

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-H₂O system at 25°C is shown in Figure 3.1.

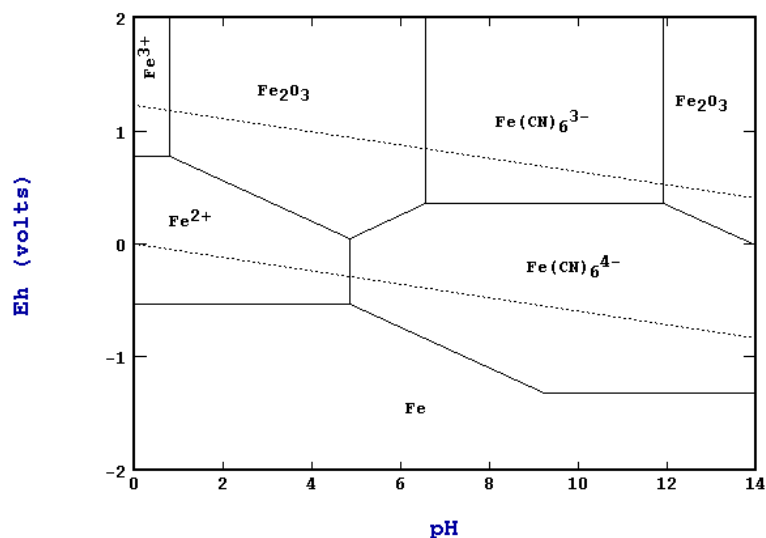


Figure 3.1. Pourbaix diagram of the Fe-CN-H₂O system at 25 °C. $[Fe] = 5 \times 10^{-5} M$, $[CN] = 6 \times 10^{-4} M$. Stabcal software, NBS database (Huang, 2003).

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 ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) onto the surface of pyrite:



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 $\text{Fe}(\text{OH})_3$ 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):



Arbiter (1985) postulated that the cupro-cyanide complex, $\text{Cu}(\text{CN})_2^-$, 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).

