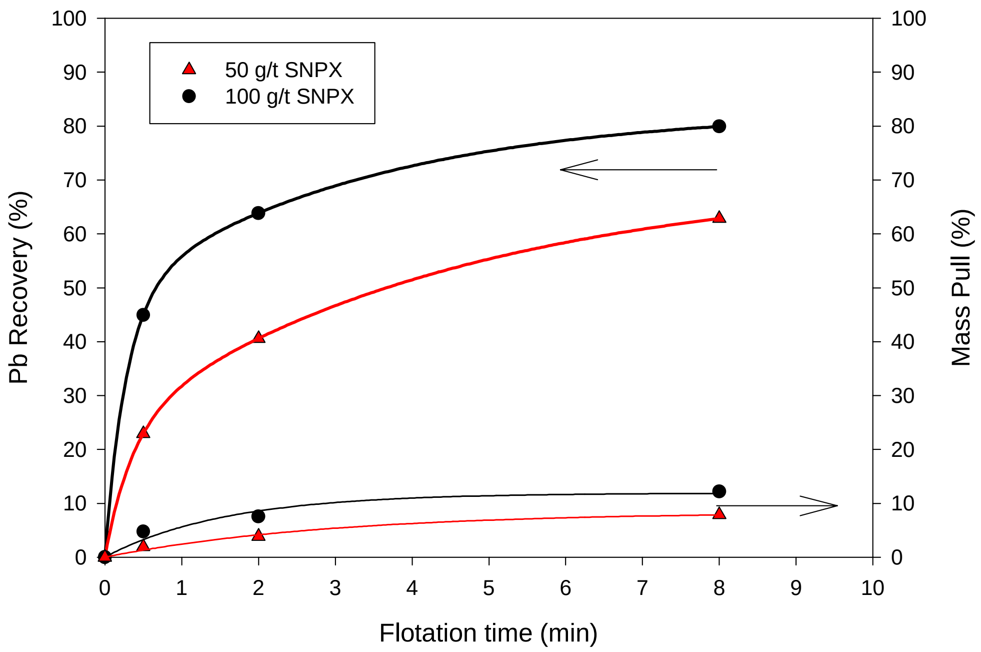


Figure 5.7. Flotation recovery of Pb and rougher concentrate mass pull at two SNPX dosages at pH 8.5. Solid lines represent fitted curves.

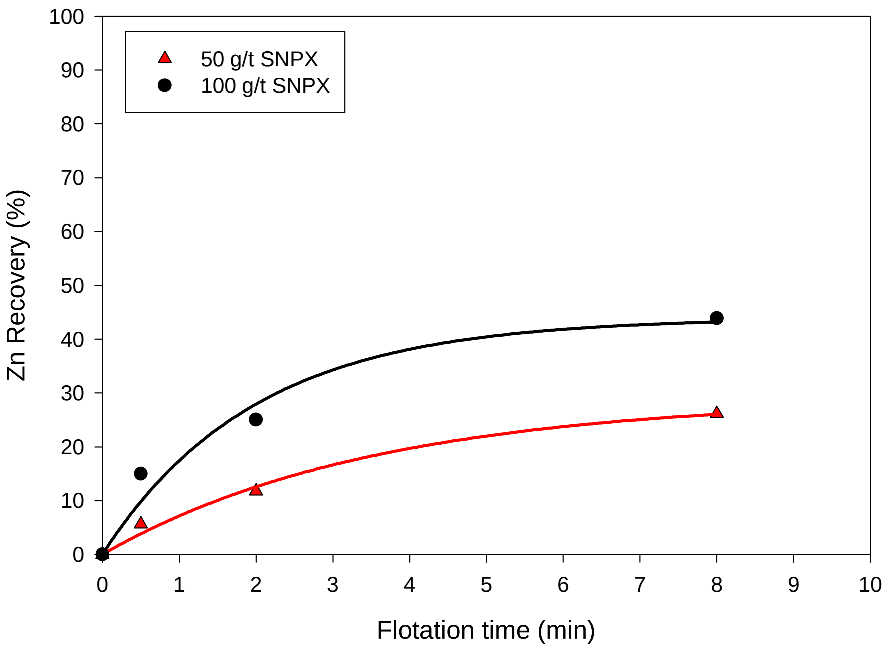


Figure 5.8. Flotation recovery of Zn in the lead rougher concentrate at two SNPX dosages at pH 8.5. Solid lines represent fitted curves.

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.

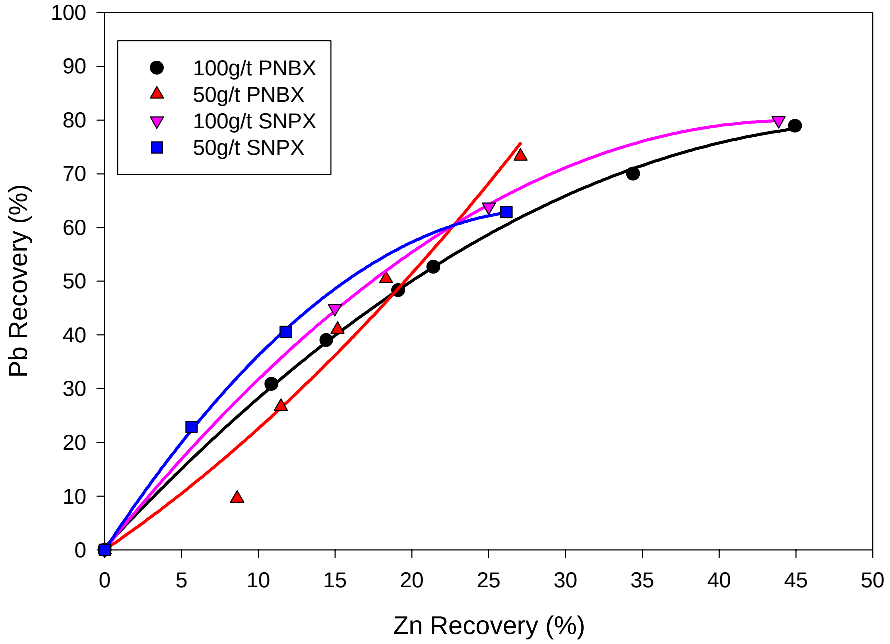


Figure 5.9. Flotation selectivity between galena and sphalerite from the Rosh Pinah ore at pH 8.5 after 8 minute of flotation time at various dosages of SNPX and PNBX

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.

