Chapter 4. Experimental

4.1. Materials, reagents and solutions

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

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

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

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

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

4.2. Flotation

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

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

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

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

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

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

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

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

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

4.3. X-ray photoelectron spectroscopy

4.3.1. Activation of sphalerite with Pb(II) ions

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

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

4.3.2. Copper activation and deactivation of sphalerite

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

4.4. Fourier transform infrared spectroscopy

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

4.5. Scanning electron microscopy (SEM)

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