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.

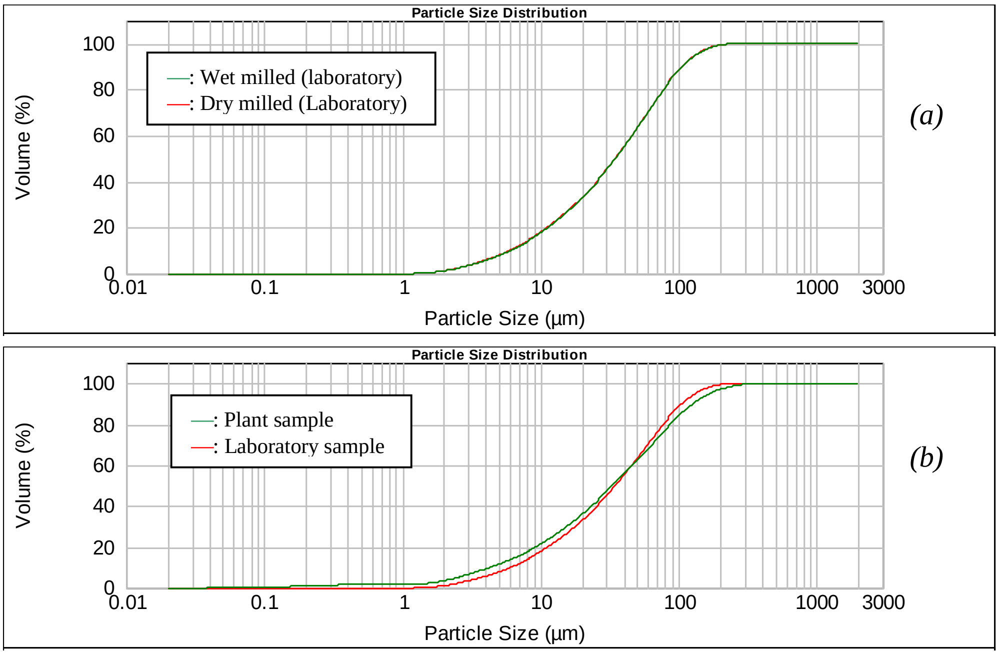


Figure 6.1 Particle size distributions of Roh Pinah ore samples. (a) Laboratory milled (wet and dry milling); (b) laboratory milled and sample from the feed of the lead flotation circuit at Rosh Pinah Mine (November 2002).

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.

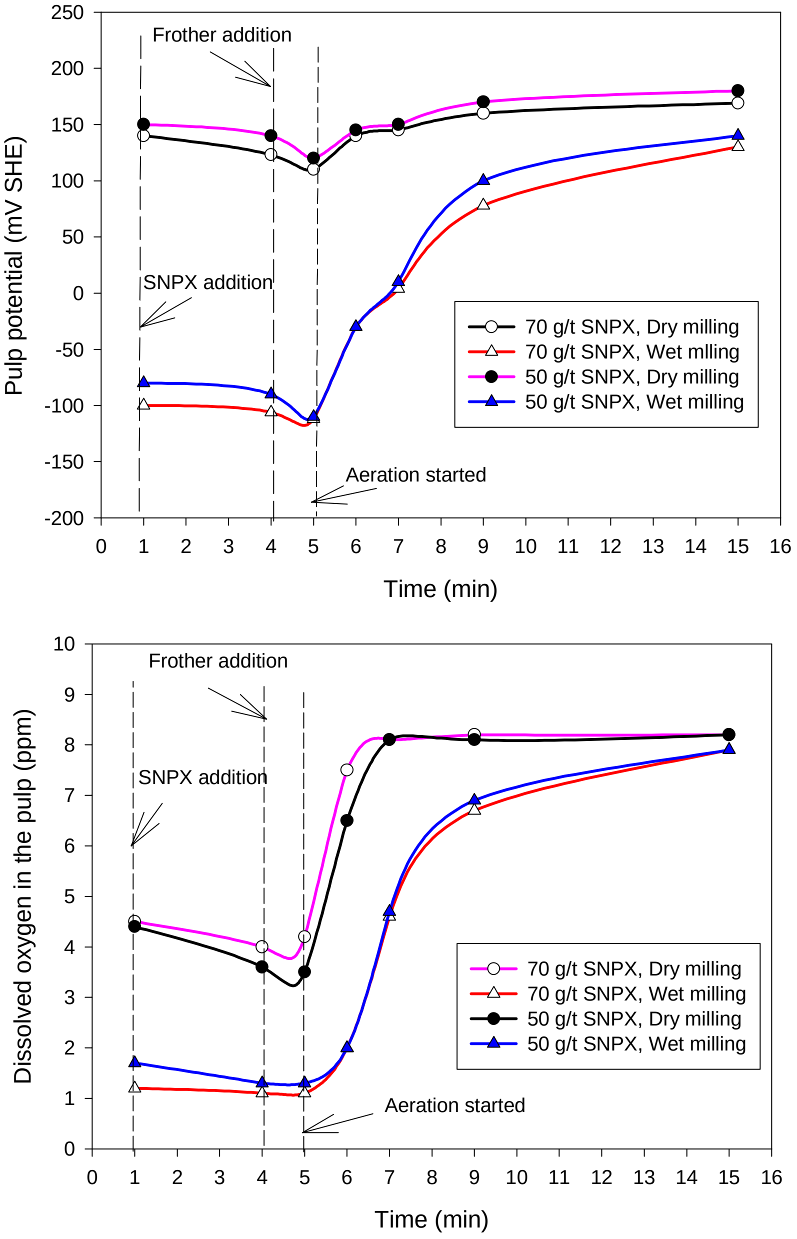


Figure 6.2. Evolution of the pulp potential and the dissolved oxygen concentration in the flotation cell during the flotation of a Rosh Pinah composite ground in either a dry or wet environment in a steel mill. Tests were carried out before the activation with cuprous cyanide species.

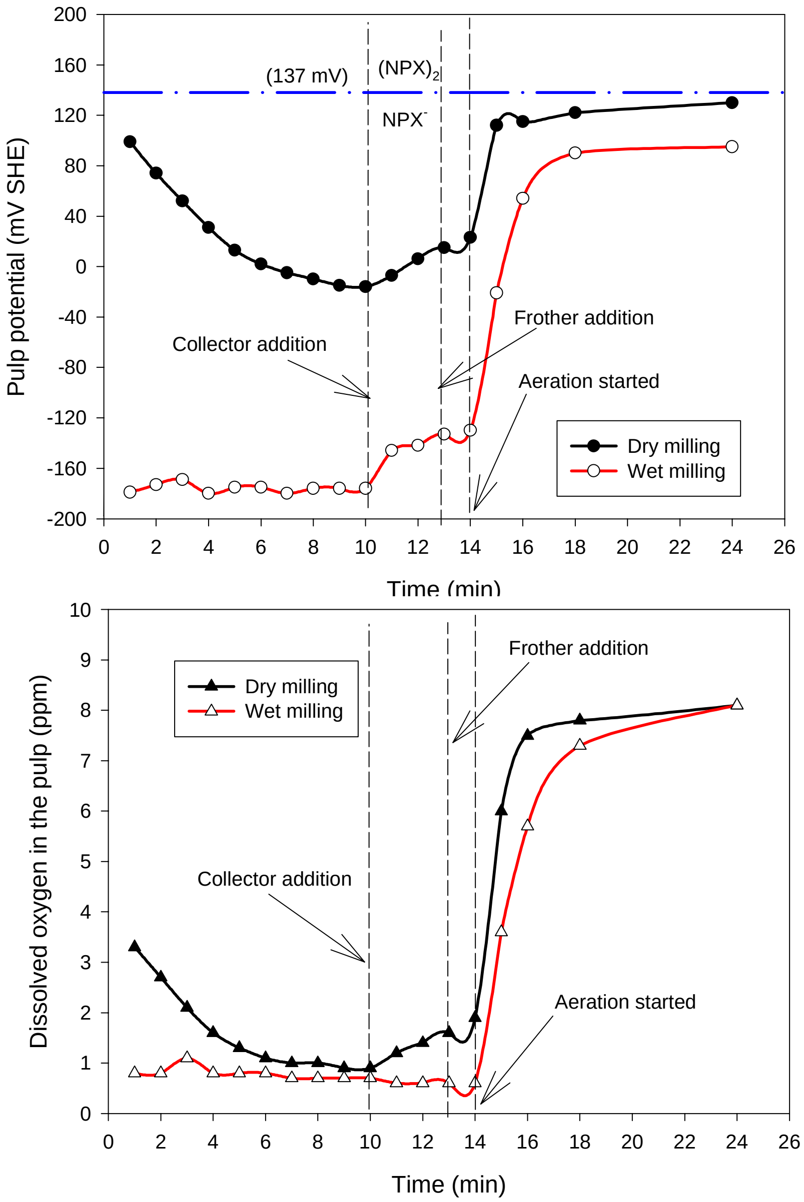


Figure 6.3. Evolution of the pulp potential and the dissolved oxygen concentration in the flotation cell during the flotation of a Rosh Pinah composite ground in either a dry or wet environment in a steel mill. Flotation tests were carried out in the presence of 10^{-4}M cuprous cyanide complexes. The 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.

