CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 THERMOGRAVIMETRY

Thermogravimetry is the technique whereby the mass of a sample is measured as a function of time or temperature, while subjected to a controlled heating programme in a specified atmosphere.

The technique has a wide range of applications, some of which are:

- investigation of phase changes;
- evaluation of thermal stability of materials;
- investigation of chemical reactivity; and
- kinetic studies.

Figure 3.1 Thermogravimetric instrument

The thermogravimetric instrument is composed of the following:

3.1.1 Sensor

The sensor is the heart of the instrument. It provides the basic information on the sample behaviour. Usually, the output of the sensor is a small DC voltage with a value related to the measured property or an AC voltage with a frequency related to the measured property.

3.1.2 Furnace

In the instrument, the sensor is in contact with the sample, which is placed in the furnace in such a way that it can be heated easily. The construction of the furnace for thermogravimetrc instruments is designed to withstand high temperatures. The furnace has a cylindrical shape and is heated by means of resistance wire, which is wound around the outer wall.

3.1.3 Programmable temperature controller

The programmable temperature controller is linked directly to the furnace and controls the heating. The instrument can measure samples in a temperature range of 20-1 600 °C. A thermocouple that is chemically inert, measures the furnace temperature. The signal from the thermocouple is transmitted to the programmer, and the temperature it represents is compared with the temperature required by the programme. The system will respond by supplying more or less power to the furnace, depending on whether the temperature of the furnace is too low or too high. The response times of the controller and the furnace govern the thermal lag of the instrument, and the range of heating rates that is achievable. The accuracy or resolution of the controller greatly depends on the technique.

3.1.4 Instrument Control

The instrument is digitally operated and controlled by a microprocessor. The processor controls

- power supply to the furnace;
- takes care of temperature programming;
- measures the signals from the sensor;
- sends the data either to a printer or via an interface to a computer; and
- ensures the correct functioning of the instrument.

3.1.5 Amplifier

The basic signal from the sensor is frequently a small analog signal. Before it can be digitized and processed further, it must be amplified. The signal amplifier is therefore a very important part of the instrument and is largely responsible for determining the quality of the resulting curve.

3.1.6 Data acquisition device (computer)

The computer produces a record of the sample mass as a function of time and temperature. It makes the collection, interpretation, storage and retrieval of the instrumental data easier. It allows the user to calculate and compare results accurately (Brown, 1988, Charsley and Warrington, 1992)

3.1.7 Sources of error during thermogravimetry

Errors lead to inaccuracy of the results. The following precautions must be taken in the design of an accurate thermobalance:

- insulation of microbalance from furnace heat;
- accurate control of the reaction temperature;
- effective earthing of glass components to avoid electrostatic charging;

- correction of weight readings for buoyancy forces. The buoyancy effect is due to thermomolecular flow that can occur when the balances are operating at low pressure. As the sample is heated, the density of the atmosphere around the sample decreases, and the upthrust, caused by the gas, will decrease. The crucible will therefore show an apparent gain in measured mass.
- use of a narrow reaction tube and smaller sample masses to minimize turbulence.

3.1.8 Operational conditions

The measurement in this instrument is performed in a defined atmosphere, usually in inert conditions (nitrogen) or in an oxidative environment (air or possibly oxygen). The mass is measured with a highly sensitive electronic balance. Currently, electronic balances are available having sensitivities as low as 0.1 µg. The sample is mostly suspended from the balance by long platinum or quartz wires and hangs in a furnace that can be heated or cooled at a given rate.

3.2 X-RAY ANALYSIS

X-rays were first discovered by the German physicist W.E Roentgen in 1895 (Graham, 1995). X-rays can be defined as wave or electromagnetic radiation of relative short wavelengths, high energy. All electromagnetic radiation is characterized by its wave character using its *wavelength* λ (the distance between the peaks), its *frequency* v (the number of points that pass a point in unit time) or by its photon *energy E*. The relationships between these quantities are as follows:

$$v = \frac{c}{\lambda} \tag{70}$$

and

$$E = hv \tag{71}$$

c = the speed of light, h = the Planck's constant

From these two equations (70 and 71) it follows that the energy equivalent to an X-ray photon is:

$$E = \frac{hc}{\lambda} \tag{72}$$

They are produced when any electrically charged particle of sufficient kinetic energy is rapidly decelerated. The radiation is produced in an X-ray tube containing a source of electrons and two metal electrodes. Figure 3.2 shows a cutaway view of an X-ray tube. The tungsten filament is heated by the filament current producing a cloud of electrons, which are accelerated along the focussing tube by the potential difference between the filament and the anode. The generated X-rays then pass through the window to the outside. The conversion of electrons to X-rays is a very inefficient process because most of the energy is converted to heat. The tube must therefore be cooled with water.

