

EXPERIMENTAL**Chapter
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3.1 Experimental approach

The extent and mechanism of the Activox[®] process can be investigated by using the two basic techniques of, in the first place ultra fine milling and subsequently pressure-acid leaching.

3.1.1 Ultra fine milling

Mechanical activation, usually done via energetic milling, enhances the leaching efficiency by changing the physicochemical properties, leading to an increase of surface area and reactivity of the sulphide concentrate (Amer, 1995:225).

In this experiment, the sulphide concentrate was mechanical ground to a desired particle target size of 80% - 10 μm . Samples of the ground slurry were collected and size analysis was conducted on the ground product to determine the relationship between grind time and resulting grind size. From these results the grind time required to produce the target grind size (80% - 10 μm) was established.

3.1.2 Activox[®] tests (pressure-acid leaching)

This approach consists of the selective dissolution of nickel, copper and cobalt from a iron containing sulphide concentrate by means of pressure leaching in the presence of oxygen and sulphuric acid.

The effect of *leaching time, percentage solids, temperature, sulphuric acid concentration, oxygen partial pressure, aeration and agitation* upon the leaching of the mechanical ground sulphide concentrate was investigated in order to determine the optimum conditions under which the nickel, copper and cobalt could be extracted from the massive sulphide ore. The samples were submitted for *AA, SEM, sulphur and Mössbauer* analysis.

3.2 Materials and chemical reagents

In section 3.2 the specific sulphide concentrate, materials used for experimental work and the specifications of the chemical reagents is described.

3.2.1 Test concentrate used for experimental investigation

The ultra fine milling and the pressure-acid leaching test work were performed on a Nkomati nickel-copper-cobalt sulphide concentrate from the Nkomati project, undertaken by Avmin (Anglovaal Mining Limited) in South Africa.

The concentrate consisted mainly of the minerals pentlandite ($(\text{FeNi})_9\text{S}_8$), pyrrhotite (Fe_{1-x}S), chalcopyrite (CuFeS_2) and traces of pyrite (FeS_2) which was identified in an unpublished thesis on the geology of the area. Elemental assays were performed on the concentrate at the Nkomati mine and are shown in Table 3.1. The concentrate was received dry and 80% of the particles were smaller than 62 μm according to Malvern size analyses conducted by the University of Potchefstroom.

Table 3.1 Elemental assay of the Nkomati concentrate

Element	Percentage present
Nickel (Ni)	10.11
Cobalt (Co)	0.39
Copper (Cu)	7.05
Iron (Fe)	38.85
Total sulphur (S)	32.90

3.2.2 Equipment and materials used for ultra fine milling experiments

The Svedala Laboratory Stirred Media Detritor (see Figure 3.1) consists of a pot mounted on a rotating baseplate located on a swivel table. A geared motor above the pot rotated a stirrer within the pot. The rotational torque was measured by a load cell and is transmitted to the integrated totaliser and rate display unit. Table 3.2 represents the Svedala Stirred Media Detritor specifications.