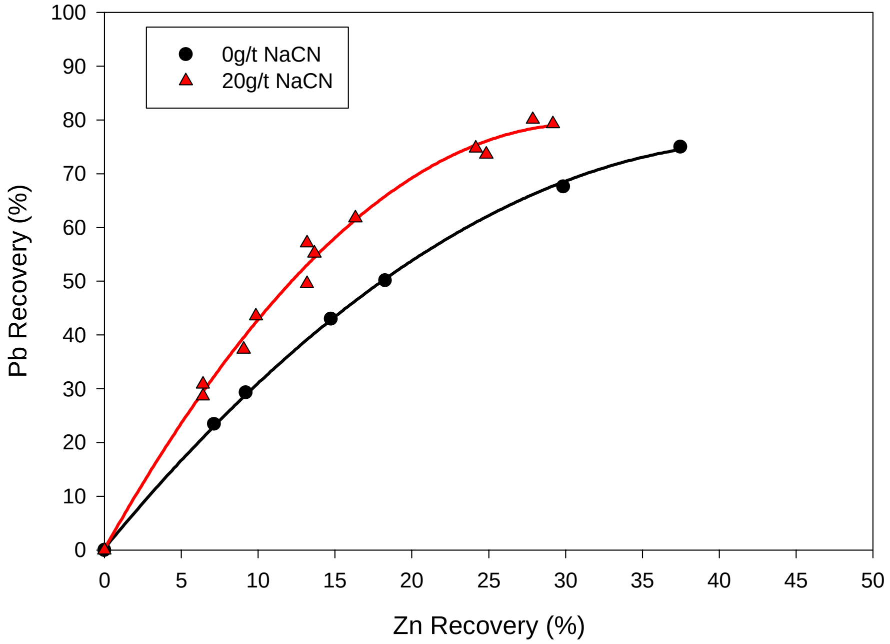


Figure 5.10. Flotation selectivity between galena and sphalerite from the Rosh Pinah composite at pH 8.5 after 12 minutes of flotation time at various dosages of NaCN and 50g/t PNBX.

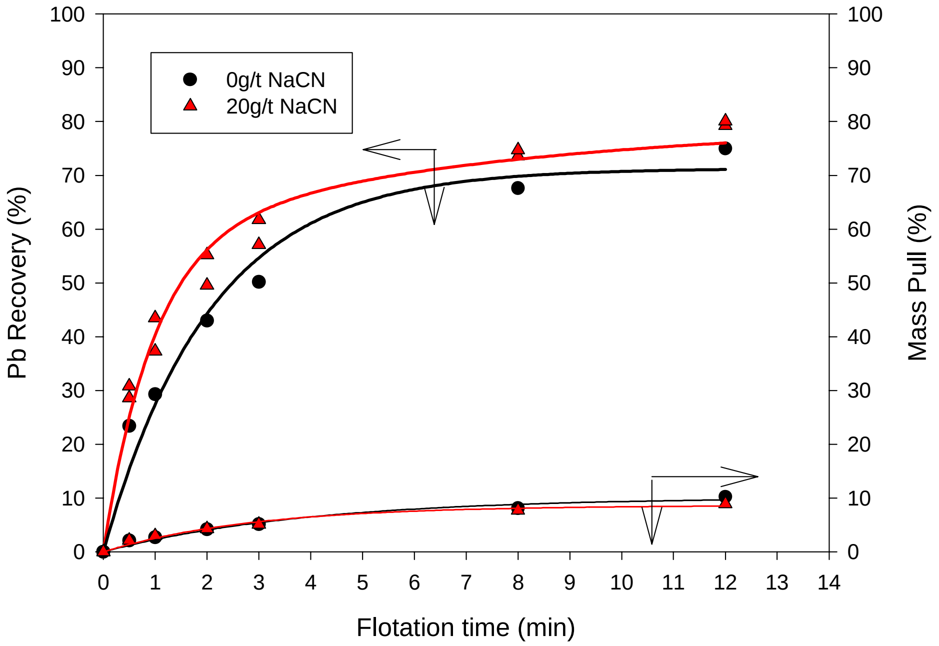


Figure 5.11. Flotation recovery of Pb in the lead rougher concentrate as a function of NaCN dosage in the presence of 50g/t PNBX. Solid lines represent fitted curves.