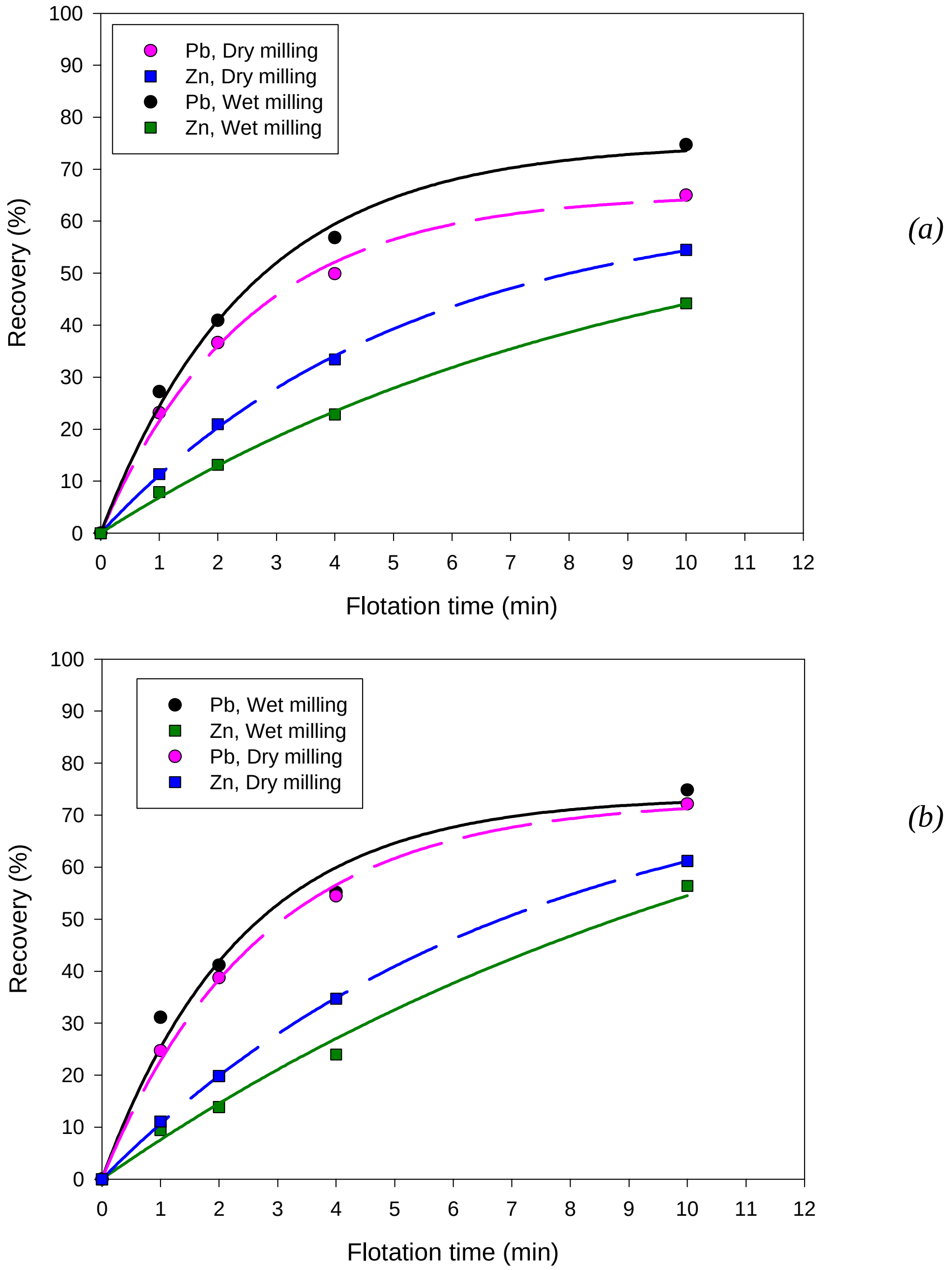


Figure 6.4. Flotation recovery of galena and sphalerite from a Rosh Pinah composite at pH 8.5 under various grinding conditions. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines (after wet milling, 67% solids), dashed line (after dry milling).

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.

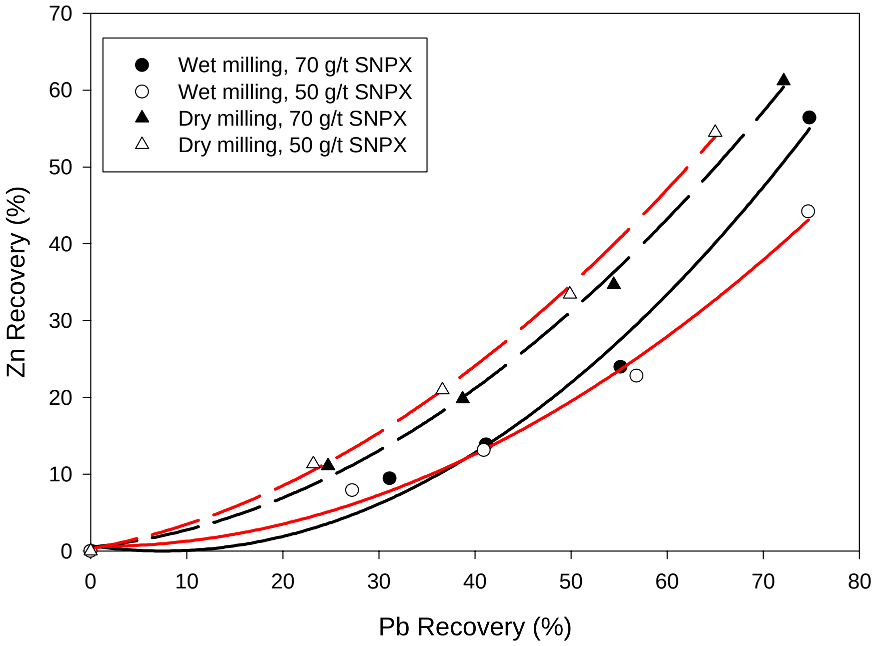


Figure 6.5. Effect of milling environment on the flotation recoveries of sphalerite and galena at various dosages of xanthate. Solid lines (after wet milling, 67% solids), dashed line (after dry milling).

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).

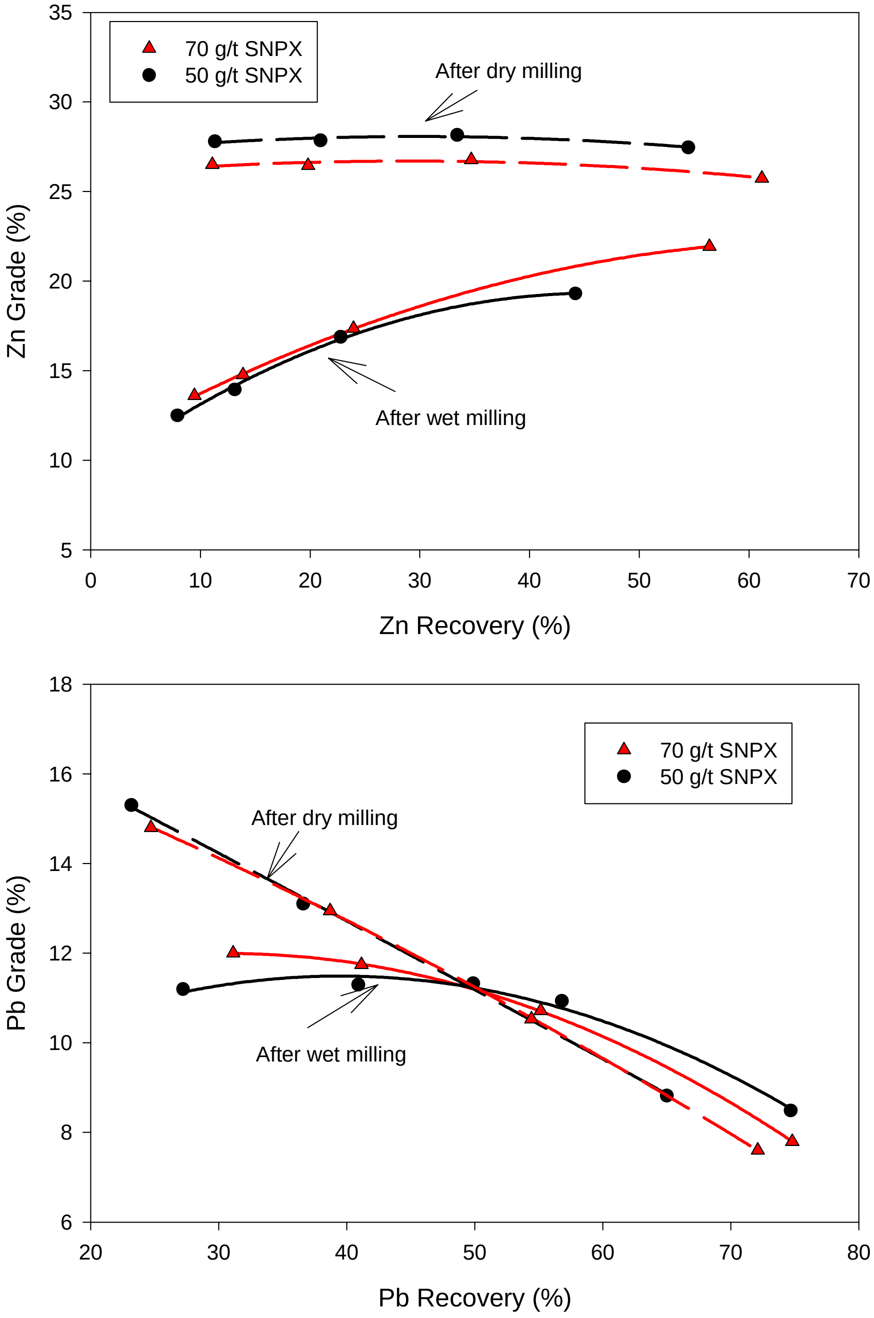


Figure 6.6. Effect of the milling environment on the recovery-grade of galena and sphalerite from a Rosh Pinah composite at pH 8.5 and in the presence of 50 and 70 g/t SNPX. Solid lines: after wet milling, 67% solids; dashed line: after dry milling.