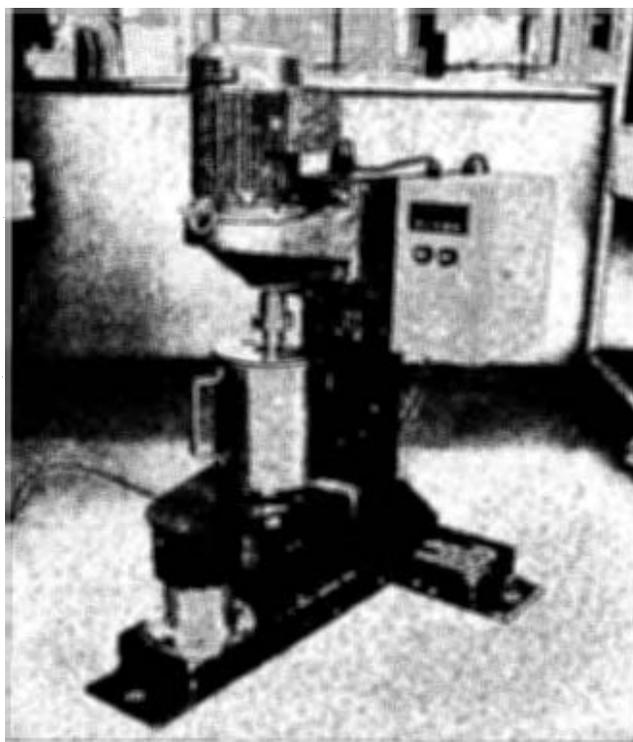


Figure 3.1 Photograph representing the Svedala Laboratory Stirred Media Detritor

Table 3.2 Specifications of the Svedala Stirred Media Detritor

Specification	Unit size
Voltage	415 volts
Frequency	50 Hertz
Load current	2 amps
Mill speed	555 r.p.m.
Working capacity	1400 ml

The Svedala Stirred Media Detritor was constructed of stainless steel with a thick rubber lining. As shown in Figure 3.2, the rotor was composed of crossed rubber bars at the bottom of the shaft. Mixed ceramic balls of approximately 5 and 2 mm were used as grinding media in all tests (see Figure 3.3).

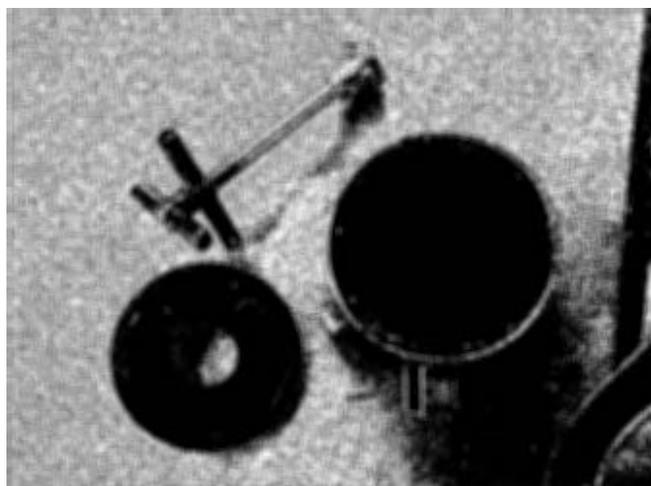


Figure 3.2 Photograph of the Stirred Media Detritor pot and stirrer

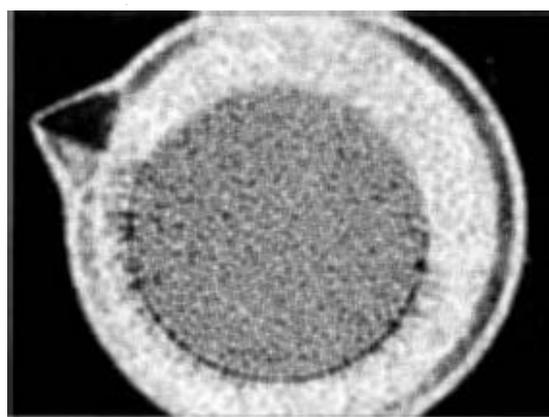
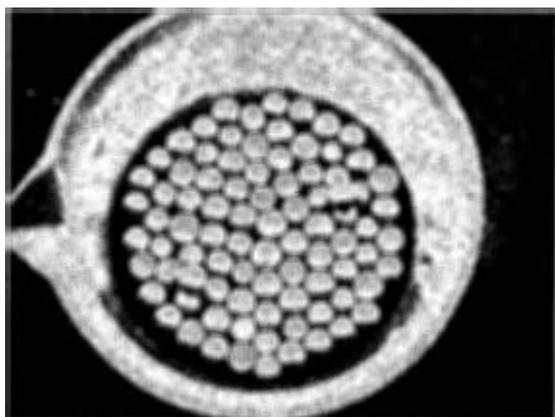


Figure 3.3 Photograph showing the grinding media consisting of ceramic balls with diameters of 5mm and 2mm respectively

3.2.3 Equipment and materials used for the Activox[®] tests

The laboratory autoclave was constructed of 904 L Austenitic stainless steel containing 0.02% carbon, 1.0% silicon, 21% chromium, 24.5% nickel and 4.5% molybdenum. The agitator shaft was composed of 316 stainless steel and the two impellers from Ertelon. The agitator shaft as well as the sampling dip tube were coated with a teflon (PTFE) layer to protect the metal from the acid conditions inside the vessel. Figure 3.4 illustrates the experimental set-up used to perform the Activox[®] testwork.

