
CHAPTER 8

ACTIVATION OF PYRITE BY Pb^{2+} and Cu^{2+} IN THE PRESENCE OF CYANIDE

8.1 Introduction

The feed to the flotation circuit at No 2 Gold Plant consists of de-slimed cyanidation tailings. Cyanide acts as a depressant in pyrite flotation (De Wet et al., 1997; O'Connor et al., 1988; Janetski et al., 1977, Elgillani and Fuerstenau, 1968). This effect is partially overcome by oxidation of the cyanide using SO_2 -containing calcine water followed by activation with copper sulphate. Work conducted by Miller (2003) indicated that in the presence of cyanide, Pb^{2+} ions in lead nitrate proved to be a better pyrite activator than Cu^{2+} in copper sulphate. In this section, the two activators are compared using release curves. After addition of $2 \times 10^{-3}M$ (100ppm) sodium cyanide and three minutes of conditioning, the respective activators were dosed at 440mmol/t (equivalent to 70g/t copper sulphate and 145.7g/t lead nitrate). Flotation was carried out at pH 7.2. There was no flotation with either copper or lead addition.

8.2 Results and Discussion

8.2.1 Copper Sulphate

In order to understand the possible mechanisms contributing to the failure of copper sulphate to activate pyrite, it is necessary to review the response of pyrite surfaces to the presence of cyanide and copper (II) ions. The Pourbaix diagram of the Fe-S-CN- H_2O system in Figure 8.1 shows that $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ are the stable species formed at pH 7.2 used in the present study.

Seke (2005) has highlighted that most practical pulp potentials are in the range where the formation of $Fe(CN)_6^{2-}$ is thermodynamically favourable. This implies that when cyanide was dosed to the flotation feed in the experiment, ferrocyanide should have formed. Early work by Elgillani and Fuerstenau (1968) has shown that in the presence of cyanide, the depression of pyrite is a result of the formation of ferrocyanide (equation 4.4) followed by the precipitation of ferric ferrocyanide ($Fe_4[Fe(CN)_6]_3$) on the sulphide surface.

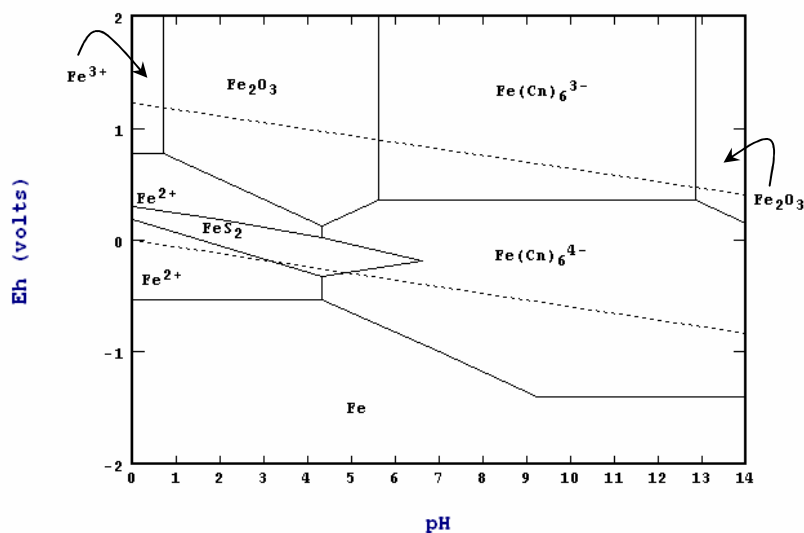
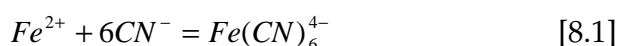


Figure 8.1 A Pourbaix diagram for the Fe-S-CN-H₂O system drawn using STABCAL software for $10^{-4}M [S]$, $10^{-4}M [Fe]$ and $2 \times 10^{-3}M [CN^{-}]$, NBS Database

The speciation of copper (II) at different pH values is shown in Figure 8.2. It is clear that at around pH 7, approximately 70% of the copper is available in the form of Cu^{2+} while the balance exists as aqueous $Cu(OH)_2$ and a very small proportion in complex form: $CuOH^{+}$. Since Cu^{2+} makes up the largest proportion, it is bound to have a strong influence on the behaviour of copper (II) at the flotation pH used in the experiment.