The high voltage maintained across the tube electrodes rapidly draws the electrons to the anode or target which they strike at high velocity. The x-rays are produced as the electrons strike the atoms of the target material and radiate in all directions (Figure 3.3).

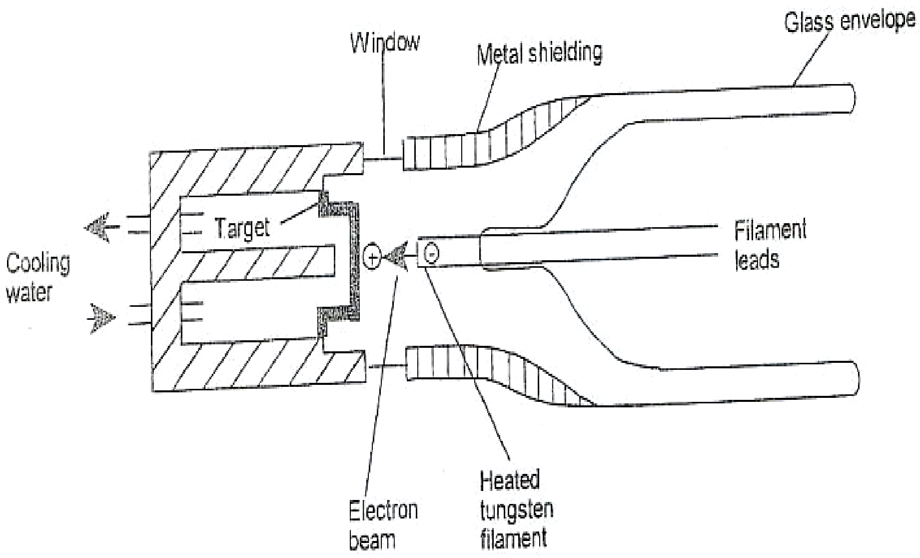

Figure 3.2 **Schematic diagram of X-ray tube (courtesy: Shimadzu Corp.)**

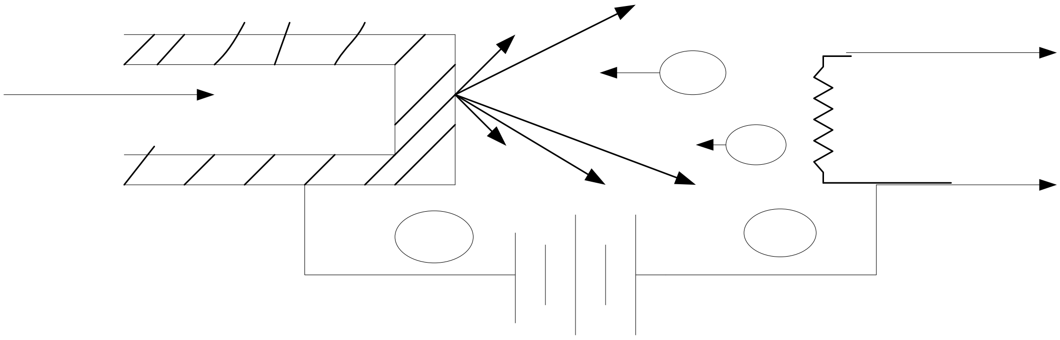

Figure 3.3 **Schematic diagram of X-ray generation**

Rays coming from a target consist of a mixture of different wavelengths and the tube spectrum consists of two parts:

1) Continuous spectrum

It is caused by the deceleration of the electrons hitting the target and in that way emitting their energy or by the stepwise loss of energy of bombarding electrons in a series of encounters with atoms of the target material.

X-RA

TARGET

COOLING WATER

No X-rays are produced before the minimum voltage is not reached for the specific target material. The intensity of the X-rays at a specific voltage also depends on the target material.