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).

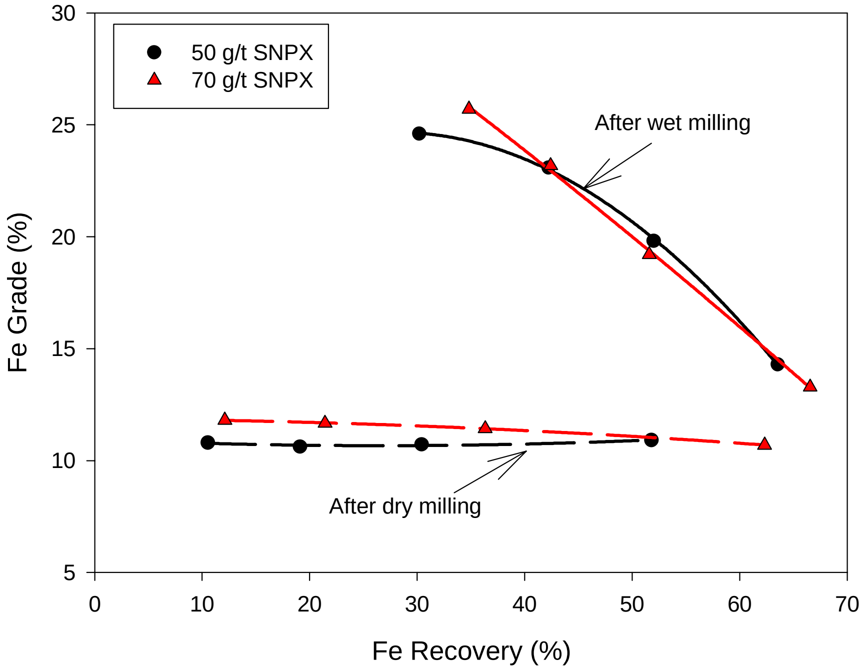


Figure 6.7. Effect of the milling environment on the recovery-grade of pyrite from a Rosh Pinah composite at pH 8.5 and in the presence of 50 and 70 g/t SNPX, respectively. Solid lines (after wet milling, 67% solids), dashed line (after dry milling).

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.

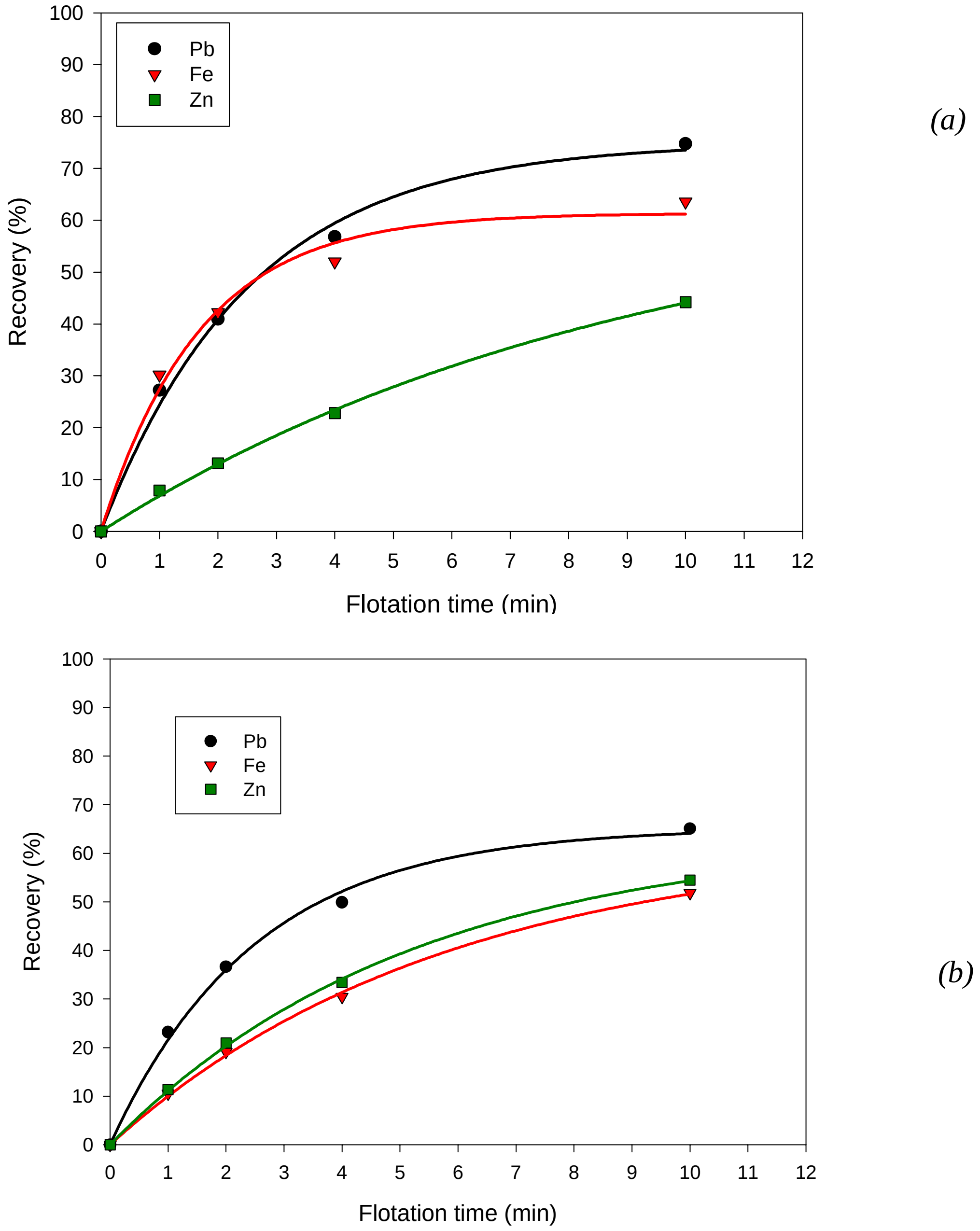


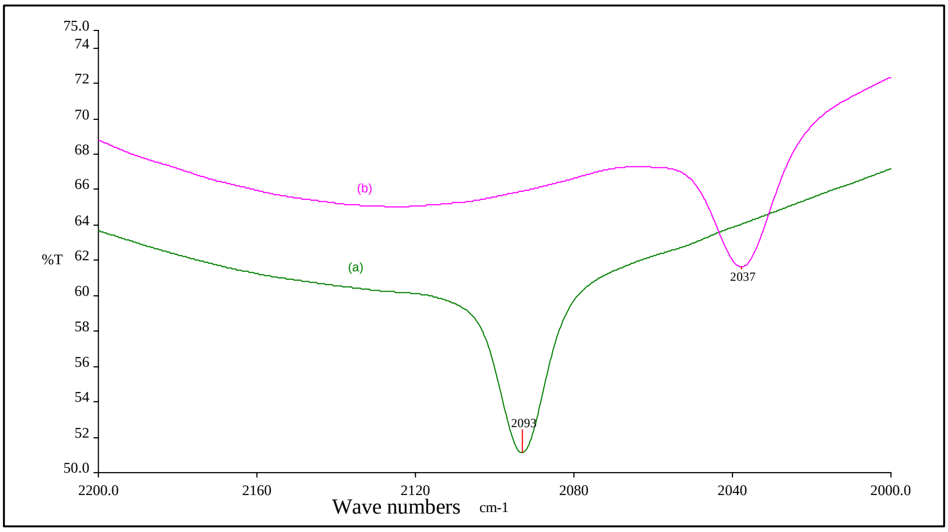
Figure 6.8. Flotation recovery of galena, pyrite and sphalerite in the presence of 50 g/t SNPX at pH 8.5. (a) Wet milling, (b) Dry milling. Solid lines represent fitted curves.