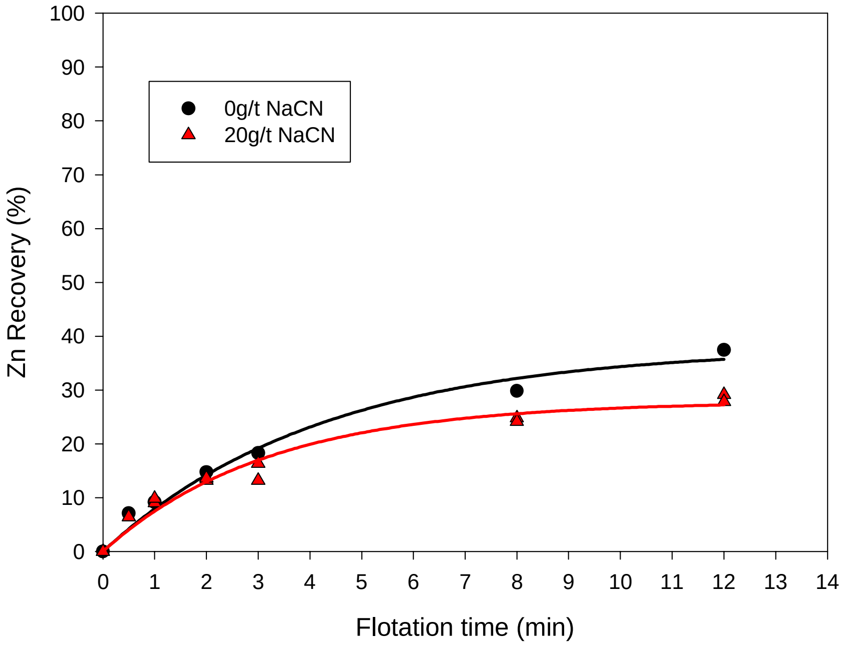


Figure 5.12. Flotation recovery of Zn in the lead rougher concentrate as a function of NaCN dosage in the presence of 50g/t PNBX. Solid lines represent fitted curves.

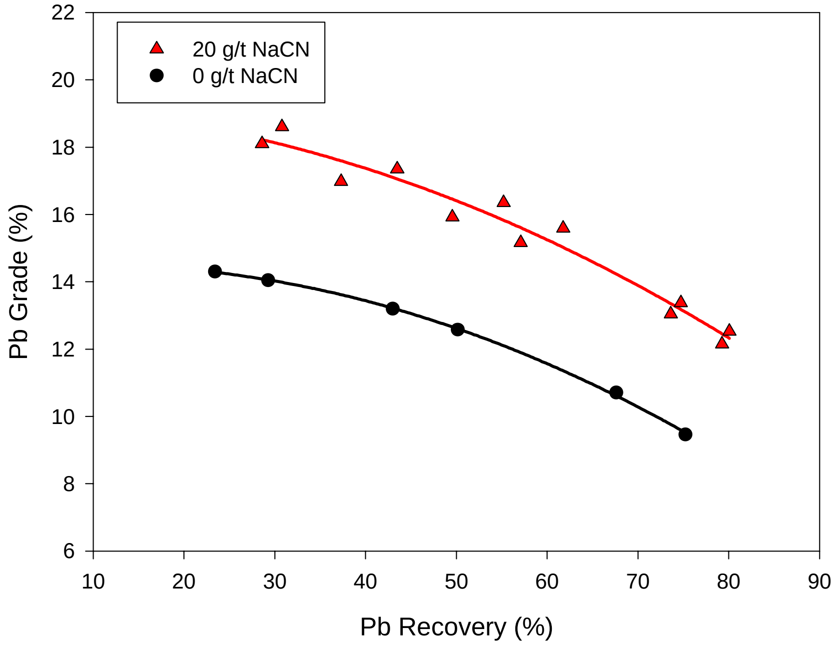


Figure 5.13. Lead recovery-grade relationship in the lead rougher concentrate at various concentration of NaCN in the presence of 50g/t PNBX. Solid lines represent fitted curves.

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.