When the voltage on an X-ray tube is raised above a certain critical value, sharp intensity maxima, characteristic of the target metal, appear at certain wavelengths. These lines fall into several sets referred to as K, L, M, etc. lines. The K lines are useful in X-ray diffraction, because the larger wavelength lines L and M are too easily absorbed. The intensities of the lines are dependant on the X-ray tube current and the voltage. The continuous spectrum consists of “bremsstrahlung” radiation: radiation produced when high energy electrons passing through the tube are progressively decelerated by the material of the tube anode (the "target").

2) Characteristic spectrum

It is produced through interaction between the atomic electrons of the target and the incident particles, which can be high voltage electrons, an X-ray photon, a gamma ray or a photon. Each will produce similar effects if the energy of the particle is greater than the energy binding the electrons to the nucleus. The radiation is generated when the bombarding electrons have sufficient energy to dislodge electrons from the inner electron shells in the atoms of the target material. There are two de-excitation processes, the photoelectric and the Auger effects.

The photoelectric effect is produced when an electron is removed form its original position leaving the atom in an ionized state. The free electron, called the photoelectron will leave the atom with a kinetic energy $E - E_0$ (where $E =$ energy of the incident photon and $E_0 =$ the binding energy of the electron). This leaves the atom with a vacancy, which can be filled by transferring an outer orbital electron to fill its place. Following the transfer and lowering of the ionized energy of the atom is the production of a fluorescent X-ray photon with an energy $E_{X\text{-ray}}$. The final resting place of the transferred electron determines the type of radiation, i.e K, L, M etc. If a K electron is ejected, the atom is in the high energy K^+ state. Transfer of an electron from the L shell reduces the electron energy state from K^+ to L^+ and the excess energy is emitted as $K\alpha$ radiation. L radiation is produced in a similar way. Each element has a unique set of binding energies and unique energy state differences.

- ***Absorption of X-rays***

X-rays, unlike ordinary light, are invisible but travel in straight lines. They have a significant attribute which is the ability to penetrate different materials to different depths. When a monochromatic beam of radiation of wavelength λ and intensity I_0 falls onto an absorber of thickness t and density ρ, a certain portion, I, of the radiation may pass through the absorber. The wavelength of the transmitted beam is unchanged and the intensity is lower depending on the thickness and the mass absorption coefficient.

Some rays do not pass through the material and are reflected by the surface causing coherent and incoherent scattering. When X-rays strike an atom in the material, tightly bound electrons in the atom also scatter X-rays of the same wavelength as that of the incident beam (coherent scatter), and loosely bound electrons scatter X-rays of the slightly increased wavelength (incoherent scatter) (Azaroff, 1968).

3.2.1 X- ray Fluorescence analysis

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays (Beckhoff *et al.,* 2006). The phenomenon is widely used for chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology.

When materials are exposed to short-wavelength X-rays or to gamma rays, ionization of their component atoms may take place. Ionisation consists of the ejection of one or more electrons from the atom, and may take place if the atom is exposed to radiation with the energy greater than its ionization potential. X-rays and gamma rays can be energetic enough to expel tightly-held electrons from the inner orbitals of the atom. The removal of an electron in this way renders the electronic structure of the atom unstable, and electrons in higher orbitals "fall" into the lower orbital to fill the hole left behind. In falling, energy is released in the form of a photon, the energy of which is equal to the energy difference of the two orbitals involved. Thus, the material emits radiation, which has energy characteristic of the atoms present. The term fluorescence is applied to phenomena in which the absorption of higher-energy radiation results in the re-emission of lower-energy radiation.

The fluorescent radiation can be analysed either by sorting the energies of the photons (energy-dispersive analysis) or by separating the wavelengths of the radiation (wavelength-dispersive analysis). Once sorted, the intensity of each characteristic radiation is directly related to the amount of each element in the material (Van Grieken and Markowicz, 2002).