The inside of the reactor is shown in Figure 3.5. The gas inlet and sampling dip tube have separate valves but are connected to the same tube to ensure that the slurry in the tube, after sampling, is purged back into the vessel.

The heating element was situated around the outside of the vessel, inside a stainless steel water jacket. The heating and cooling mechanisms were provided to control the exothermic reaction. The complete autoclave, or leaching vessel, with a working volume of 2 litre was situated inside a steel frame to facilitate the complete experimental set-up. A detailed schematic diagram of the experimental set-up is presented in Figure 3.6.

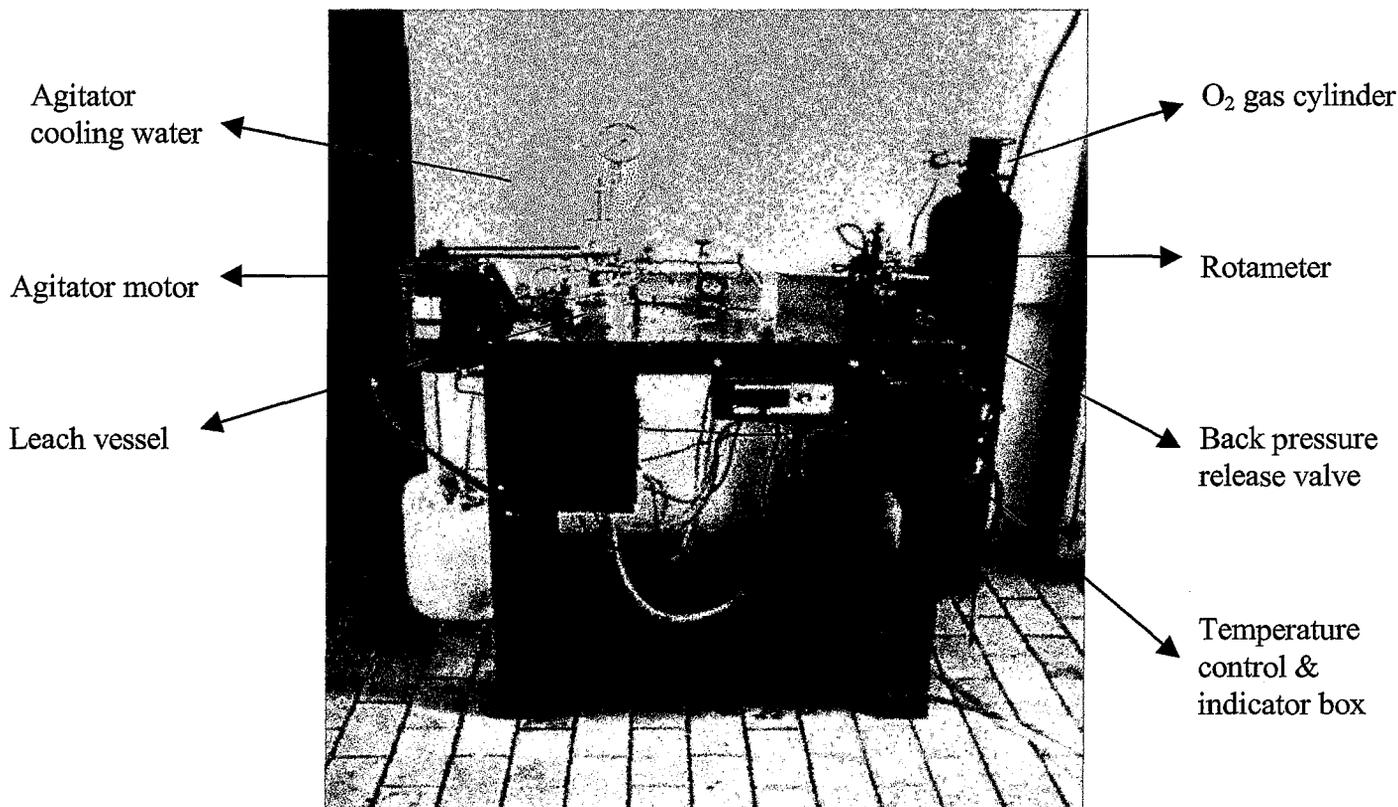


Figure 3.4 Photograph of the experimental set-up for Activox[®] testwork

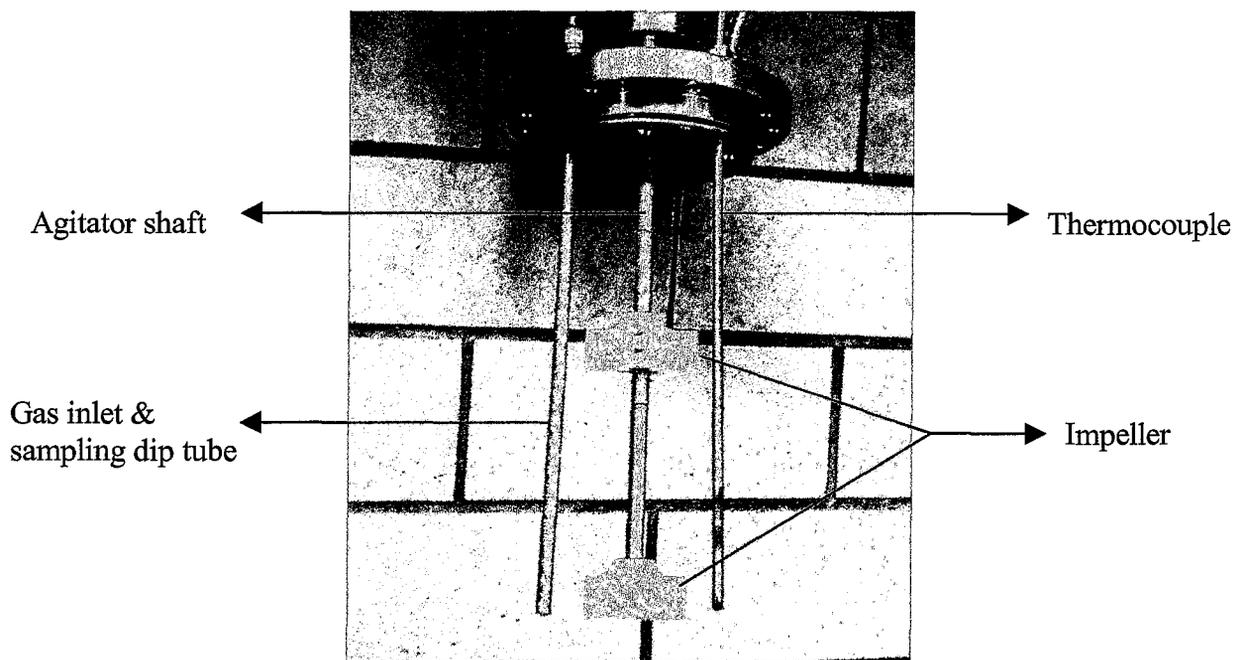


Figure 3.5 Photograph representing the inside of the leach reactor

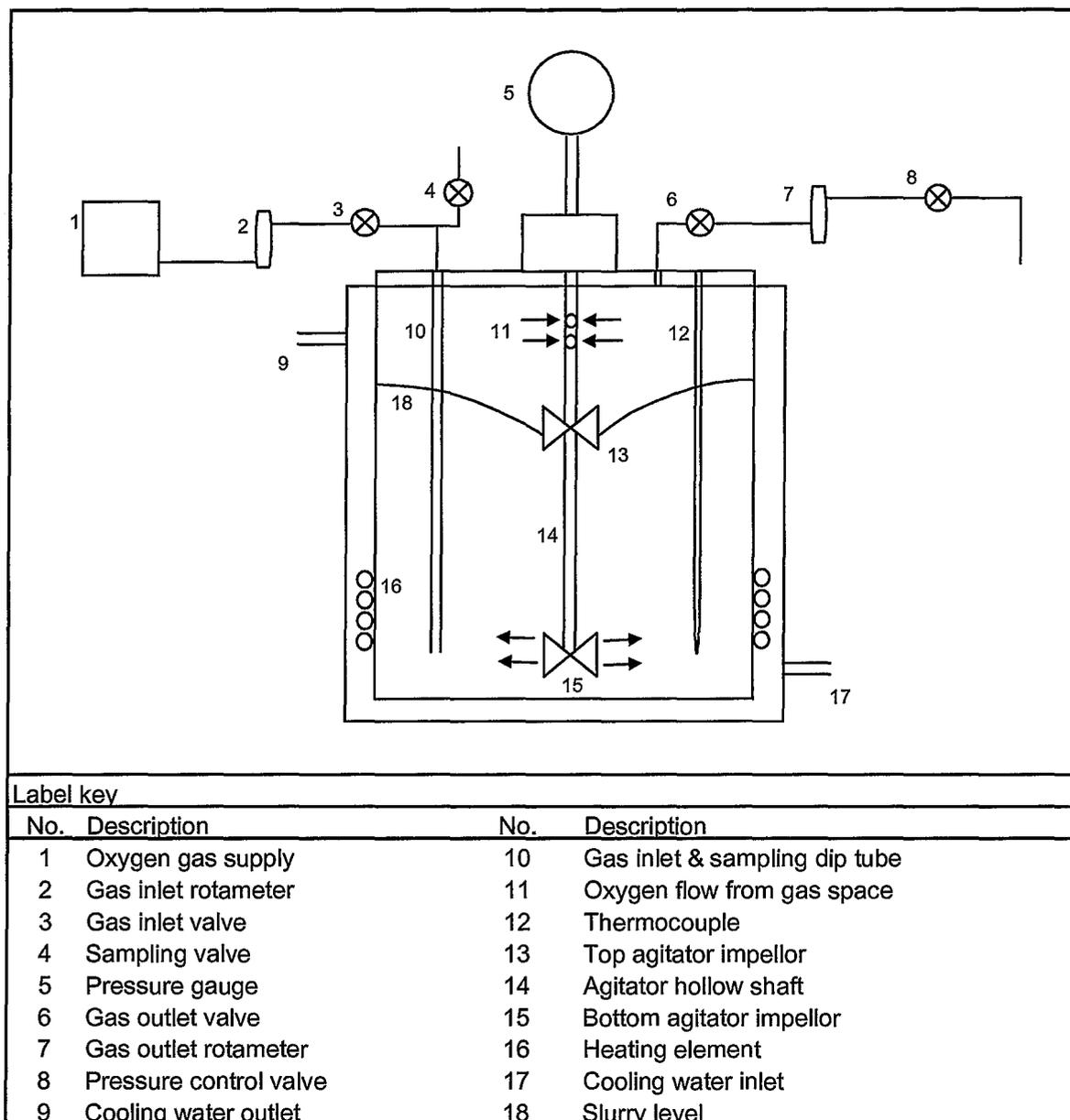


Figure 3.6 Schematic diagram of the experimental set-up for Activox[®] testwork

3.2.4 Chemical reagents used during the experimental testwork

The chemicals used during the investigation are listed in Table 3.3. The reagents were used without any further purification.

Table 3.3 Physical properties of chemical reagents

Chemical	Chemical composition	Supplier	Grade
Sulphuric acid	H ₂ SO ₄	Chemworld	98 %
Hydrochloric acid	HCl	Merck	33 %
Nitric acid	HNO ₃	Halpro Lovasz	55 %
Silver nitrate	AgNO ₃	PAL chemical	99.9 %
Oxygen	O ₂	Afrox	90-95 %

3.2.5 Elemental analysis of the water used for experimental testwork

All milling as well as leach experiments were conducted with normal Potchefstroom tap water. The chemical analysis of the water is shown in Table 3.4.