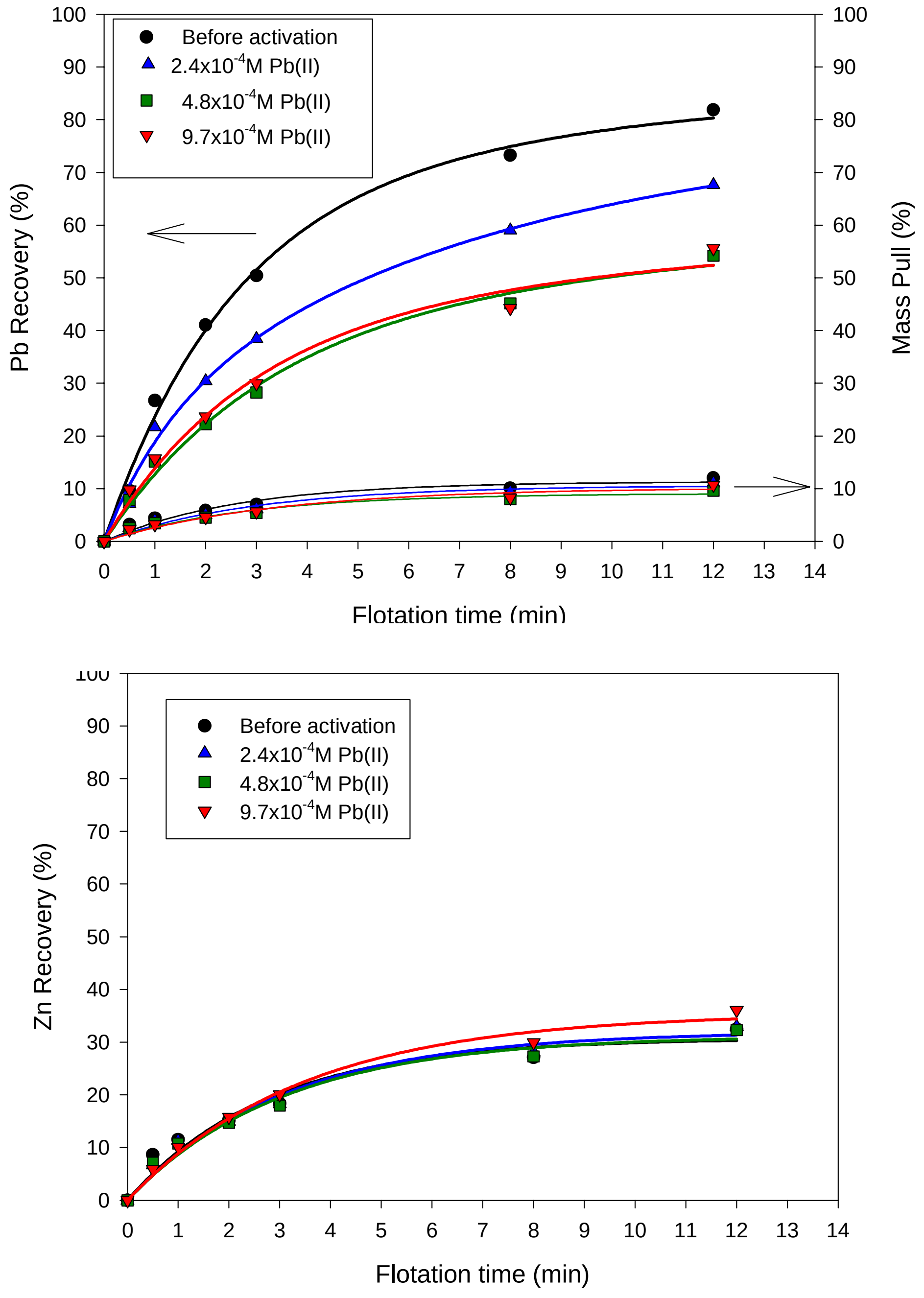


Figure 5.14. Recoveries of galena and sphalerite in the presence of various concentrations of Pb(II) and 50 g/t (1.2x10^{-4}M) PNBX at pH 8.5. Solid lines represent fitted curves.

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.

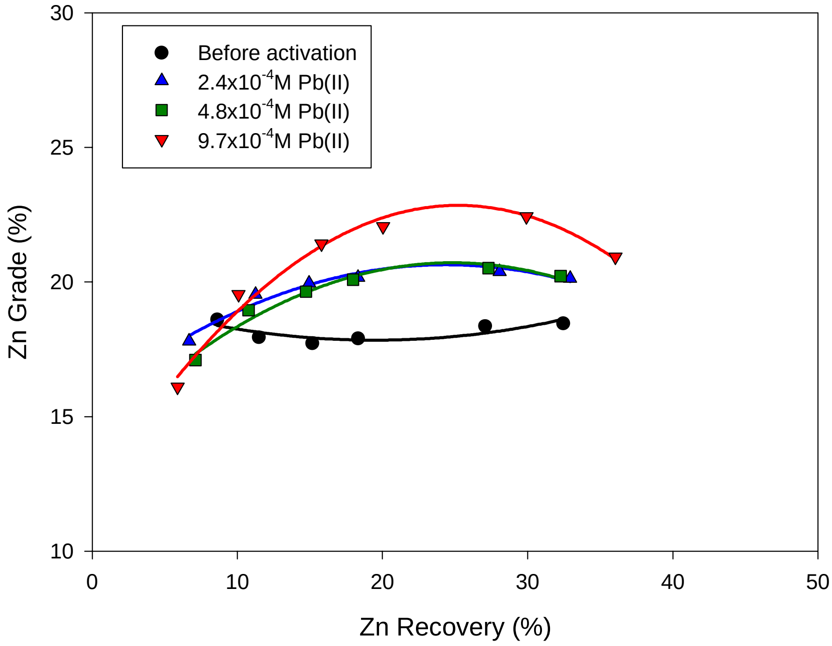


Figure 5.15. Zinc recovery-grade relationship in the absence and presence of various concentration of lead nitrate and 50 g/t (1.2x10^{-4}M) PNBX at pH 8.5

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).