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 (g/t)	Milling Type	Cu(I) concentration ([CN$^-$]/[Cu] = 3)	Mass Pull (%)	Recovery (%) Pb	Recovery (%) Zn	Grade (%) Pb	Grade (%) 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

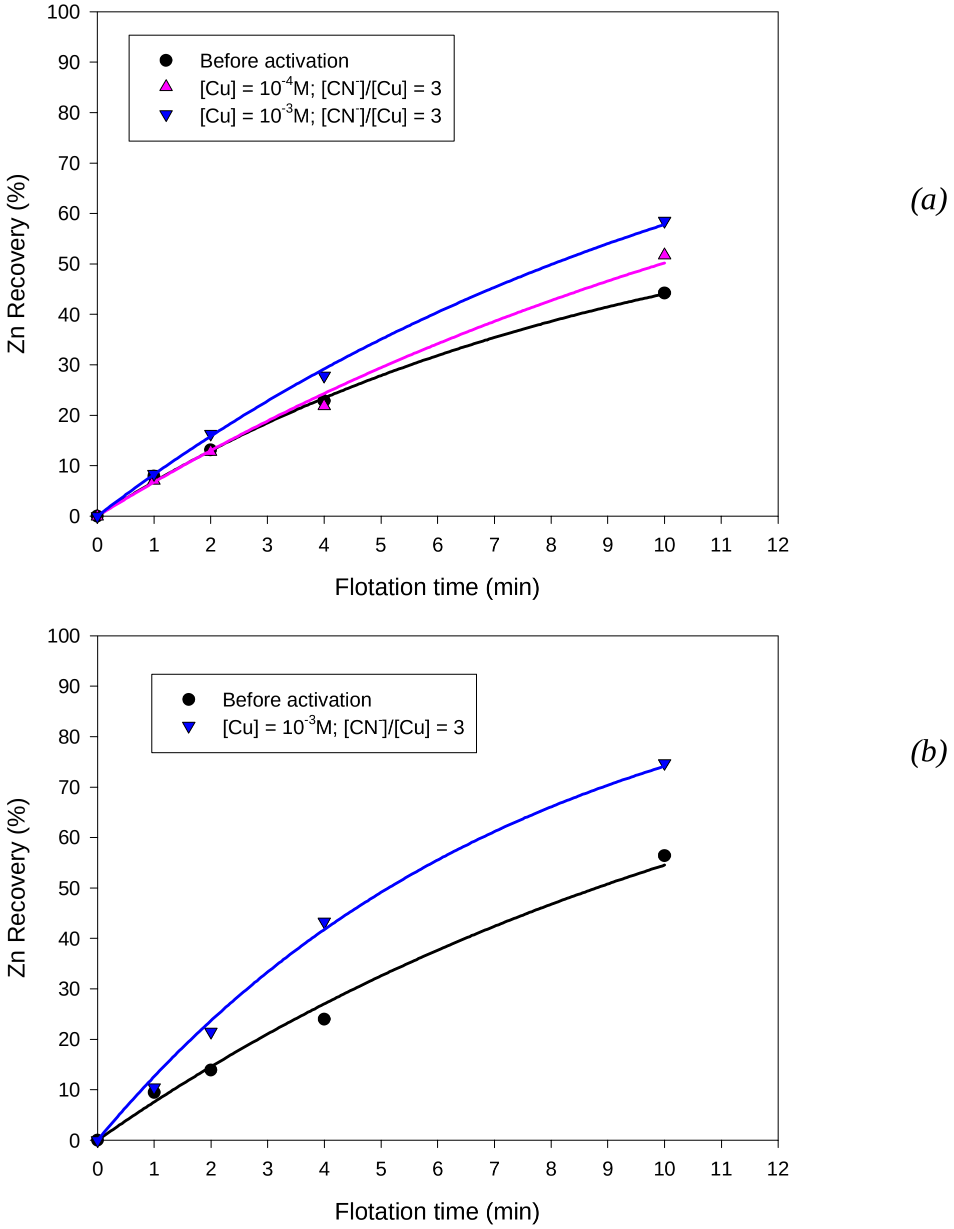


Figure 6.10. Flotation recovery of sphalerite from a wet milled Rosh Pinah composite before and after activation with cuprous cyanide at pH 8.5. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.

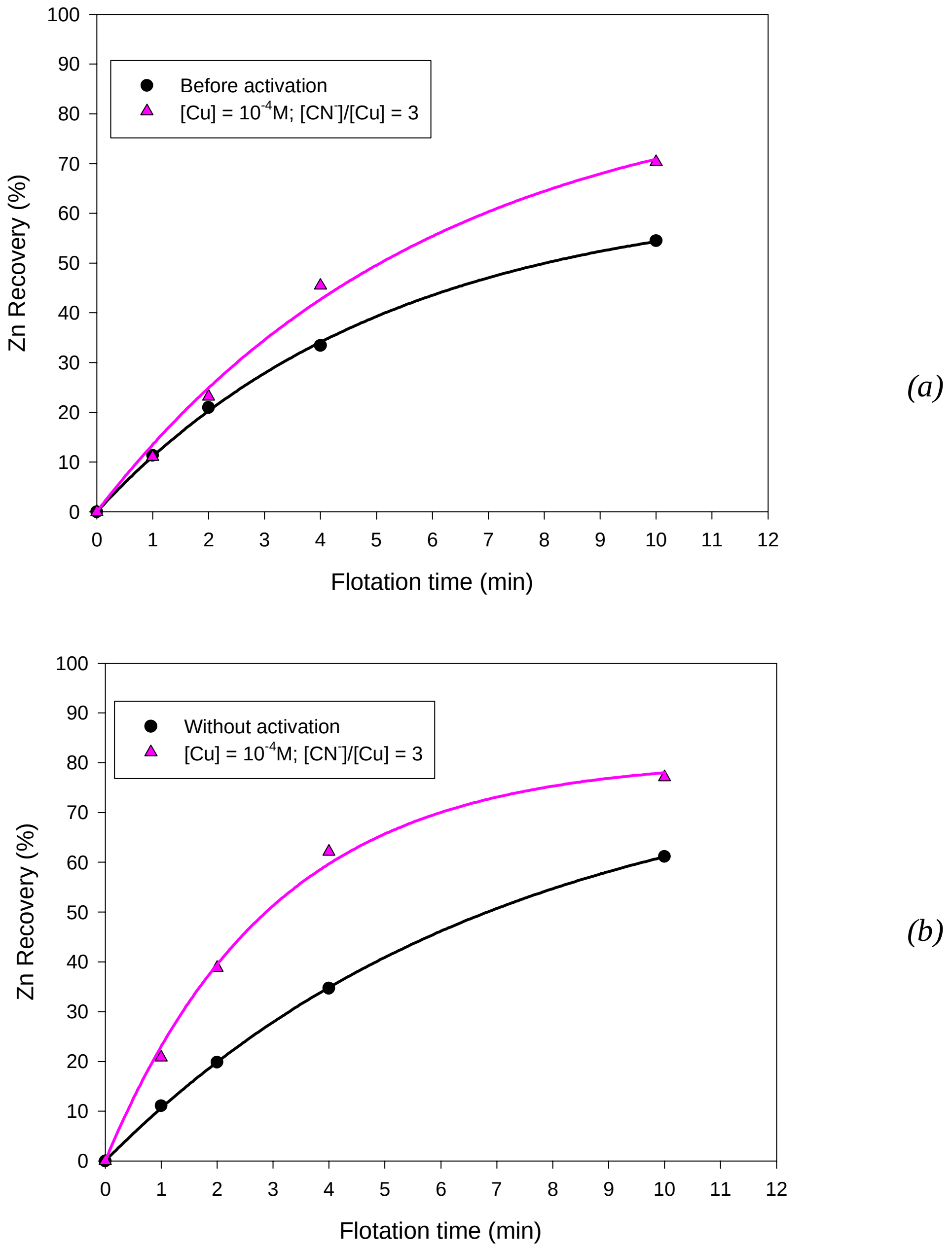


Figure 6.11. Flotation recovery of sphalerite from a dry milled Rosh Pinah composite before and after activation with cuprous cyanide at pH 8.5. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.

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.

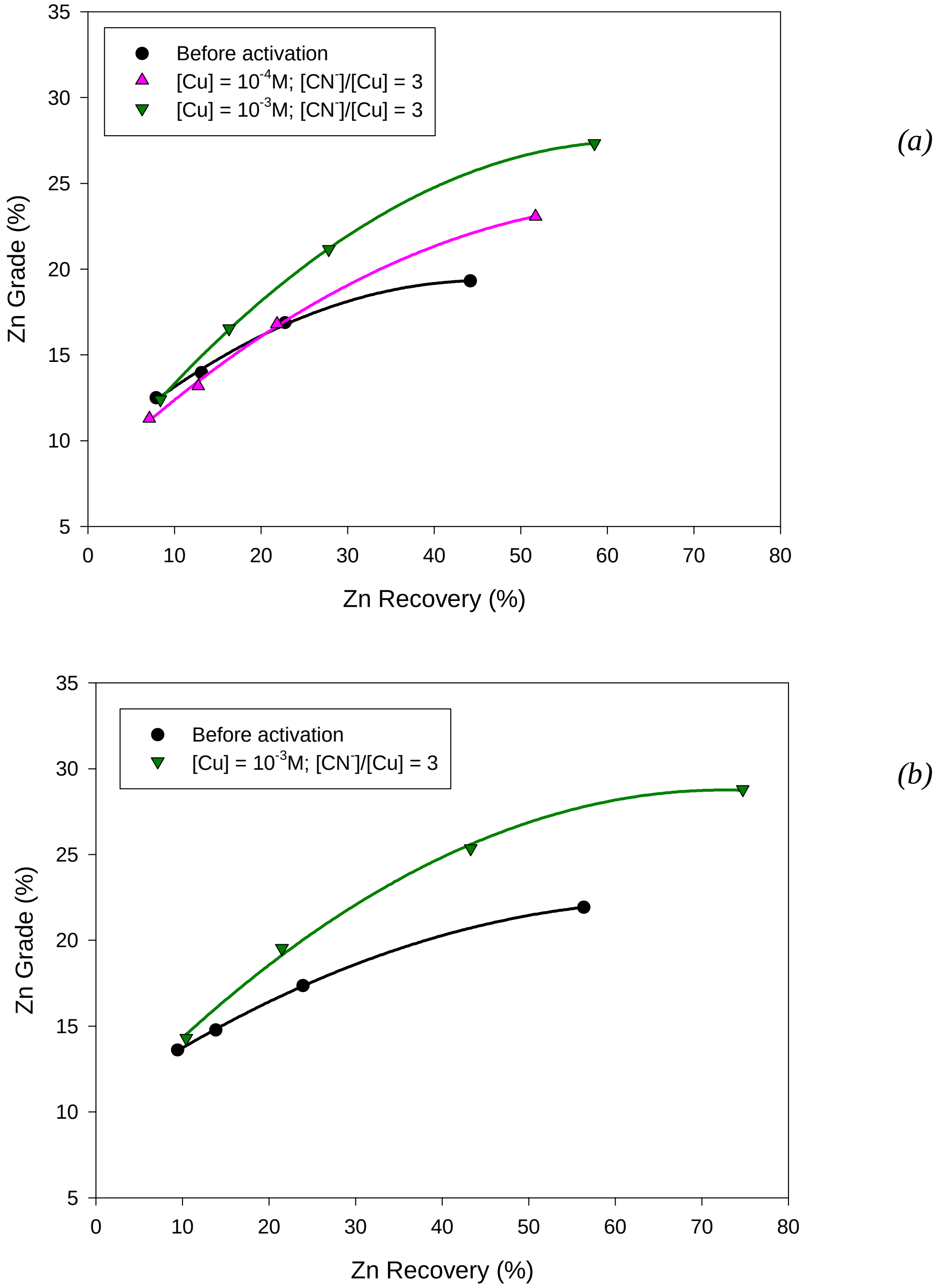


Figure 6.12. Recovery and grade of sphalerite from a Rosh Pinah composite after activation with cuprous cyanide at pH 8.5 and wet milling. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.