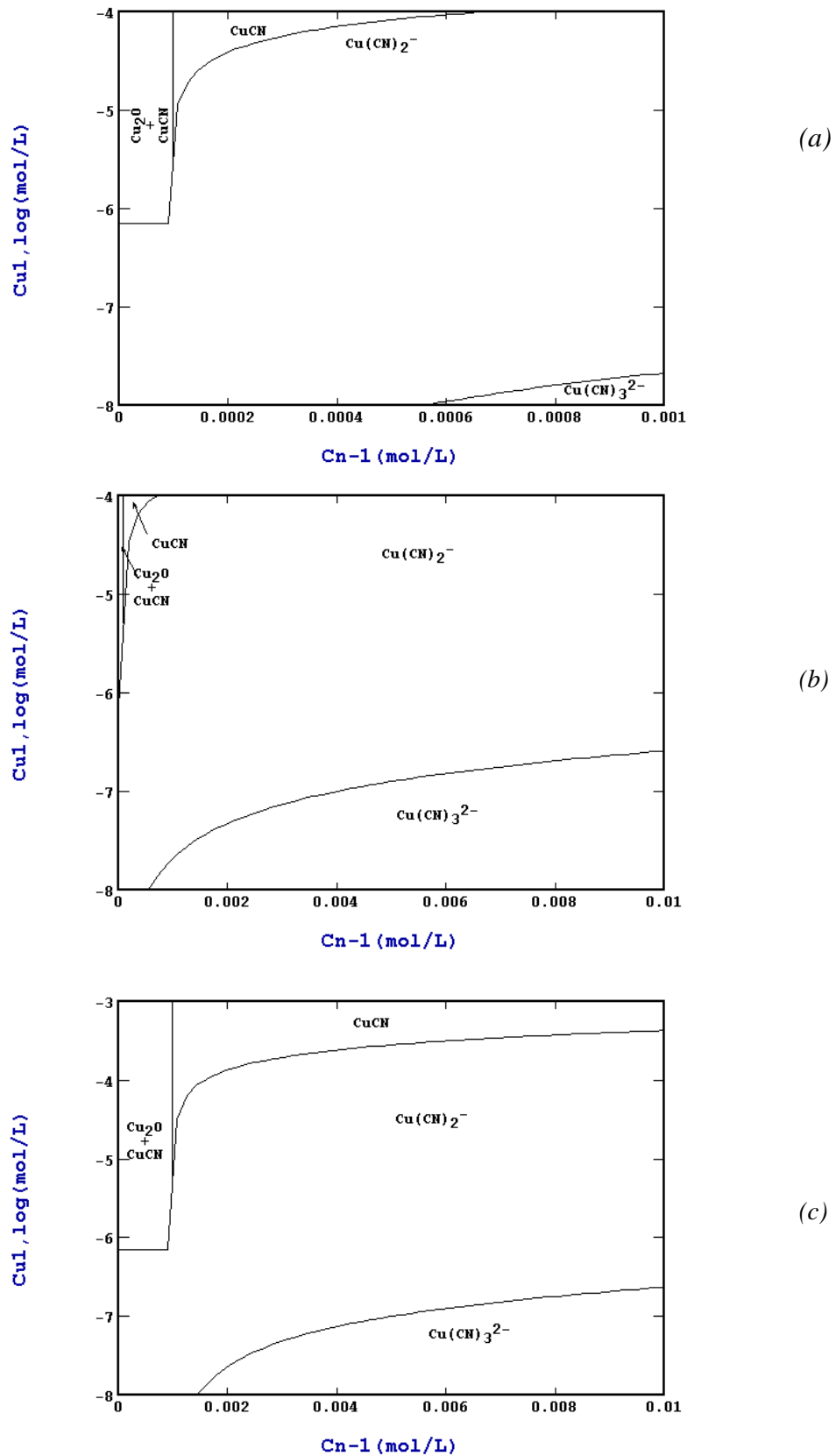


Figure 3.2. Solubility of Cu(I) as a function of cyanide concentration at pH 8 and 25 °C. Total Cu(I) of 10^{-4} M (a and b) and 10^{-3} M (c). Stabal software, NBS database (Huang, 2003). Note different cyanide concentration range in (a), (b) and (c).

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 $\text{Cu}(\text{CN})_2^-$ and $\text{Cu}(\text{CN})_3^{2-}$. For a total copper concentration of 10^{-4}M , the domain of stability of $\text{Cu}(\text{CN})_2^-$ and $\text{Cu}(\text{CN})_3^{2-}$ 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 $\text{Cu}(\text{CN})_2^-$ and $\text{Cu}(\text{CN})_3^{2-}$ 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 $\text{Cu}(\text{CN})_2^-$ and $\text{Cu}(\text{CN})_3^{2-}$ 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.

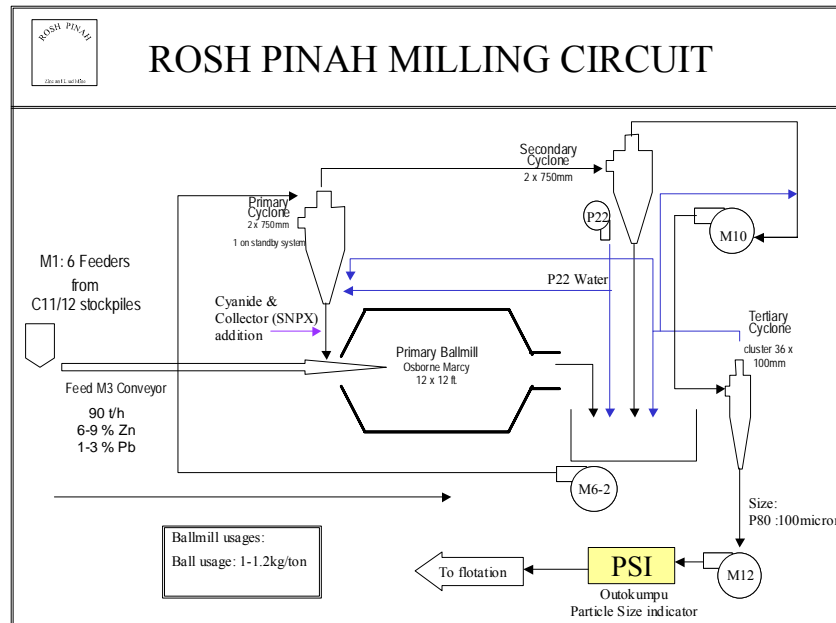


Figure 3.3. Schematic diagram of the milling circuit at Rosh Pinah Mine (Minsiomi, 2001).