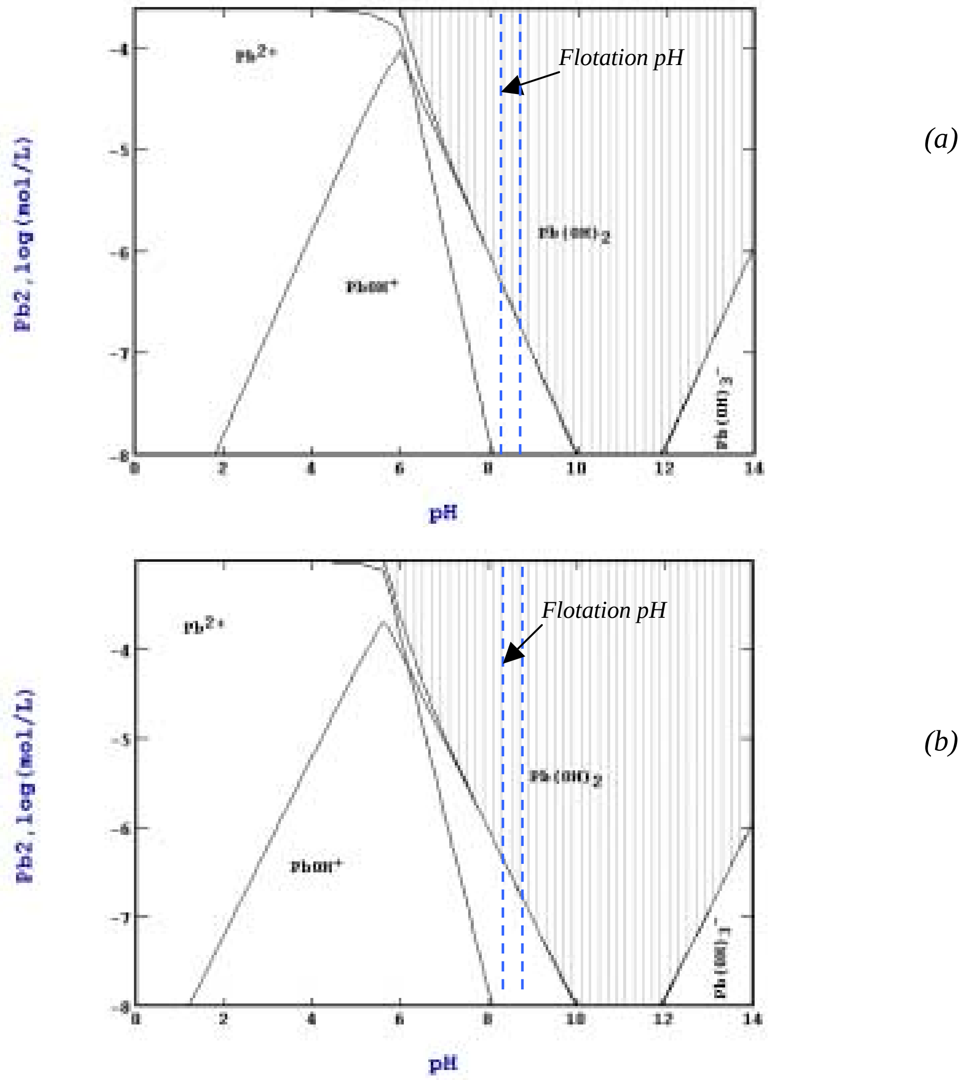


Figure 5.16. Solubility diagram for Pb(II) as a function of pH at 25°C. Total lead concentration: (a) $2.4x10^{-4}$M and (b) $9.7x10^{-4}$M. Stabcal software, NBS database (Huang, 2003). Shaded area shows the solid species.

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.

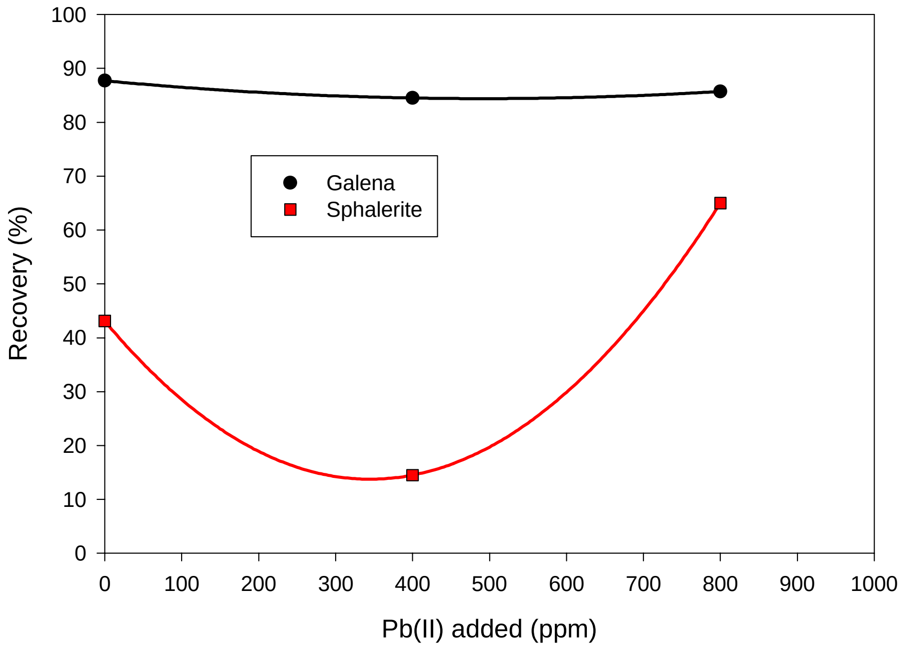


Figure 5.17. Effect of added Pb(II) on the recovery of galena and sphalerite with 50g/t SNPX and Senforth 6005 (Bredenhann et al., 2001). Solid lines represent fitted curves.

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.

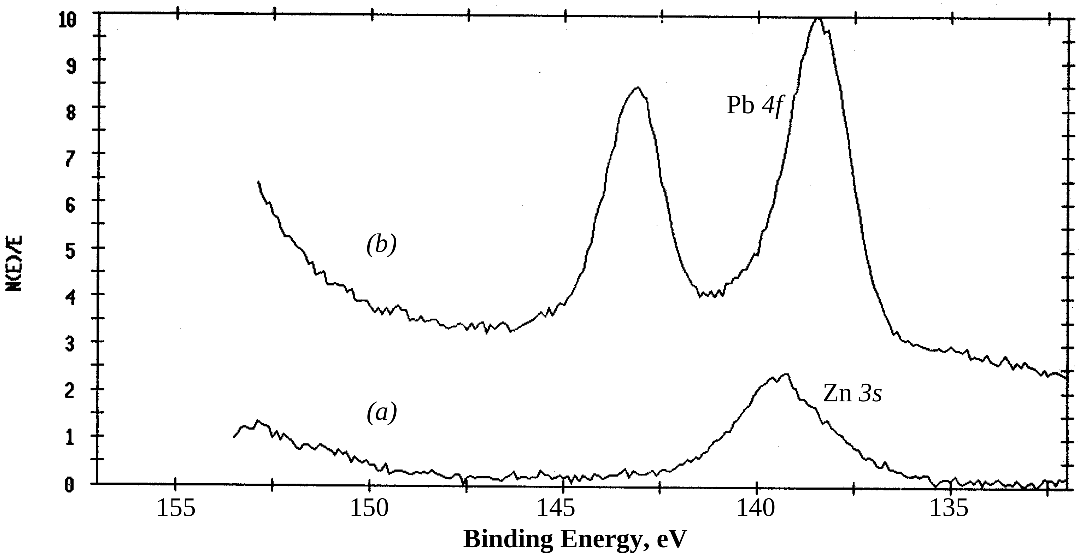


Figure 5.18. XPS photoelectron spectra obtained on a sphalerite surface at pH 9.2. (a) in the absence of Pb(II), (b) and in the presence of $3x10^{-3}$M Pb(II).