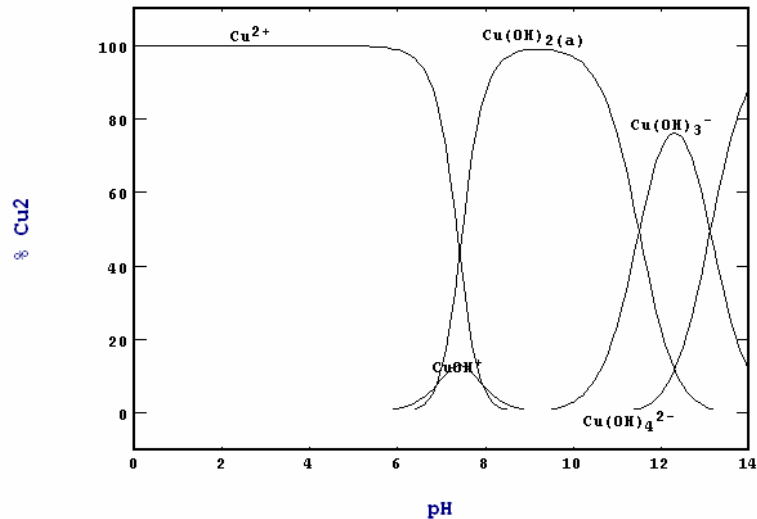
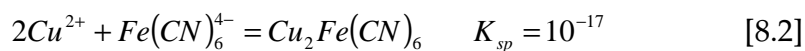


Figure 8.2 Copper (II) speciation at different pH values. Diagram drawn using STABCAL Software for $2 \times 10^{-4}M [Cu^{2+}]$, NBS Database

Reference has been made to the formation of ferrocyanide at E_h -pH conditions typical of most pyrite flotation circuits. Any interaction between Cu^{2+} and the iron cyanide complex is likely to affect the capacity of copper sulphate to activate pyrite. In the work conducted by Bellomo (1970), titration of copper (II) with ferrocyanide yielded a reddish brown precipitate of $Cu_2Fe(CN)_6$ according to:



Bellomo (1970) also showed that the copper ferrocyanide precipitate formed has a solubility of $2 \times 10^{-6} M$ and its formation was accompanied by a change in standard free energy of $-75kJ/mol$. This present work tested $2 \times 10^{-4}M$ copper sulphate. Considering the negative free energy change, it is reasonable to assume that copper ferrocyanide was formed spontaneously when copper sulphate was dosed to the flotation slurry. Since the resulting concentration of copper (II) was greater than the solubility, some of the salt formed should have precipitated. This shows that copper sulphate dosed was consumed in the formation of copper ferrocyanide salt so that none was available to adsorb

on pyrite and activate it. Consequently, xanthate could not adsorb and pyrite could not float.

Addition of copper sulphate to flotation streams treating cyanidation tailings has been reported to enhance pyrite recovery through formation of copper-cyanide complexes (O'connor et al., 1988). These eliminate free cyanide so that it cannot depress pyrite. Westwood and co-workers (1970) have however emphasised that treatment with copper sulphate alone is not sufficient to render pyrite floatable. This is consistent with the findings of this present work where $2 \times 10^{-4}M$ copper (II) failed to activate pyrite in the presence of $2 \times 10^{-3}M$ sodium cyanide. The authors also mentioned that low pH treatment is essential for pyrite to float. It is most likely that the low pH destroys cyanide through hydrolysis; completely eliminating ferrocyanide (Figure 8.1) so that copper (II) can adsorb and activate pyrite without any interference from complex ion formation. Since Elgillani and Fuerstenau (1968) proposed that precipitation of ferric ferrocyanide in flotation pulps containing cyanide depresses pyrite, there is a possibility that copper ferrocyanide has a similar effect. Given that gold and uranium are hosted by pyrite, their flotation responses are bound to be affected as well.

8.2.2 Lead Nitrate

The complete depression of pyrite observed despite the dosage of 0.44mol/t lead nitrate (equivalent to $2 \times 10^{-4}M$ Pb^{2+}) activator can possibly be understood by studying the speciation of lead (II) at the flotation pH of 7.2. Figure 8.3 shows that at around pH 7, approximately 80% of lead (II) at the concentration dosed in the experiment [$2 \times 10^{-4}M$] exists in the form of $PbOH^+$ and only about 20% as Pb^{2+} . Because lead (II) does not interact with cyanide (Miller, 2003), the probability that it will activate pyrite essentially depends on the dominant species: $PbOH^+$. Since complete depression of pyrite was

observed in the experiment, it appears that this species is incapable of activating pyrite.