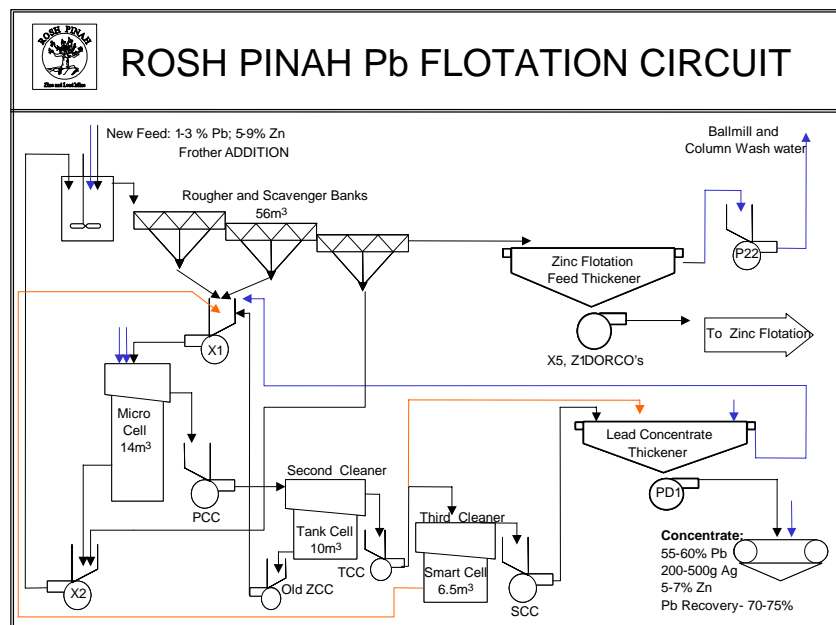


Figure 3.4. Schematic diagram of the lead flotation circuit at Rosh Pinah Mine (Minsiomi, 2001).

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 mg/l	E _H mV	DISSOLVED ION (MG/L)	
			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.

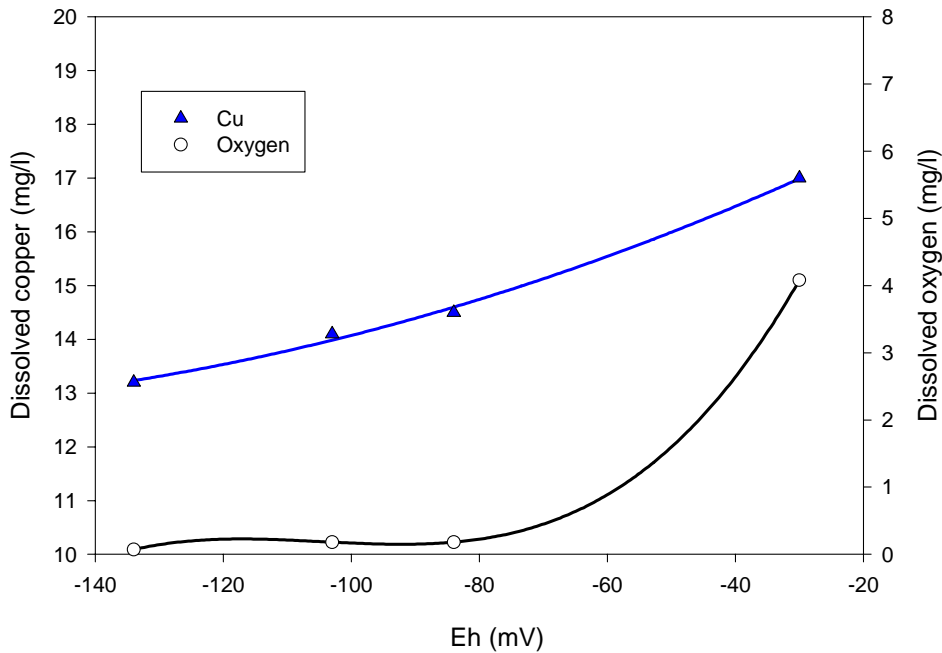


Figure 3.5. Variation of the dissolved copper and dissolved oxygen as functions of the pulp potential at the Rosh Pinah Mine milling circuit. Data of Table 3.3

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 $\text{Cu}(\text{CN})_2^-$ and $\text{Cu}(\text{CN})_3^{2-}$ can be deposited as $\text{Cu}(\text{OH})_2$, 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).