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

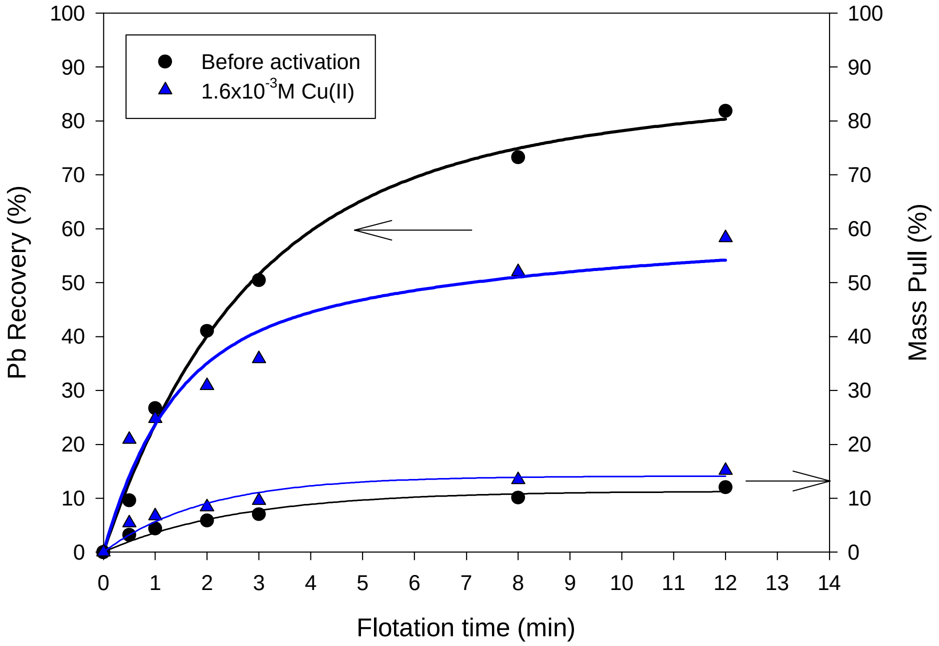
Pb/Zn atomic concentration ratio of 0.085 after the activation of a sphalerite probe in a 10^{-4}M Pb(II) solution for 1 minute. They also showed the presence of lead xanthate and dixanthogen when the activated sphalerite probe was conditioned in the presence of 10^{-4}M PAX.

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) (1.6×10^{-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 1.6×10^{-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).



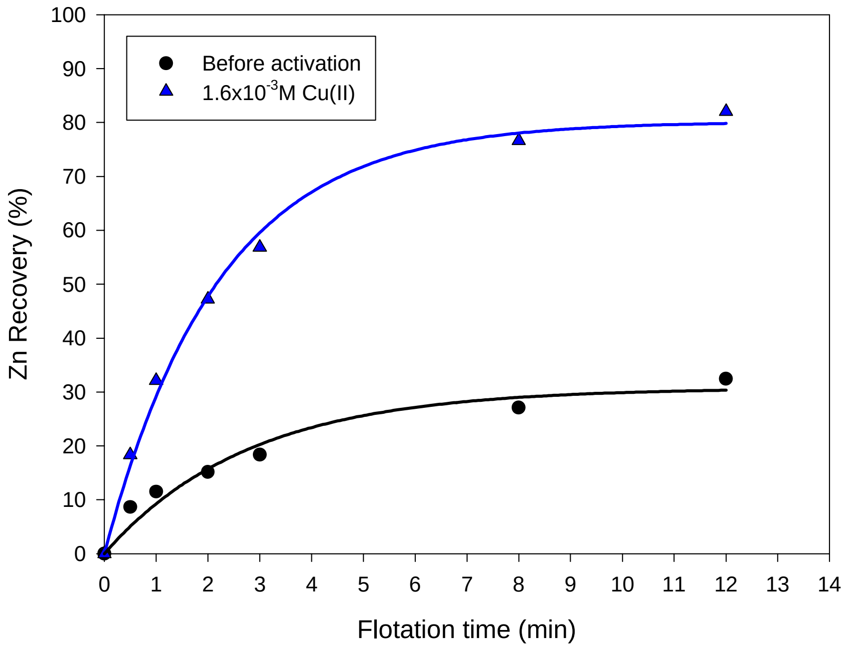


Figure 5.19. Effect of copper sulphate activation on the recovery of lead and zinc with 50 g/t (1.2x10^{-4}M) PNBX at pH 8.5. Solid lines represent fitted curves.

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.

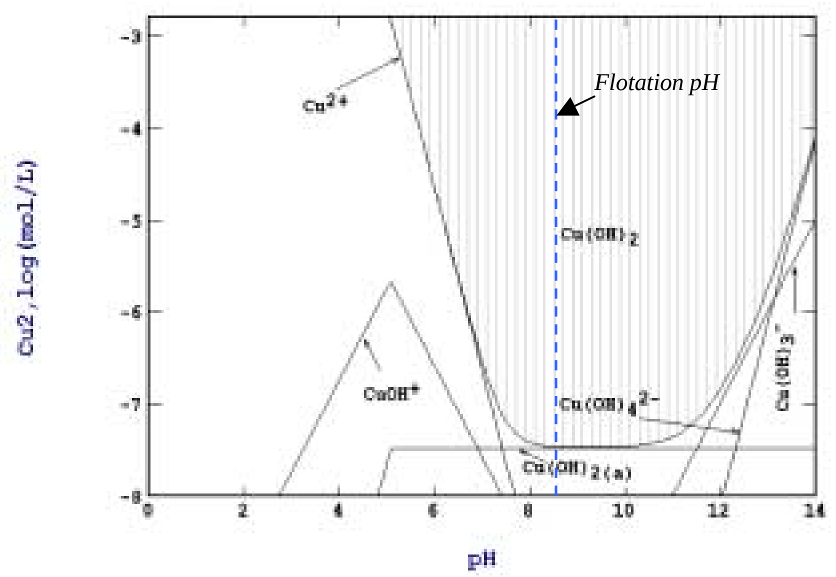


Figure 5.20. Speciation diagram for Cu(II) as a function of pH for [Cu] = 1.6x10^{-3}M at 25°C. Stabcal software. NBS database (Huang, 2003). Shaded area shows the solid species.