Table 3.4 Elemental analysis of tap water

Analysis	Result	Analysis	Result
Aluminium	0.05-0.06 mg/l	Manganese	0.005 mg/l
Barium	0.01-0.02 mg/l	Mercury	0 mg/l
Boron	0.005 mg/l	Molybdenum	0.0002 mg/l
Cadmium	0.0005 mg/l	Nickel	0.004 mg/l
Calcium	50 mg/l	Silver	0 mg/l
Chromium	0.006 mg/l	Strontium	0.05 mg/l
Chlorine	0.2-0.3 mg/l	Sulphur	32 mg/l
Cobalt	0.001 mg/l	Thallium	0 mg/l
Copper	0.005 mg/l	Titanium	0.008 mg/l
Iron	0.1-0.2 mg/l	Uranium	0.001 mg/l
Lead	0.001 mg/l	Vanadium	0.0004 mg/l
Lithium	0.001 mg/l	Zinc	0.06 mg/l
Magnesium	35-40 mg/l	Zirconium	0 mg/l

3.3 Experimental procedure

In order to ensure reliable results, a detailed experimental design and process measures are necessary prior to any testwork. This section involves the experimental procedure followed to perform the ultra fine milling and Activox[®] tests.

3.3.1 Experimental procedure for the ultra fine milling

The total charge volume of the mill is 1400 ml. The ratio of solids to liquid was 40% by mass and slurry to media was 50% by volume. To maintain a working capacity of 1400 ml, 402 g of the as-received concentrate was mixed with 599 ml of tap water, which ensured that 40% solids were present. After the slurry was allowed to mix for approximately two minutes, 1890 g of the ceramic media were then added and the reset button was pressed to reset the work input display. The slurry was then ground for one hour and samples were taken at 5, 10, 20, 30, 40, 50 and 60 minutes respectively. Size analyses, by means of Malvern laser sizer facilitated at the University of Potchefstroom, was conducted on the ground product to determine the relationship between grind time and resulting grind size. The results (particle size distribution curves) are presented in Appendix A.

From these results the grind time required to produce the target grind sizes of 80%-10 μm particles was found to be 30 minutes. The rest of the as-received concentrate was milled just prior to the leaching tests for this determined period. The pot content was screened to remove the grinding media, once the milling was completed. The 80%-10 μm product was filtered and the filter cake was split into 200g (dry mass) batches and transferred to the leach reactor.

3.3.2 Experimental procedure for the Activox[®] tests

From the preceding literature study, it was possible to compile the experimental design parameters, for the different leaching variables, from which the pressure-acid leaching tests were done (see Table 3.5).

Table 3.5 Experimental variables and ranges used for the present pressure-acid leach tests

Variable	Amount
Temperature	90 – 120 °C
Oxygen partial pressure	4 – 13 bar
Percentage solids	5 – 20 %
Oxygen concentration	15 – 90 l/h O ₂
Sulphuric acid concentration	0 – 90 kg/t H ₂ SO ₄
Agitation	400 – 1000 r/min
Leach time	0 – 2.5 h

The freshly ground sample, obtained from the ultra fine milling, was mixed with water to make up a slurry of 1.7 litres. The slurry was poured into the autoclave and all the parameters were set at target values. Once the temperature reached 85°C the oxygen valve was opened and oxygen was purged through the slurry at a specific flow rate, via the gas inlet tube as shown in Figure 3.5.

The slurry was then leached for 2.5 hours with intermediate sampling performed at 15, 30, 50, 90 and 150 minutes via the sampling dip tube. Approximately 60-80 ml of slurry was removed (with the agitator on) via the sample dip tube. The slurry was filtered and the volume of the filtrate was measured and retained in a labelled vial, which was then submitted for E_H and pH measurements and elemental assays. The residue solid was dried, weighed and recorded.

After completion of the leaching process the final slurry was removed from the autoclave and transferred to a clean dry filter press. Once the primary filtration was complete, the filtrate was removed, measured and stored without washing or dilution at this point. The filter cake was re-slurried in a diluted sulphuric acid solution (pH equal to leach solution pH) and re-filtered after it was well mixed. The liquor obtained from this filtering process was discarded and the filter cake re-slurried again with 4 litres of tap water and filtered. This re-slurry and filtration process was repeated until the pH of the filtrate exceeded 3.5.