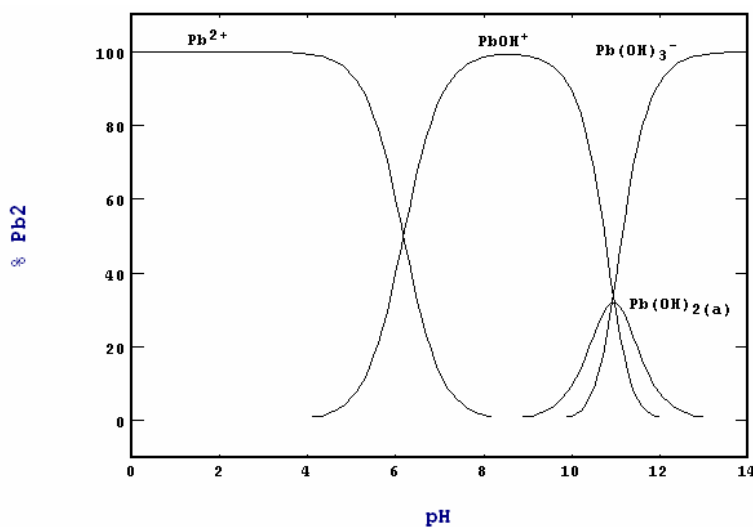
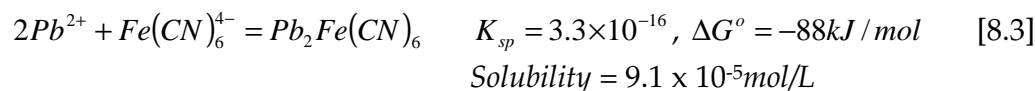


Figure 8.3 Lead (II) speciation at $2 \times 10^{-4}M [Pb^{2+}]$. Diagram drawn with STABCAL software, NBS database

Electrochemically controlled contact angle measurements by Miller (2003) on pyrite using potassium amyl xanthate in the presence of cyanide showed high contact angles in lead nitrate-treated pyrite compared to untreated sulphide. This work was conducted at pH 4.7 and from Figure 8.3; almost 100% of lead (II) is as a cation (Pb^{2+}). It appears that for lead (II) to activate pyrite, it is essential that it must be in this form. In view of this background, the flotation experiment was repeated at pH 5.5. Approximately 90% of lead (II) would be in the form: Pb^{2+} (Figure 8.3) and 100% of copper (II) as Cu^{2+} (Figure 8.2). Viljoen (1998) has shown that SIBX has a half life of 63.2 hours at pH 6 so that at pH 5.5, there is little risk of collector losses through hydrolysis. As in Cu^{2+} , Bellomo (1970) reported that Pb^{2+} reacts with ferrocyanide to give $Pb_2Fe(CN)_6$, a white powdery precipitate soluble in strong acids and bases.



The author however noted that the kinetics of the reaction are very slow at room temperature so that its effects might be insignificant within the time frame of the flotation experiment.