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.

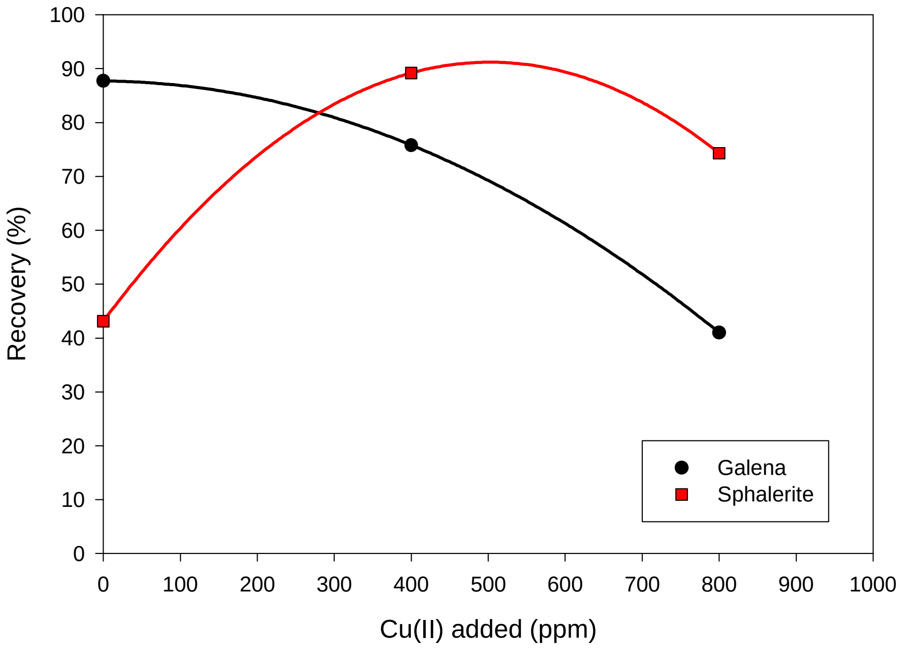


Figure 5.21. Effect of added Cu(II) on the recovery of galena and sphalerite with 50g/t SNPX and Senforth 6005 (Bredenhann et al., 2001). Solid lines represent fitted curves.

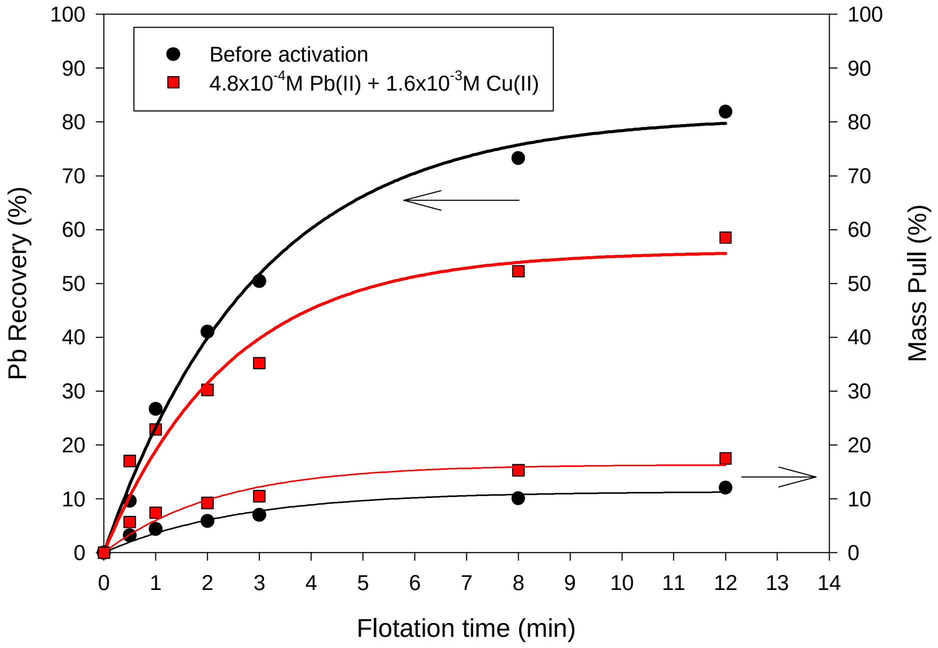


Figure 5.22. Flotation recovery of galena with and without added Cu(II) and Pb(II) in the presence of 50 g/t (1.2×10^{-4}M) PNBX at pH 8.5. Solid lines represent fitted curves.