The final residue filter cake was dried over night at a temperature of 110°C after which it was weighed and the mass recorded. A homogenous sample was drawn from this filter cake and the sample was submitted for elemental assays.

3.4 Experimental measurements

Different experimental techniques were used to obtain relevant data, from the experiments performed, for further processing and interpretation.

3.4.1 pH and E_H measurements

The pH and E_H of all solutions were measured using a Metrohm Ion Analysis 744 pH meter, fitted with an AG 9101 pH electrode and a built-in temperature probe. The meter was calibrated regularly using standard buffer solutions (pH 7.0 and 4.0) and after use the glass electrode was rinsed with de-ionised water and stored in a 3M potassium chloride solution.

3.4.2 Atomic Absorption (AA) measurements

Atomic Absorption (AA) spectrophotometry is one of the most widely used methods for the determination of the concentrations of single elements in an analytical sample. The different components used in the instrument for AA spectrophotometry consists of a radiation source, a sample holder, a wavelength selector, a detector and a signal processor.

The metal concentration in the solution, in terms of mg/l was determined by means of a Varian SpectrAA-10 Atomic Absorption spectrophotometer (see Figure 3.7). The liquid, as well as the solid samples, was analysed using this spectrophotometer. Before the composition of the solid residue could be determined, the residue was decomposed by hydrochloric and nitric acid. The data obtained was used to calculate the metal recovery.

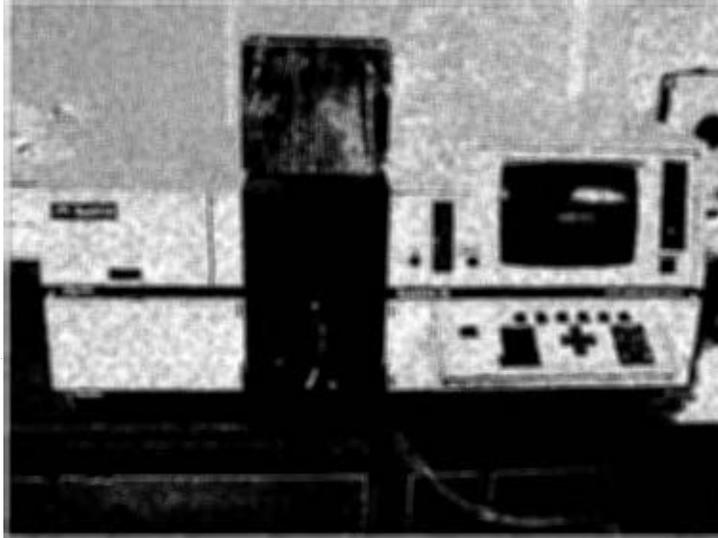


Figure 3.7 Photograph of the atomic absorption (AA) spectrophotometer used in the present investigation

3.4.3 Scanning Electron Microscope (SEM) analysis

The SEM is used to produce a surface picture of a scanned particle surface using a tightly focused electron beam. When the surface of the solid is scanned, several types of signals are produced via the back-scattered electrons, secondary and Auger electrons, X-ray fluorescence photons and other photons of varying energies. Figure 3.8 represents the Scanning Electron Microscope used in this research project.

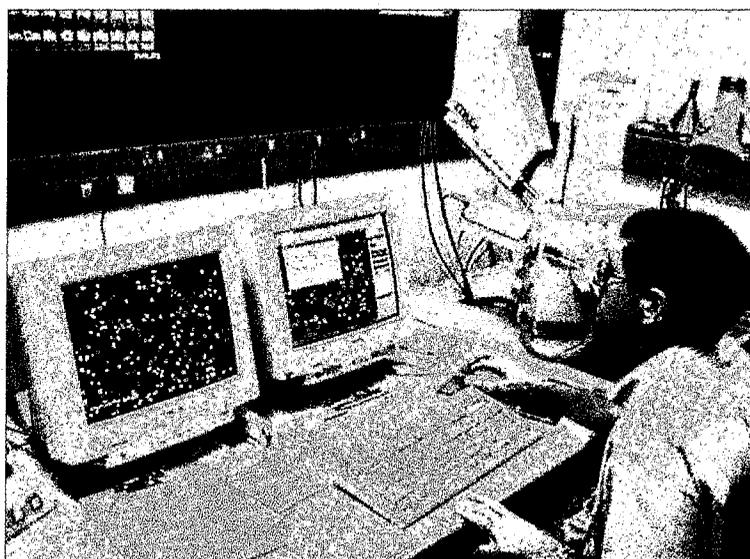


Figure 3.8 Photograph of the Scanning Electron Microscope (SEM) with dr. L.J. Tiedt performing an analyses