3.2.1.1 Energy dispersion

In energy dispersive analysis, the fluorescent X-rays emitted by the material sample are directed into a solid-state detector which produces a continuous distribution of pulses, the voltages of which are proportional to the incoming photon energies. This signal is processed by a multichannel analyzer (MCA) which produces an accumulating digital spectrum that can be processed to obtain analytical data. In wavelength dispersive analysis, the fluorescent X-rays emitted by the material sample are directed into a diffraction grating monochromator. The diffraction grating used is usually a single crystal. By varying the angle of incidence and take-off on the crystal, a single X-ray wavelength can be selected. The wavelength obtained is given by the Bragg equation (Buhrke *et al*., 1998):

$$n.\lambda = 2d.\sin(\theta) \tag{73}$$

where d is the interplanar spacing
θ is the angle between the planes and the X-ray beam (Bragg angle),
λ is the X-ray wavelength and
n is the order of reflection.

3.2.1.2 Wavelength dispersion

In wavelength dispersive spectrometers (WDX or WDS), the photons are separated by diffraction on a single crystal before being detected. Although wavelength dispersive spectrometers are occasionally used to scan a wide range of wavelengths, they are usually set up to make measurements only at the wavelength of the emission lines of the elements of interest. This is achieved in two different ways:
"Simultaneous" spectrometers have a number of "channels" dedicated to analysis of a single element, each consisting of a fixed-geometry crystal monochromator, a detector, and processing electronics.

This allows a number of elements to be measured simultaneously, and in the case of high-powered instruments, complete high-precision analyses can be obtained in under 30 s. "Sequential" instruments have a single variable-geometry monochromator (but usually with an arrangement for selecting from a choice of crystals), a single detector assembly (but usually with more than one detector arranged in tandem), and a single electronic pack. The instrument is programmed to move through a sequence of wavelengths, in each case selecting the appropriate X-ray tube power, the appropriate crystal, and the appropriate detector arrangement.

3.2.1.3 Sample analysis by XRF

- ***Qualitative analysis by XRF***

For qualitative analysis, the crystal is rotated so that all angles between approximately 15 ° and 145 ° are presented to the x-ray beam. Detected X-rays are amplified and recorded as a series of peaks. A scale of 2θ is automatically recorded, and elements are identified from their 2θ values in conjunction with an appropriate set of tables.

- ***Quantitative analysis by XRF***

For quantitative analysis, the crystal remains stationary, set at the appropriate angle to reflect a particular element's radiation. The recorded intensity is related to the element's concentration in the sample.

3.2.2 X-ray Diffraction

X-ray diffraction is coherent elastic scattering of X-rays by atoms or ions in a crystal. Because the wavelength of photons with energy of order 10 KeV is a little smaller than the spacing of atoms in solids, a crystal will act as a diffraction grating for X-ray. As a crystal is three dimensional, the diffraction conditions are more stringent than for a two-dimensional grating. This technique is widely used in chemistry and biochemistry to determine the structures of an immense variety of molecules, including inorganic compounds, DNA, and proteins. X-ray diffraction is commonly carried out using single crystals of a material, but if these are not available, microcrystalline powdered samples may also be used.

3.2.2.1 Principle of X-ray diffraction

The principle involved is, that a beam of X-rays striking a crystal will pass through it, but with scattering or diffraction of the photons in the beam. Since the particles in the crystal are in a regular or symmetrical arrangement, the X-rays will be scattered in a regular pattern. X-rays wavelength used in diffraction lie between approximately 0.5 and 2.5 Aº.

When X-rays are incident on any form of matter, they are partly scattered in all directions by the atoms in the matter. When these atoms have three dimensionally regular arrangements, these scattered X-rays mutually reinforce one another to show the phenomenon of diffraction.

X-ray diffraction by crystals can simply be explained by the Bragg model (equation 78). Measuring distances (d) between units in crystals by X-ray diffraction is done by the Bragg method. The units in each Bragg plane act as the X-ray scattering sources and the X-ray beam striking the crystal will act as if it had been reflected from these evenly spaced planes. This will give rise to reinforcement of the beam at certain angles and destruction at others, so that the spacing between the planes can be determined.

3.2.2.2 Methods in Quantitative XRD

In a multicomponent crystalline mixture, each component of the mixture produces its characteristic pattern independently of the others, making it possible to identify the various components. Additionally, the intensity of each component pattern is proportional to the amount present. Absorption corrections, however, have to be performed, so that a quantitative analysis for the various components may be developed. The following three quantitative methods will be discussed: Reference Intensity Ratios (RIR) method, Whole Pattern Method and Rietveld Method.

- ***Reference Intensity Ratios***

The ratio has been given the notation I/I_c, meaning 'analyte intensity I over corundum intensity I_c'.