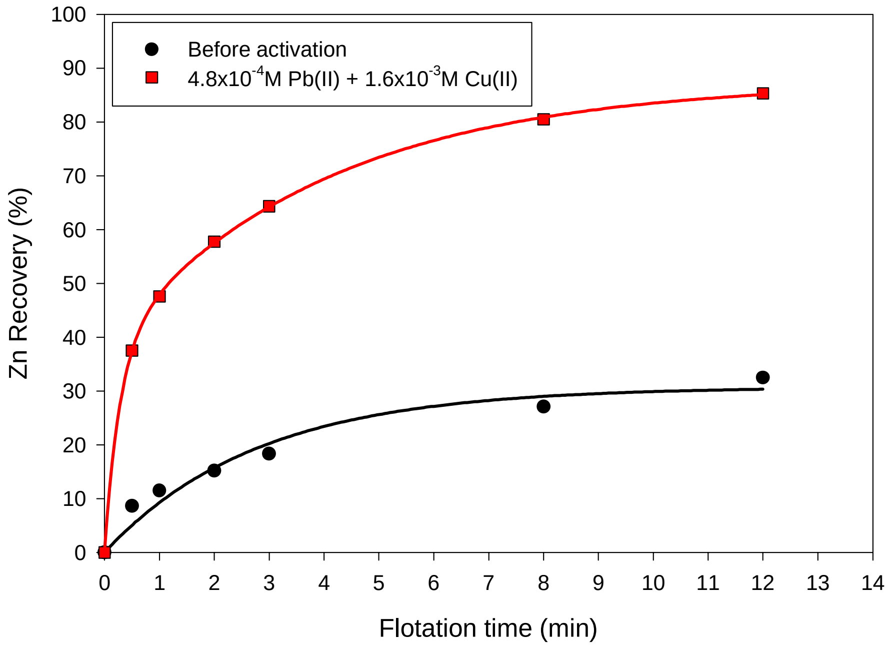


Figure 5.23. Flotation recovery of sphalerite with added Cu(II) and Pb(II) in the presence of 50 g/t (1.2x10^{-4}M) PNBX at pH 8.5. Solid lines represent fitted curves.

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.

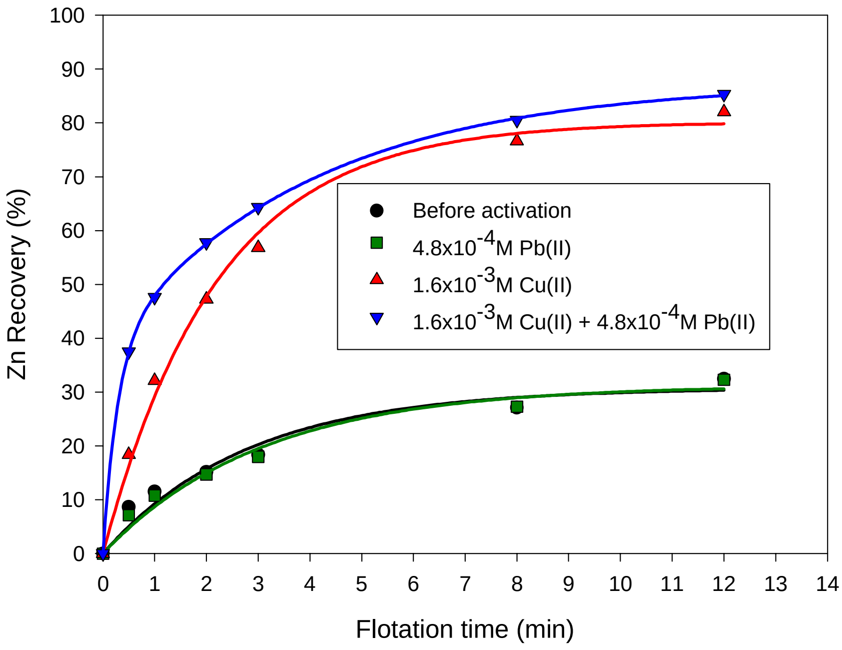


Figure 5.24. Zinc recovery-grade relationship with added Cu(II) and Pb(II) in the presence of 50 g/t (1.2x10^{-4}M) PNBX at pH 8.5. Solid lines represent fitted curves.

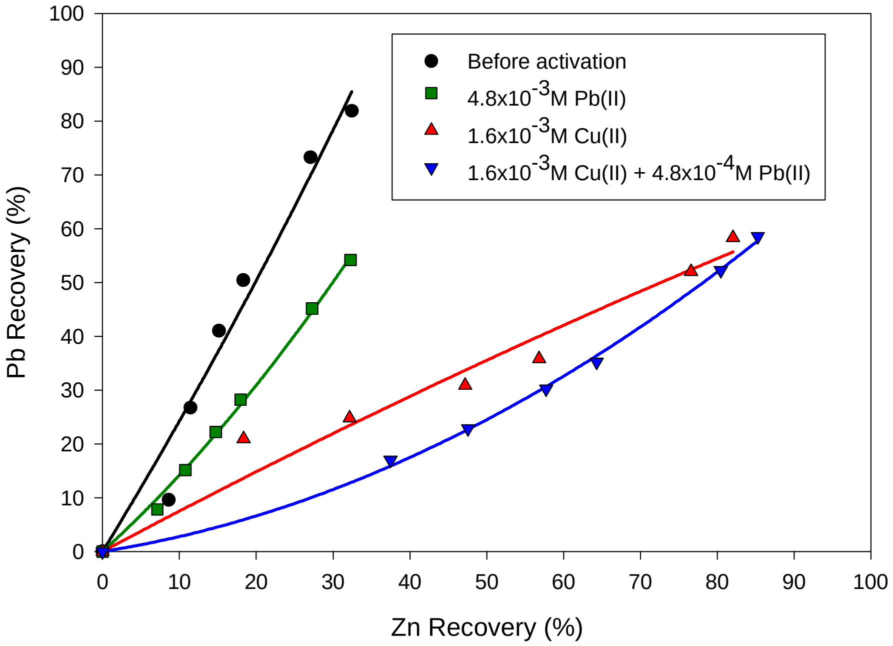


Figure 5.25. Flotation selectivity between galena and sphalerite as a function of added Cu(II) and Pb(II) in the presence of 50 g/t (1.2x10^{-4}M) PNBX at pH 8.5. Solid lines represent fitted curves.

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.