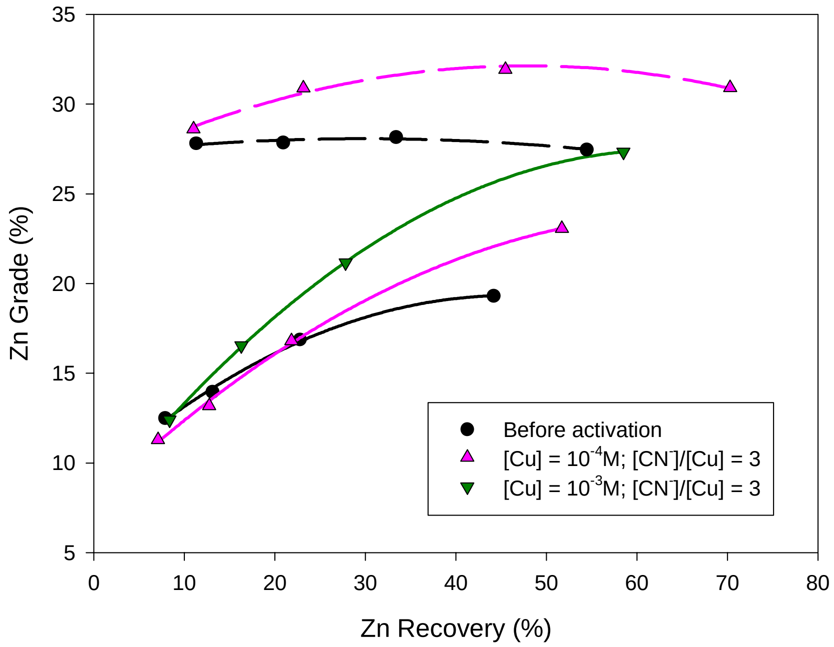


Figure 6.13. Effect of the milling environment on the recovery-grade of sphalerite from a Rosh Pinah composite at pH 8.5 and in the presence of 50 g/t SNPX and various concentration of cuprous cyanide. Solid lines: after wet milling, 67% solids; dashed line: after dry milling.

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.

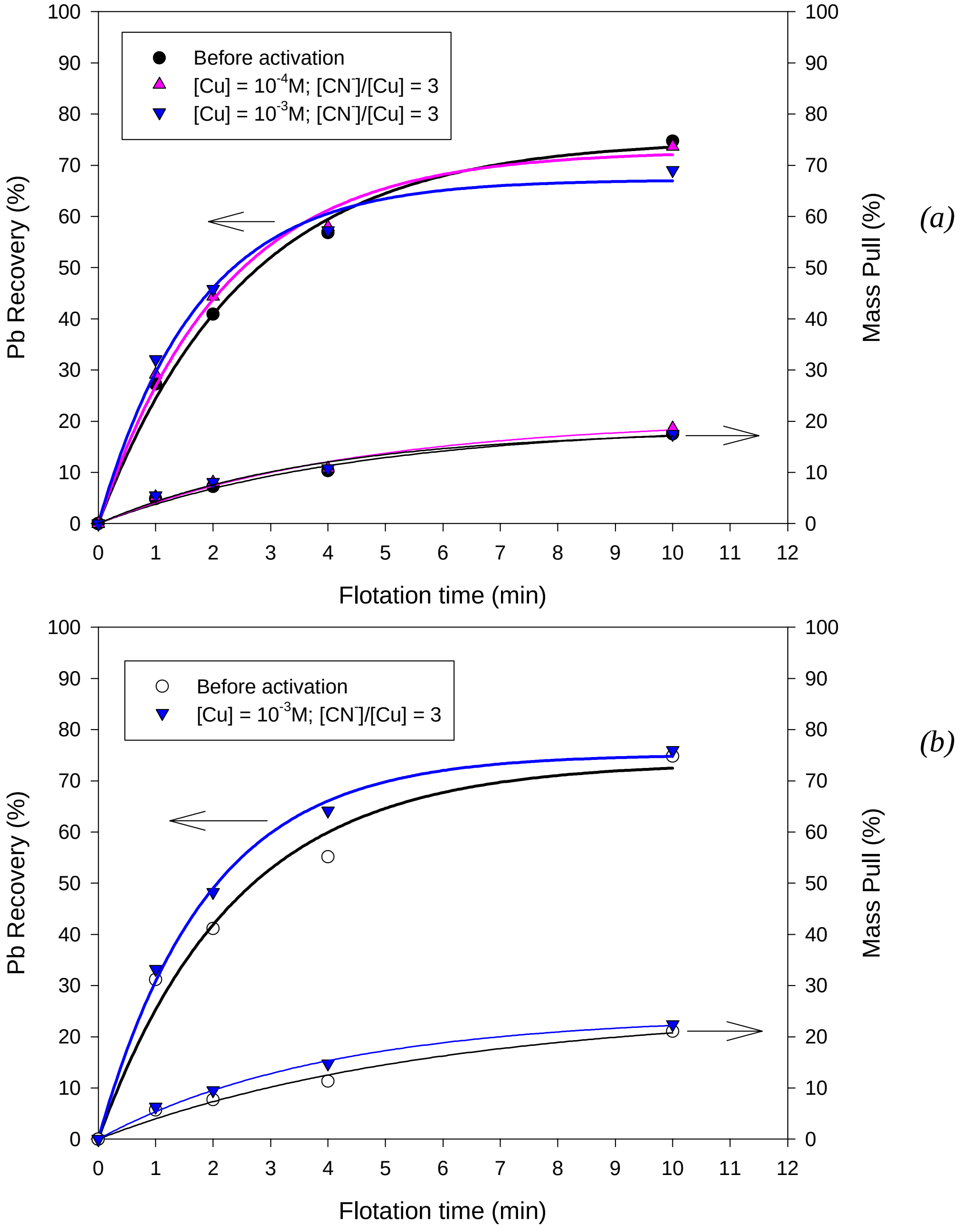


Figure 6.14. Flotation recovery of galena from a Rosh Pinah composite after activation with cuprous cyanide at pH 8.5 and wet milling. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.

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).