Two methods are used to measure the RIR:

1) measuring intensities of the strongest peaks from samples prepared by mixing the analyte and standard together in a known weight ration; and
2) measuring separately the intensities for the analyte peak and the reference standard peak from pure phase preparations and by correcting the intensities with mass absorption coefficients. Both methods are independent of the difference in mass absorption coefficients between analyte and standard (Davis, 1992).

The general RIR definition for component j, when components j and c are mixed together in a 1:1 weight ratio or are corrected from the known value of w_c is (Davis *et al.*, 1990):

$$I_j = \frac{I_j}{I_c}, \qquad w_j = w_c \tag{74}$$

- ***Whole Pattern Method***

The method uses the full diffraction pattern collected over a specified 2θ range preselected to cover all the major peaks of all the phases analyzed (Smith *et al.,* 1987). The key feature of this method is that all the information in the diffraction pattern is used for the analysis.

- ***Quantitative Phase Analysis using the Rietveld Method***

Rietveld method is used in the characterisation of crystalline materials and needs a complete structure model (Bish and Howard, 1988).

This method fits calculated rather than measured reference patterns to the pattern from the unknown. It can also use a pattern-fitting algorithm where all lines for each phase are considered. This method allows to correct for preferred orientation, but corrections only appear to work in samples with minor amounts of preferred orientation (Bish and Howard, 1988). The use of an internal standard will allow the determination of total amorphous phase content in a mixture. Hill (1991) states that the Rietveld method of phase analysis is only as accurate as the modelling provided in the pattern calculation.

In the Rietveld Method, an entire calculated diffraction pattern is compared with the observed pattern, point by point. Six factors affecting the relative intensity of the diffraction lines of a powder pattern (Klug and Alexander, 1974):

- Polarization factor when radiation is scattered or diffracted.
- Structure factor – the ratio of the amplitude scattered by the plane relative to the amplitude scattered by a single electron.
- Multiplicity factor – the number of different planes in a form having the same spacing.
- Lorentz factor – a reflection time factor
- Absorption factor-factor affecting the intensities of diffracted rays
- Temperature factor – when atoms undergo thermal vibration. The amplitude of this vibration increases as the temperature increases.

Basic equation of the Rietveld method (Wiles and Young, 1981):

$$y_i = \sum \left[S_p \sum_k \left[APL\Psi M_k \left| F_k \right|^2 G(\Delta\Theta_{ik}) po_k \right] \right] + y_{bi} \tag{75}$$

where,

y_i - Intensity of the angular position, i in the powder pattern

S_p - Scale factor of the phase p, relates the phase intensities to the pattern

APL - Absorption, polarisation, Lorenz factor

Ψ - Geometrical factor (powder-ring - factor)

M - Plane multiplicity factor

F - Structure factor

G - Profile shape function

po - Preferred orientation correction factor

y_{bi} - Background intensity

3.3 TUBE FURNACE

A tube furnace is designed to heat a tube that is usually 50 to 100 cm in length and from 25 to 100 mm in diameter. Samples are placed inside the tube in ceramic or metal boats using a long push rod. The tube is surrounded by heating elements which may also incorporate a thermocouple (a thermocouple can also be inserted down the tube if desired).

Different types of elements are single zone wirewound, silicon carbide and multi zone wirewound. Tube furnaces also have a significant advantage over other types of furnaces. The ends of the furnace tubes (which usually protrude 10 or more centimeters from each end of the furnace) do not get very hot and so a variety of different adapters may be placed on the ends. Furnace tubes can be made out of a variety of materials. Quartz is commonly used for temperatures below 1 200 °C and alumina or yttria-stabilized zirconia can be used for higher temperatures. The ceramics, quartz silica and metals are the worktubes suitable for this instrument. Figure 3.4 shows the picture of a tube furnace used in this study.

Figure 3.4 Tube furnace (Model TSH12/38/500)

3.4 MUFFLE FURNACE

The controller can be used in Automatic mode in which the output power is automatically adjusted to hold the temperature at the required value. It is ideal for ashing organic and inorganic samples, cement testing, heat treating small steel parts, ignition tests, gravimetric analysis, and determination of volatiles and suspended solids. Heating elements are embedded in refractory cement on top and both sides to reduce energy consumption and for structural strength. The furnace is insulated with ceramic fibre insulation which improves furnace temperature uniformity. Unit can heat up to 2 000 °C.