3.4.4 Mössbauer measurements

Mössbauer spectroscopy is an attractive tool for studying hydrometallurgical treatment of concentrates containing amongst others pyrrhotite and chalcopyrite. The technique makes it possible to distinguish between the iron-containing species present, giving a quantitative estimate of their relative abundance. Because the majority of the valuable metals are usually associated with iron-containing minerals, Mössbauer spectroscopy is an effective means of monitoring the various minerals present in a sample.

All spectra were obtained with the aid of a Halder Mössbauer spectrometer, capable of operating in conventional constant acceleration mode using a backscatter-type gas flow detector (see Figure 3.9). A 50 mCi ^{57}Co source, plated into a Rh-foil, was used to produce the γ -rays. The sample analyses were done at room temperature and data collected in a multi-channel analyser (MCA) to obtain a spectrum of count rate against source velocity. The amount of each constituent present in a sample was determined from the areas under the relevant peaks.

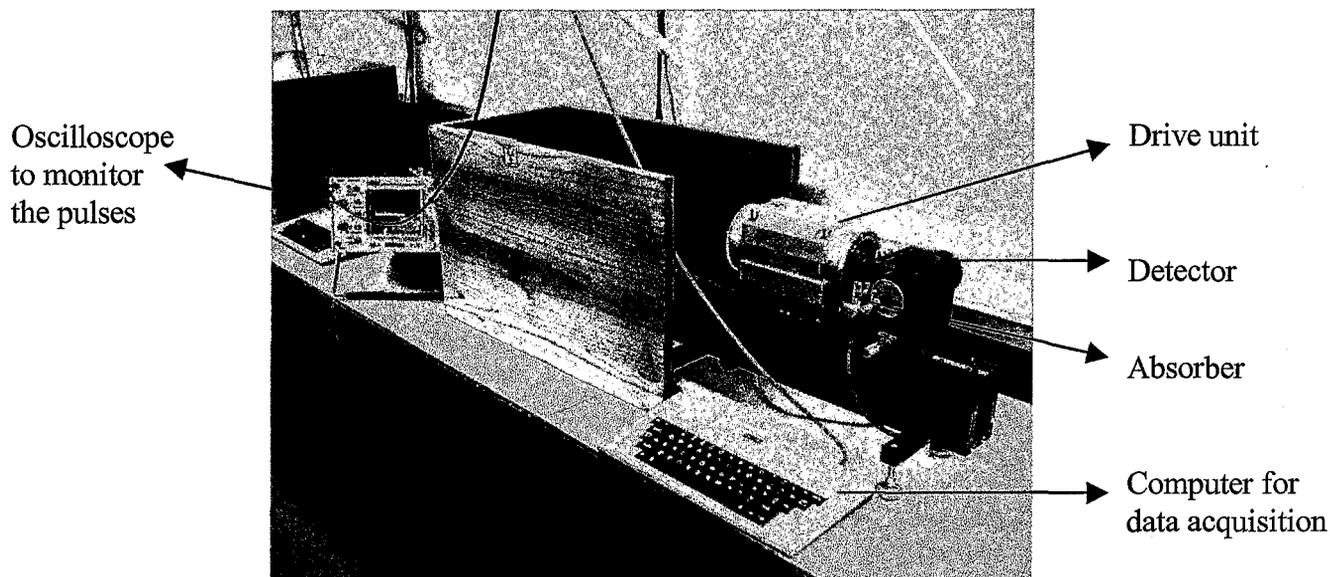


Figure 3.9 Photograph of the Halder Mössbauer spectrometer

3.4.5 Sulphur analysis

All the different sulphur analyses were performed by Mintek and the results are shown in Appendix B.