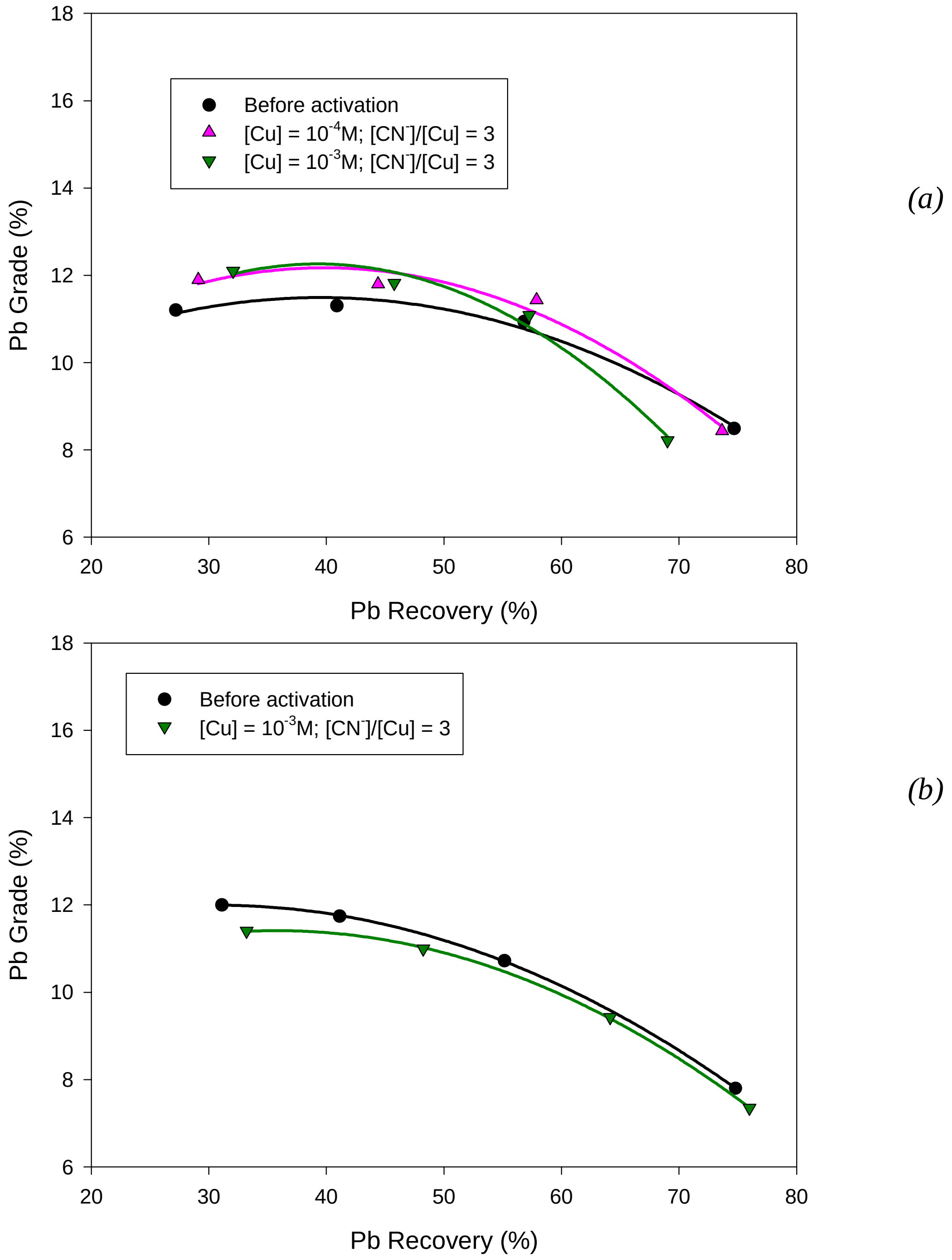


Figure 6.15. Recovery and grade of galena from a Rosh Pinah composite after activation with cuprous cyanide at pH 8.5 and wet milling. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.

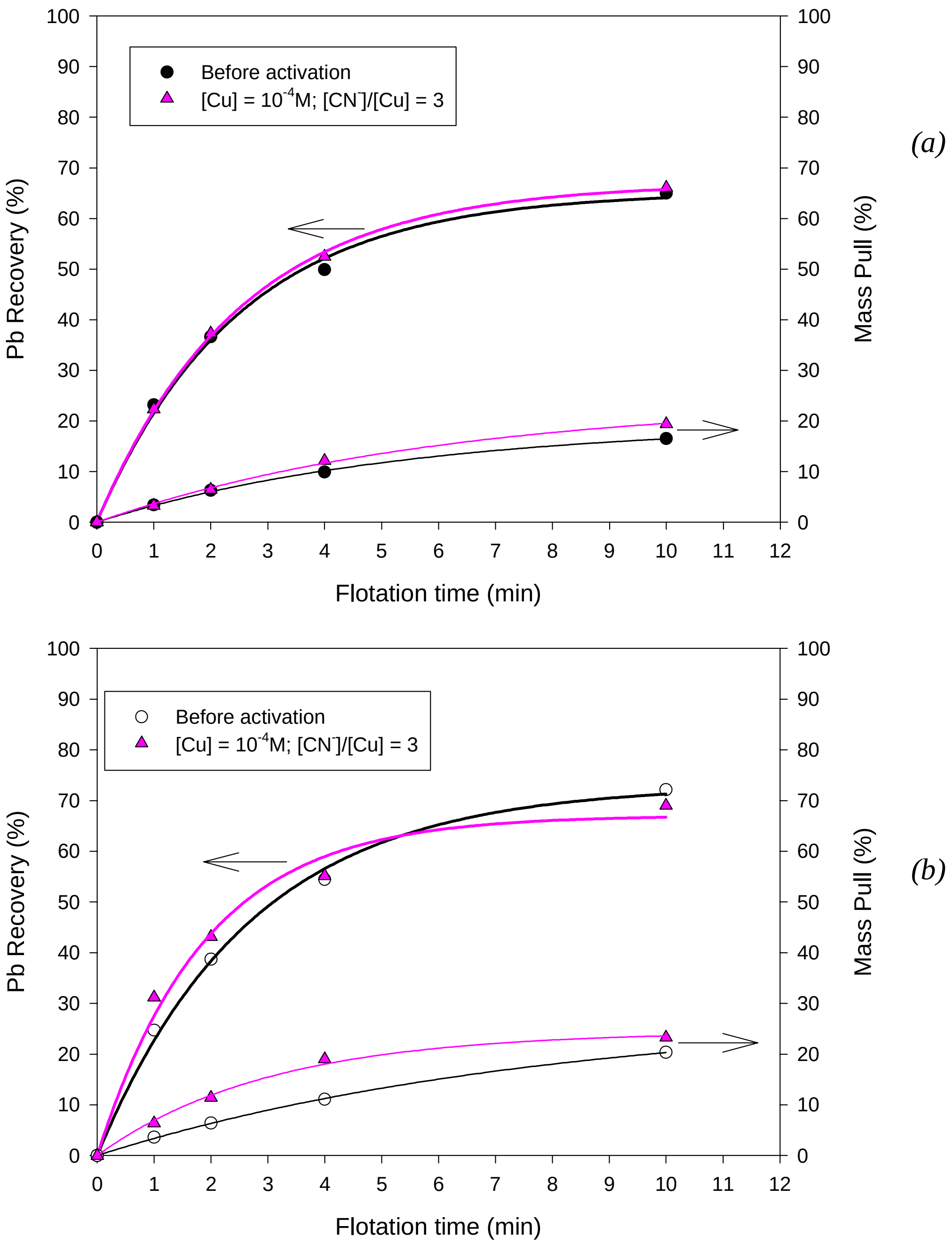


Figure 6.16. Flotation recovery of galena from a Rosh Pinah composite after activation with cuprous cyanide at pH 8.5 and dry milling. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.

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).

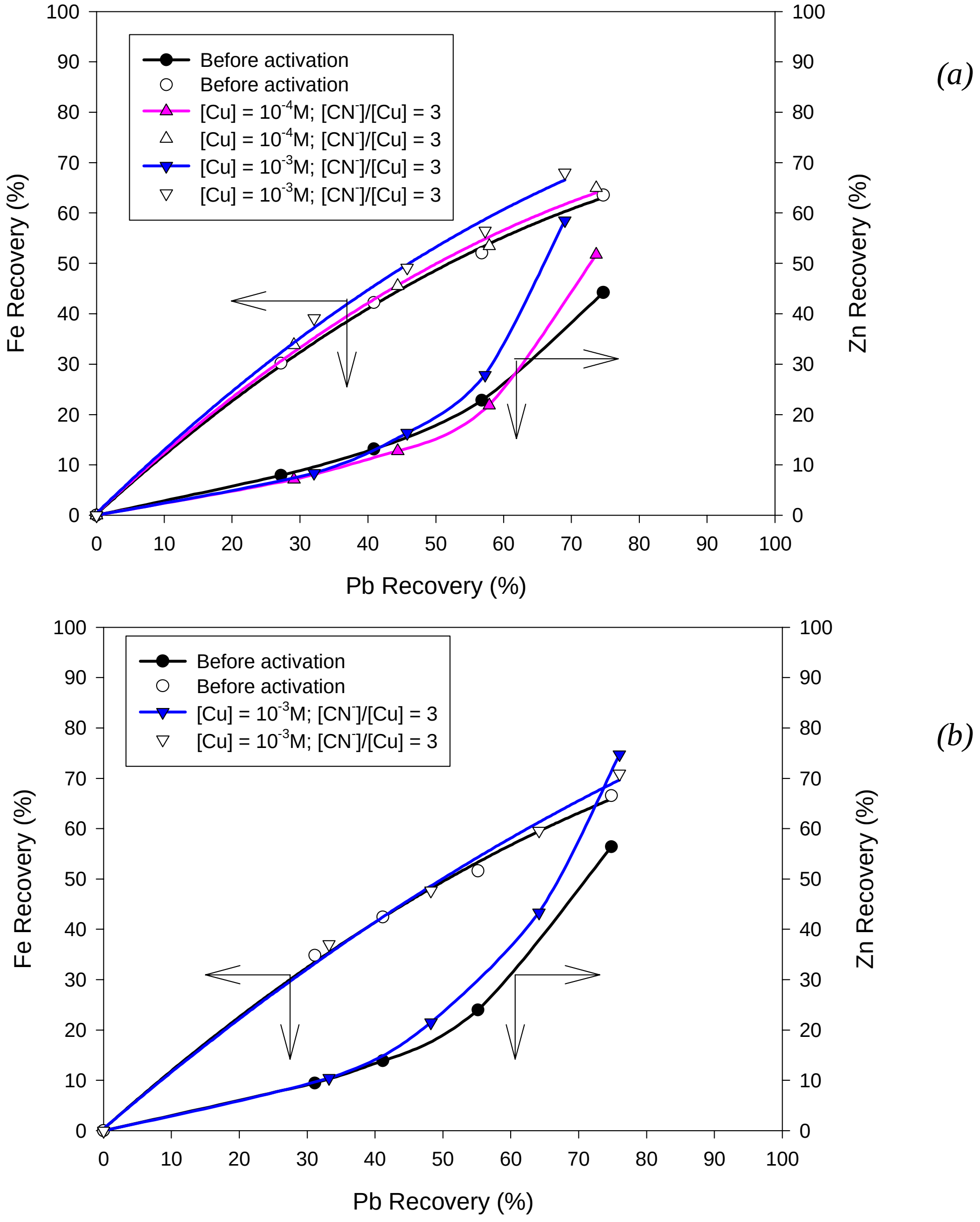


Figure 6.17. Flotation recoveries of Cu(I)- activated sphalerite, galena and iron sulphide for different copper (I) cyanide concentrations and flotation times of 1, 2, 4, and 10 minutes; after wet milling. (a) 50 g/t SNPX, (b) 70 g/t t SNPX