Figure 3.5 Muffle furnace (Model TSH12/38/500)

CHAPTER 4

AIM OF STUDY

The aim of this project was to investigate and optimize various stages of the sulphur recovery process on laboratory scale to the stage prior to pilot and full-scale implementation. Figure 4.1 shows the process flow diagram of the sulphur recovery process. The following individual stages were studied:

- Thermal decomposition of gypsum to calcium sulphide (A)
- Stripping of the H_2S from calcium sulphide slurry with CO_2 to form $CaCO_3$ (which can also be recovered as a by-product and used for neutralization of acid mine water) (B)
- Sulphur production (C)

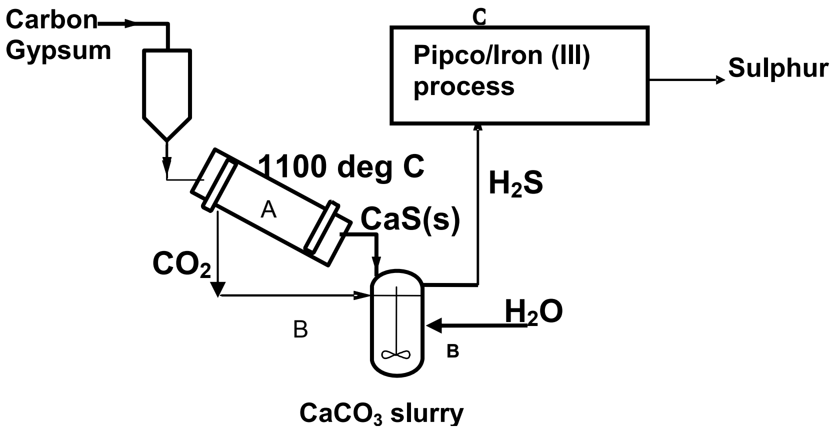

Figure 4.1 Process flow diagram for the sulphur recovery process

4.1 THERMAL STUDIES (A)

The effects of the following parameters on the reduction of gypsum to calcium sulphide were investigated

- Reaction time: Different time periods ranging from 5 min to 60 min were evaluated to optimize the time needed to thermally decompose gypsum into calcium sulphide in the furnace.

- Temperature of the furnace: The conversion of gypsum to calcium sulphide occurs at high temperature. The temperatures were varied from 900 °C to 1100 °C to obtain the optimum temperature.

- Molar ratio: The molar ratios of gypsum to activated carbon were varied from 1:0 to 1:3. The aim was to investigate the stoichiometric amount of activated carbon needed to react with gypsum for effective reduction.

- Particle sizes of gypsum: As reactivity also depends on particle size, different particle sizes of gypsum were studied (1 250 µm, 630 µm and 380 µm).

- Type of furnace: The muffle furnace, which contained oxygen, and tube furnace, which was oxygen deficient, were investigated to identify which heating unit is more efficient.

- Gypsum compounds: Gypsum from three sources were tested. Pure gypsum, Anglo gypsum and Foskor gypsum were compared in respect of CaS yield.

- Reducing agent: Two different reducing agents (activated carbon and Duff coal) were compared with respect to yields of CaS and for cost effectiveness.

Thermogravimetric analysis was conducted under isothermal and non-isothermal conditions with the aim of elucidating the influence of different kinetic parameters on the mechanism of the process. Carbon monoxide and activated carbon were used as reducing agents. The following parameters were studied:

- Heating rate: The aim of this investigation was to use the isoconversional method to estimate/calculate the activation energy. These allow the dependence of activation energy on the degree of conversion to be observed. Six different heating rates between 1 °C/min and 10 °C/min were studied using gypsum from three different sources (pure gypsum, Anglo gypsum and Foskor gypsum) and two different reducing agents (carbon monoxide and activated carbon).

- The effect of heating mixtures of gypsum and activated carbon at a constant temperature for a certain period was investigated by conducting isothermal studies using pure gypsum and activated carbon. Isothermal temperatures were between 850 °C to 1 000 °C.

- The molar ratio between gypsum and activated carbon was varied from 1:0.5 to 1:3. The aim was to investigate the optimum amount of activated carbon needed to react with gypsum for effective reduction.