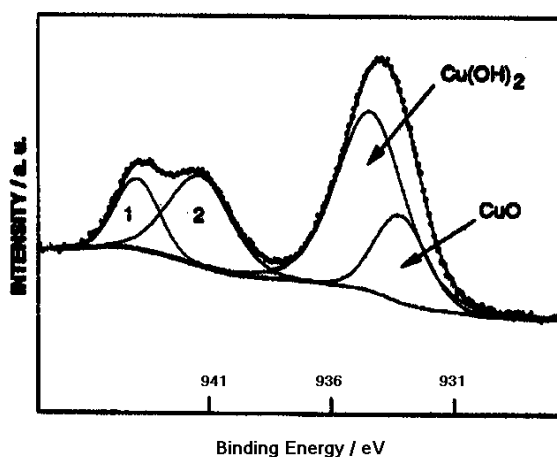


Figure 3.6. Curve fitting of $\text{Cu}2p_{3/2}$ spectrum of Cu/GC electrode just after X-ray irradiation. The copper-glassy carbon (Cu/GC) electrode was obtained by potential cycling between -0.1 and 0.65 V versus SCE in 0.2 M NaOH solution containing 0.5 g/l of $\text{KCu}(\text{CN})_2 + \text{K}_3\text{Cu}(\text{CN})_4$ (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.

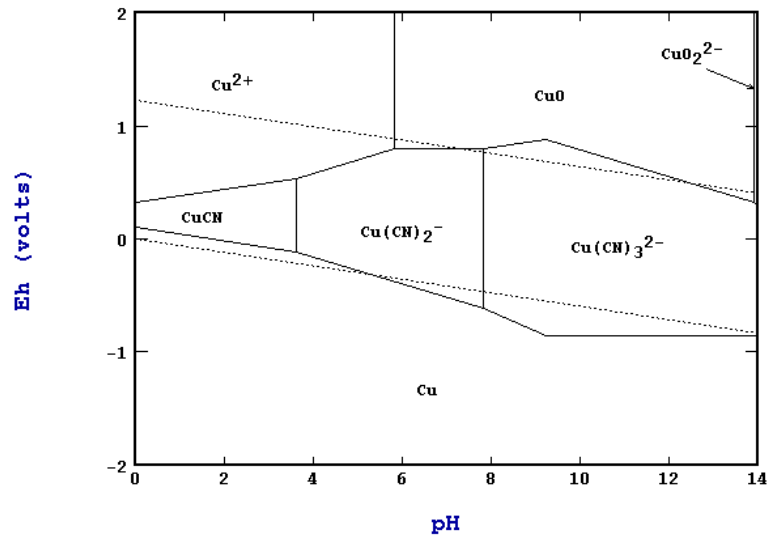


Figure 3.7. Pourbaix diagram of the Cu-CN-H₂O system at 25 °C. [Cu] = 5x10⁻⁵M, [CN] = 6x10⁻⁴M. Stabcal software, NBS database (Huang, 2003).

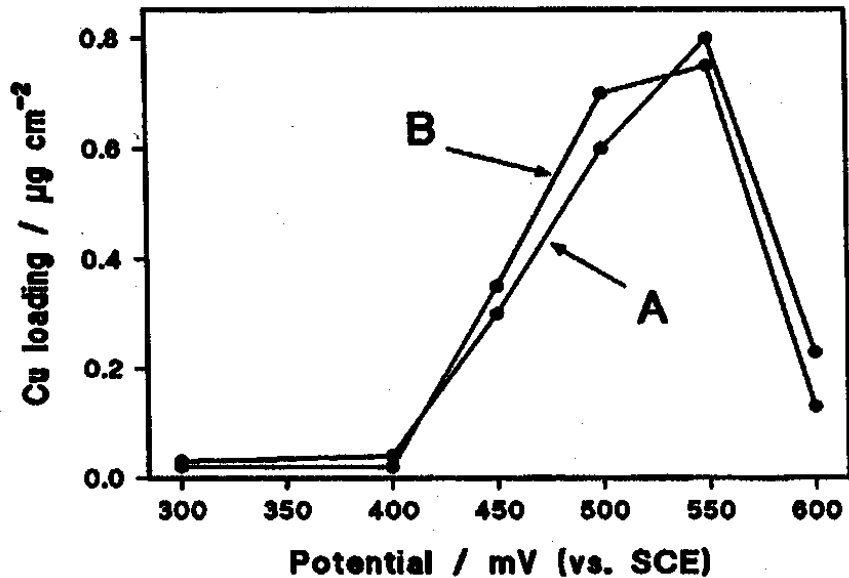


Figure 3.8. Film growth of Cu(II) oxide/hydroxide versus the applied potential at a glassy carbon (A) and platinum (B) electrodes, respectively. Potentiostatic deposition performed in 0.2 M NaOH solution containing 0.5 g/l KCu(CN)₂ + K₃Cu(CN)₄ (Casella and Gatta, 2000).

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



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; Patrick 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 the effect of process water quality on the flotation selectivity between galena and sphalerite. The experimental approach is described in the next chapter.