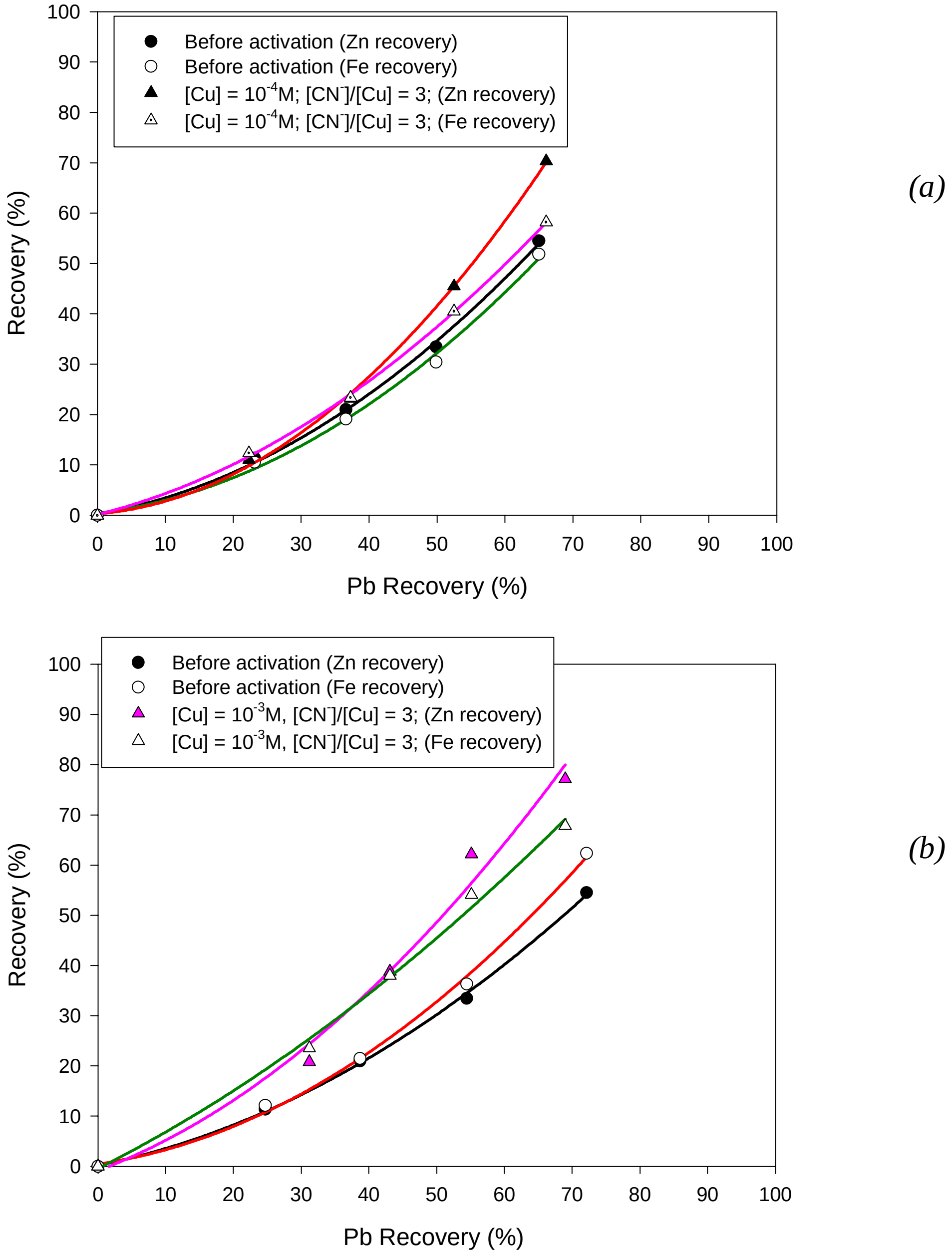


Figure 6.18. Flotation recoveries of Cu(I)- activated sphalerite, galena and iron sulphide for different copper (I) cyanide concentrations and flotation time of 1, 2, 4, and 10 minutes; after dry milling. (a) 50 g/t SNPX, (b) 70 g/t t SNPX. Solid lines represent fitted curves.

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.

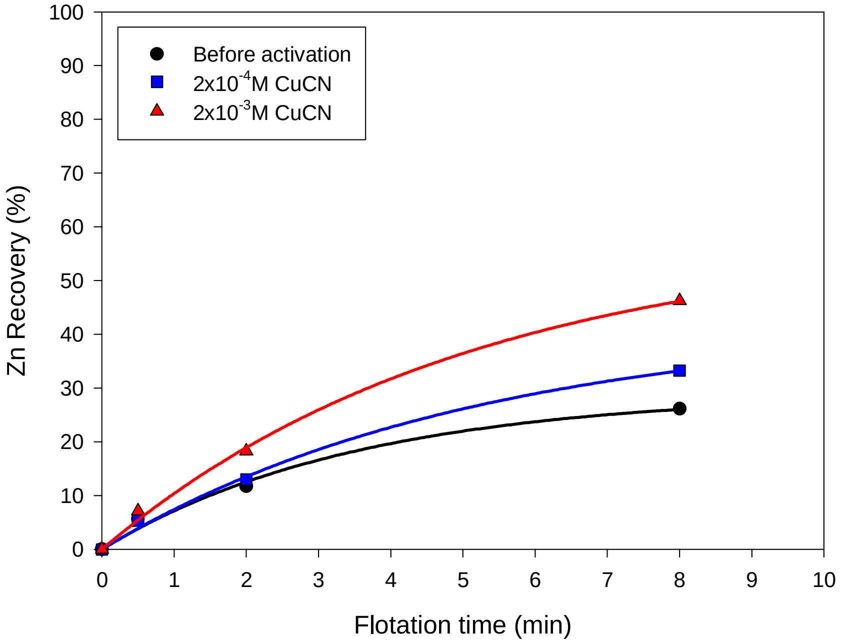


Figure 6.19. Flotation recovery of sphalerite from a dry-milled Rosh Pinah composite at pH 8.5 in the presence of various concentrations of CuCN and 50 g/t SNPX. Solid lines represent fitted curves.

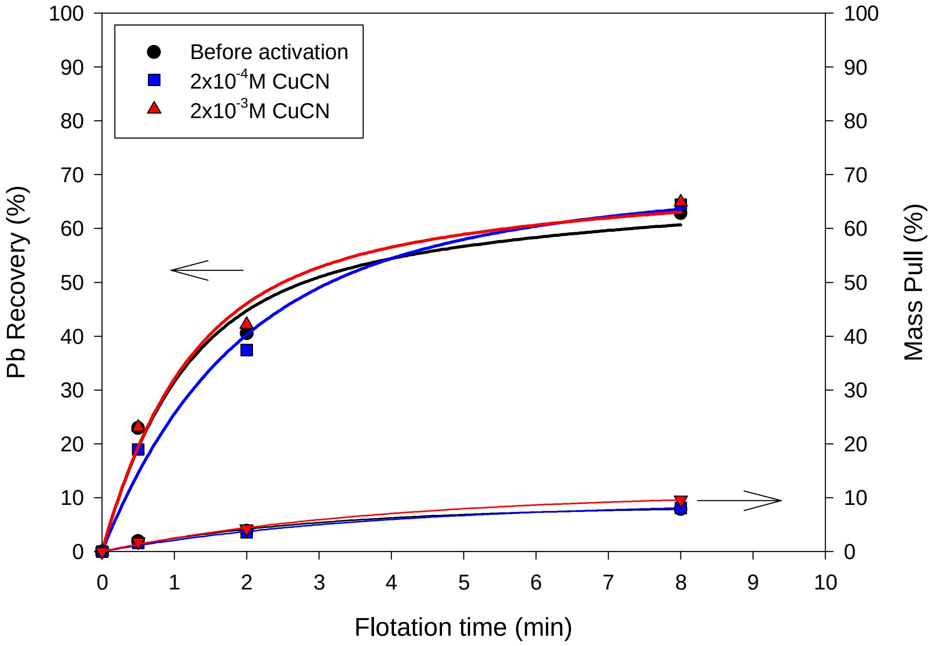


Figure 6.20. Flotation recovery of galena from a dry-milled Rosh Pinah composite in the presence of various concentrations of CuCN and 50 g/t SNPX. Solid lines represent fitted curves.