- The two different reducing agents (activated carbon and Duff coal) were compared with the aim of obtaining a suitable reducing agent to use on a full-scale plant

4.2 SOLUBILITY OF CaS

Due to the low solubility of CaS, the influence of the following parameters on the solubility of CaS were studied:

- Stirring: The influence of stirring on the solubilisation of CaS solution was studied by stirring the CaS slurry for 180 minutes.

- Temperature: The effect of temperature on the solubility of CaS was investigated by heating the CaS solution from 30 °C to 90 °C.

4.3 SULPHIDE STRIPPING AND ABSORPTION (B)

The effect of the following parameters on the stripping of sulphide using CO_2 was investigated:

- CO_2 flow rate: To obtain the equivalent amount of CO_2 gas required to strip hydrogen sulphide gas from a CaS slurry, different CO_2 flow rates (2 200 mℓ/min to 3 300 mℓ/min) were studied.
- CO_2 pressure: The effect of 100 kPa and 200 kPa CO_2 pressure on the system was studied. This work was done to identify if the effect of doubling the partial pressure of CO_2 in the system would increase the amount of CO_2 in solution, thereby displacing/reacting with more of the remaining sulphide.
- Hydrodynamics: These experiments were conducted to investigate whether increasing the agitation would speed up the liquid-gas-solid reaction and if more of the gas in the headspace would result in more gas being circulated through the mix, resulting in a greater volume of CO_2 being cycled through the liquid per unit time. Stirring rates of 500 rpm and 1000 rpm were tested.

4.4 H_2S GAS ABSORPTION AND SULPHUR FORMATION (C)

Two methods were tested for sulphur recovery to establish the more effective method:

- Iron (III) process: In this process, H_2S gas was absorbed into Fe(III) solution. A sample from the iron (III) reactor was analysed, using XRD, with the aim of identifying compounds formed other than sulphur.

- The PIPco process: In this process H_2S gas was absorbed into a SO_2 rich potassium citrate solution. The sulphur recovered was assayed for purity.

CHAPTER 5

MATERIALS AND METHODS

5.1 THERMAL STUDIES

5.1.1 Feedstock

Gypsum. Three different gypsum samples were utilised in the reduction studies.

- Pure gypsum (AR grade) was obtained from Merck.
- Anglo gypsum from Anglo Coal (Landau Colliery) was prepared from the desalination stages of a mine water treatment pilot plant.
- Foskor gypsum obtained from Foskor (Phalaborwa) was prepared by leaching of calcium phosphate, with sulphuric acid.

The results of X-ray fluorescence (XRF) analyses of the gypsum samples used are summarised in Table 5.1.

Carbon. Two types of carbon were used as the reducing agents.

- Activated carbon obtained from Merck with a carbon content of 98.7%.
- Duff Coal from Anglo Coal with 68.5% carbon content.

Analysis of the activated carbon and Duff coal is given in Table 5.2.

Carbon monoxide. 5% CO gas diluted with pure 95% nitrogen obtained from Air Liquide was used for the reduction of gypsum.

Table 5.1 XRF analyses of pure gypsum, Anglo gypsum and Foskor gypsum

Compounds	Composition (%)		
	Pure gypsum	Anglo gypsum	Foskor gypsum
SiO_2	0.01	0.01	0.17
TiO_2	0.01	0.00	0.00
Al_2O_3	0.01	0.01	0.01
Fe_2O_3	0.00	0.09	0.05
MnO	0.00	0.12	0.00
MgO	0.00	4.37	0.00
CaO	41.6	34.74	37.47
Na_2O	0.01	0.01	0.01
K_2O	0.01	0.00	0.01
P_2O_5	0.04	0.13	0.78
SO_3	56.0	50.48	53.76
Loss On Ignition	0.89	9.10	6.64
Total $CaSO_4$	97.6	85.2	91.2

Table 5.2 XRF analyses of the activated carbon and Duff coal

Sample composition	Composition (%)	
	Activated carbon	Duff Coal
Moisture	0.5	1.6
Ash	0.5	13.5
Volatile Matter	0.3	15.2
% Carbon	98.7	68.5

5.1.2 Equipment

For the thermal study, a Mettler Toledo Star e System was used for execution of thermogravimetric analysis. A tube furnace, model TSH12/38/500 and a muffle furnace model 2216e controller were used for thermal decomposition of gypsum (refer to Chapter 3). A silica tube was used for the reduction reaction.