8.2.3 Copper Sulphate at pH 5.5

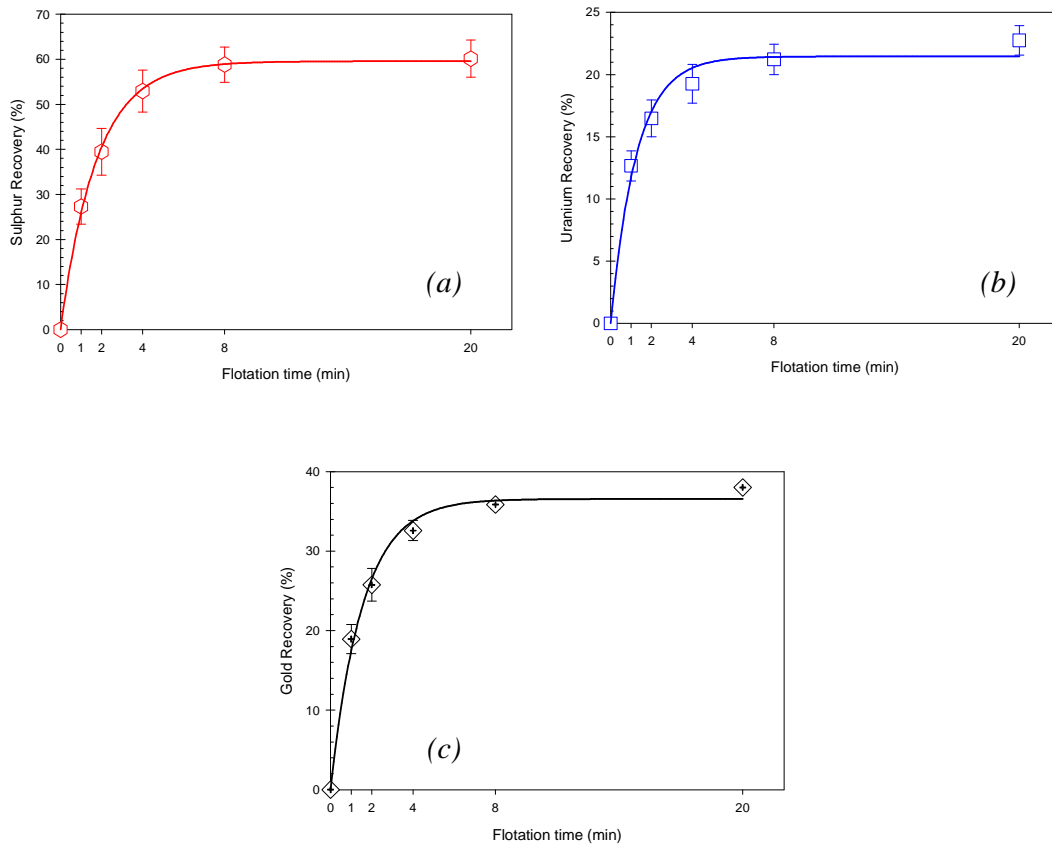
Flotation at pH 5.5 using 0.44mol/t copper sulphate as an activator in the presence of 100ppm cyanide still failed to recover pyrite. There was no froth build-up and any bubbles formed were barren and they broke down as soon as they reached the surface. Throughout conditioning, cyanide could still be smelled from the flotation pulp. Examination of the Pourbaix diagram of the Fe-S-CN-H₂O system in Figure 8.1 shows that flotation at pH 5.5 was still in the Eh-pH conditions where ferrocyanide is stable. It appears that the pH 5.5 was not low enough to destroy cyanide through hydrolysis and stabilize the ferrous ion. This means that the mechanisms thought to be operative at pH 7.2 presented earlier still dominated the flotation experiment. The presence of cyanide is so detrimental to pyrite flotation that standard practice at No 2 Gold Plant is to keep its concentration below 4ppm (Brooks, 2005).

8.2.4 Lead Nitrate at pH 5.5

The flotation responses for sulphur gold and uranium following flotation at pH 5.5 with lead nitrate as an activator are shown in Table 8.1 and Figure 8.4. The lack of interaction between the lead (II) in cationic form (Pb^{2+}) and cyanide enabled it to adsorb onto pyrite so that it was amenable to xanthate adsorption, and hence floatable (Miller 2003). The nature of the xanthate species formed on adsorption of SIBX is essentially dixanthogen (Sui *et al.*, 1997).

Table 8.1 Sulphur, gold and uranium flotation responses recorded following activation with lead nitrate in the presence of cyanide at pH 5.5

Component	Activator	k (min^{-1})	R_{max} (%)	R^2
Sulphur	Lead nitrate	0.57	59.54	0.9990
	Copper sulphate	0.00	0.00	0.0000
Uranium	Lead nitrate	0.79	21.40	0.9870
	Copper sulphate	0.00	0.00	0.0000
Gold	Lead nitrate	0.57	59.54	0.9990
	Copper sulphate	0.00	0.00	0.0000

**Figure 8.4** (a) Sulphur (b) uranium and (c) gold recovery-time graphs recorded for flotation with 440mmol/t $Pb(NO_3)_2$ in the presence of 0.001M NaCN at pH 5.5

8.2.5 Conclusions

In the presence of 100ppm sodium cyanide, and pH 5.5 lead (II) recovered sulphur, gold and uranium but copper (II) did not. Therefore the Pb^{2+} cation was necessary for activation.

The destruction of cyanide at No 2 Gold Plant is based on the INCO SO_2 /AIR process. This not only enhances the flotation of pyrite, it also removes the poisonous chemical from the system so that tailings from the flotation circuit can be dumped without any risk of contaminating the environment. Substitution of copper sulphate with lead nitrate means that the tailings will still contain cyanide and this will pose a serious environmental problem. A plan to destroy cyanide before the tailings leave the plant will have to be put in place. Whether lead nitrate is a better activator than copper sulphate therefore depends on whether any improvements in flotation performance outweigh the cost of setting up extra facilities to handle cyanide from tailings.