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

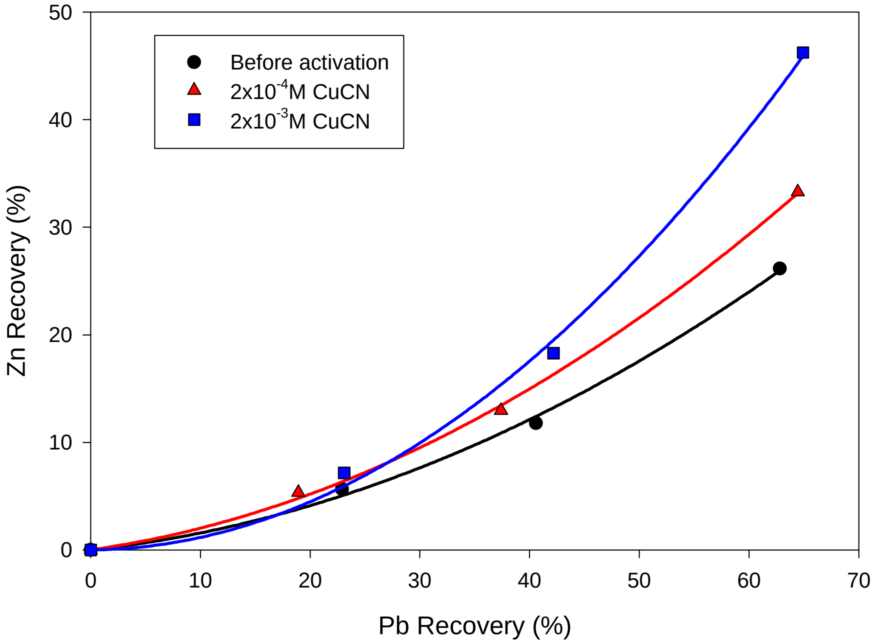


Figure 6.21. Flotation selectivity between galena and sphalerite at pH 8.5 as a function of various concentrations of CuCN and in the presence of 50g/t SNPX. Dry-milled composite.

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.

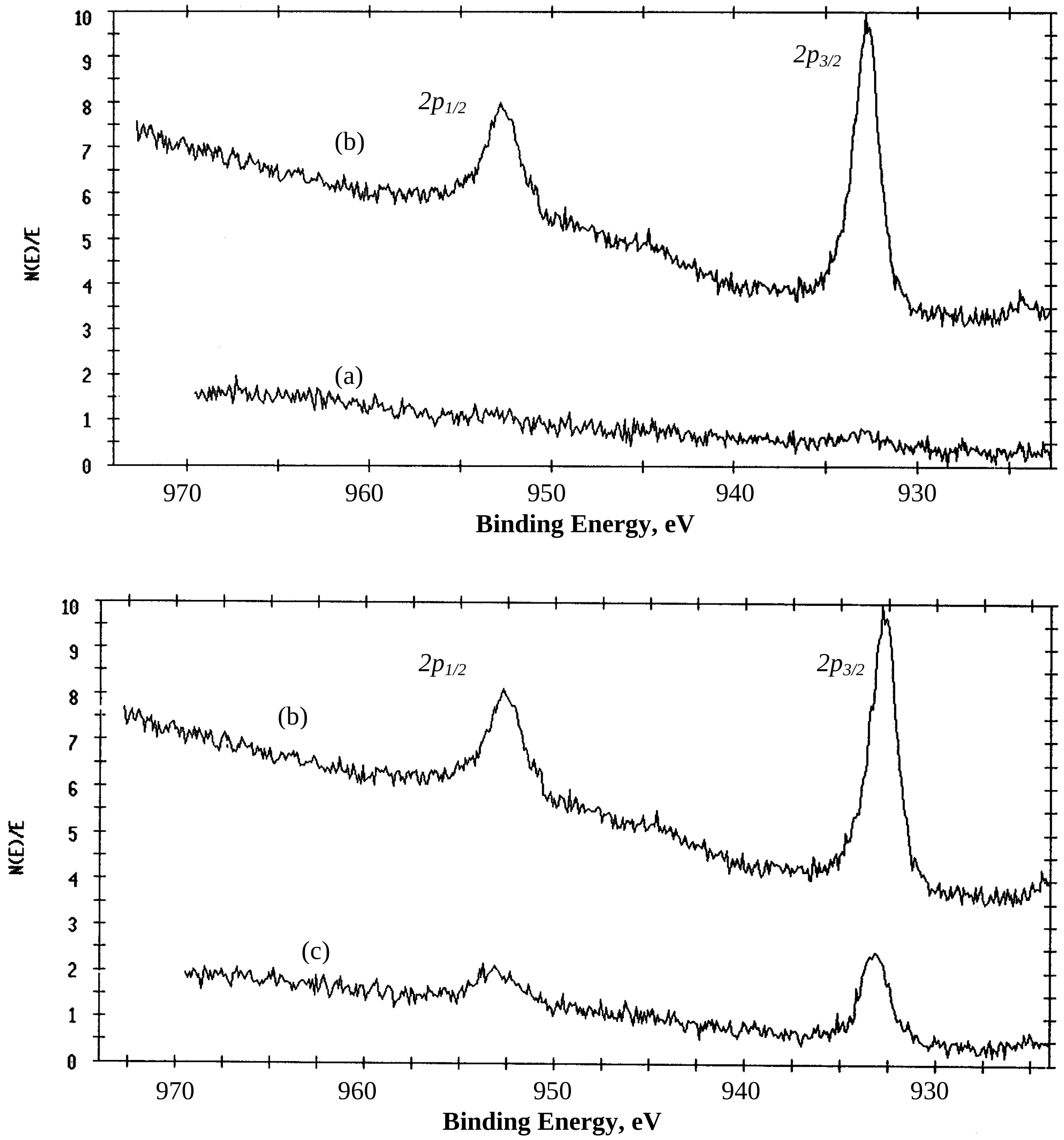


Figure 6.22. Normalised XPS spectra in the Cu 2p binding energy of the sphalerite samples treated with (a) *water (pH 10.5), (b)* 10^{-2} *M Cu(II) from* $Cu(NO_3)_2$ *, (c)* 10^{-2} *M Cu(I) from* $Cu(CN)_x^{(x-1)-}$.

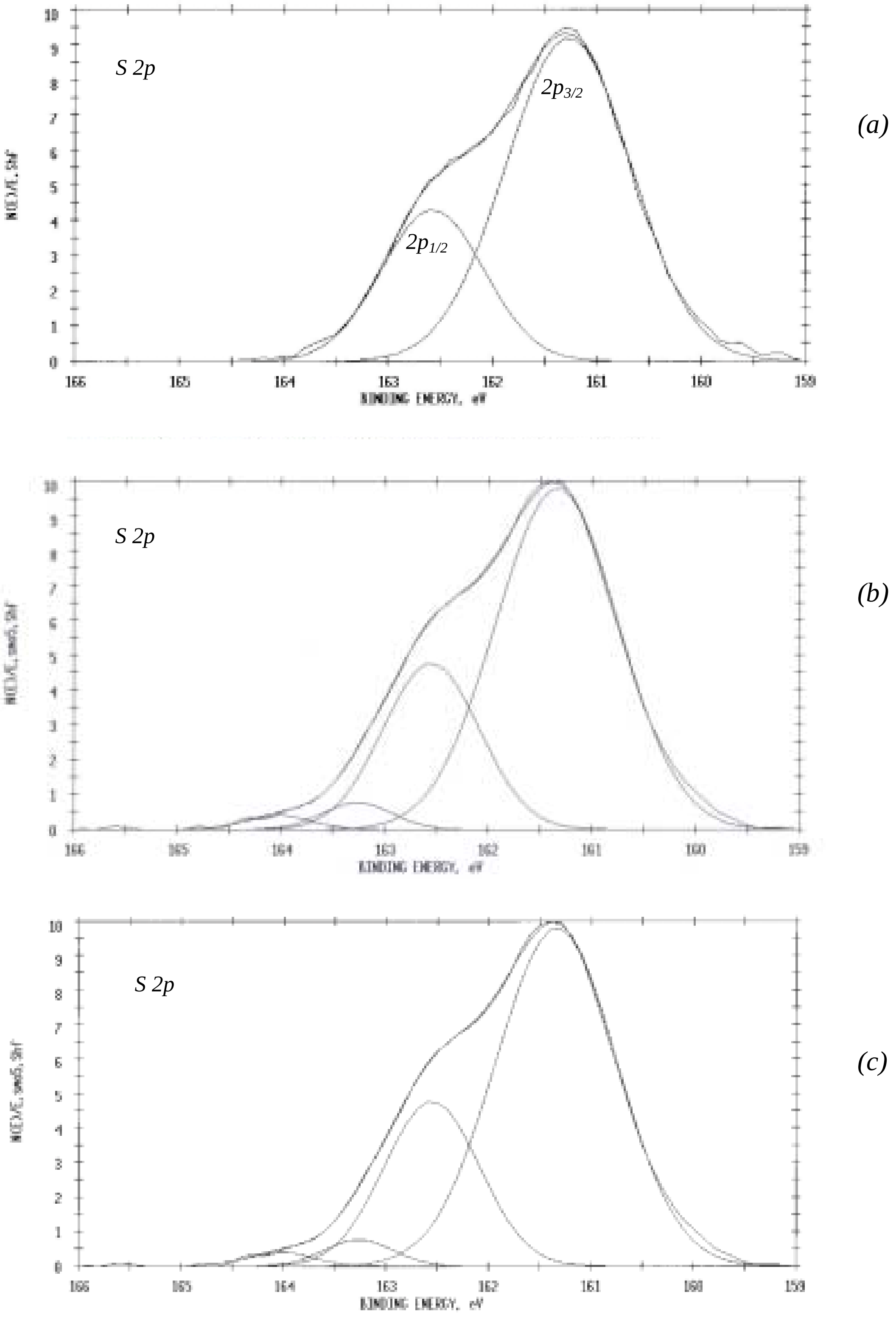


Figure 6.23. XPS spectra in the S 2p binding energy range of the sphalerite samples treated with (a) water (pH 10.5), (b) 10^{-2} M Cu(II) from $Cu(NO_3)_2$, (c) 10^{-2} M Cu(I) from $Cu(CN)_x^{(x-1)-}$.

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.