Samples were contained in silica boats, A_1 clay graphite crucibles and a platinum sample holder during the thermal studies.

5.1.3 Experimental procedure

5.1.3.1 Tube and Muffle furnace

The gypsum and carbon mixtures were thoroughly mixed by hand to ensure homogeneity. The mixtures were placed in silica boats/clay crucibles and heated in the tube furnace and muffle furnace for various times. The amounts of activated carbon or Duff coal used for the different carbon to gypsum ratios are summarized in Table 5.3. The gypsum amount was kept constant at 5 g.

The Anglo gypsum and Foskor gypsum were dried first at 150 °C - 180°C to remove excess moisture (anhydrous gypsum) as they tend to form lumps when wet and thereafter grounded to a fine powder. Nitrogen gas (50 mℓ /min) was passed through the reaction tube as an inert gas in the tube furnace. In the muffle furnace some oxygen was present. Reaction products from the tube furnace were allowed to cool in a nitrogen atmosphere.

X-Ray Diffraction (XRD) analysis was used to determine the composition of samples (described in 5.1.4).

The effect of the following parameters on the reduction of gypsum to calcium sulphide using a tube or muffle furnace were investigated:

- Reaction time (5 min, 20 min, 30 min and 60 min).
- Temperature of the furnace (900 °C, 1 000 °C, 1050 °C and 1 100 °C, 1150 °C).
- Carbon to gypsum molar ratio (0, 0.025, 0.5, 1, 2 and 3).
- Particle sizes of Foskor gypsum (1 250 µm, 630 µm and 380 µm).
- Type of furnace (muffle furnace (oxygen present) or tube furnace (oxygen deficient)).

- Gypsum compounds (pure gypsum, Anglo gypsum and Foskor gypsum).
- Reducing agent (duff coal and activated carbon).

Table 5.3 Compositions of various gypsum/carbon ratios

Gypsum compound (5g)	Ratio	Activated carbon (g) (98.7 % C)	Duff coal (g) (68.5 % C)
Pure gypsum dihydrate (97.6 %)	0.25:1	0.09	
	0.5:1	0.17	
	1:1	0.35	
	2:1	0.70	
	3:1	1.04	1.5
Anglo gypsum (anhydrite) (85.2 %)	3:1	1.14	1.6
Foskor gypsum (91.2 %)	3:1	1.22	1.7

5.1.3.2 Thermogravimetry Analysis

Carbon monoxide and activated carbon were used for the reduction of gypsum. Nitrogen gas was used as inert atmosphere at a flow rate of 50 mℓ/min. The nitrogen gas was also utilized as a diluent gas for carbon monoxide. Carbon monoxide (5% in nitrogen) was used unless otherwise stated. Samples with masses between 10 and 20 mg were held in a platinum sample holder during the thermogravimetric studies. The percentage conversion was calculated based on measured mass loss. Kinetic analysis was done using the Ozawa Flynn Wall method (Ozawa, 1965; Flynn and Wall, 1966).

For the kinetic studies on the reduction of gypsum to calcium sulphide, using carbon monoxide or activated carbon as reducing agents, the influence of following parameters were studied:

- Heating rates (1, 2, 4, 6, 8, 10 °C/min) on the reaction between pure gypsum and carbon monoxide.

- Temperature from 25 °C to 1 260 °C for the reaction between activated carbon and pure gypsum.
- Molar ratio of activated carbon to pure gypsum (0.5:1 to 3:1).
- Gypsum compounds (pure gypsum, Anglo gypsum and Foskor gypsum)
- Reducing agent (activated carbon or Duff coal) using pure gypsum, Anglo gypsum and Foskor gypsum)
- Heating rate (1, 2, 4, 6, 8 and 10 °C/min) on the reaction between the three gypsum compounds and activated carbon.
- Isothermal studies on the reaction between pure gypsum and activated carbon. The temperature of the furnace was 850 °C, 875 °C, 900 °C, 950 °C and 1000 °C. The samples were allowed to remain at each temperature for 15 minutes.

5.1.4 Analytical Procedure

To identify the composition of the samples before and after thermal treatment, XRF and XRD analyses were carried out.

5.1.4.1 XRF analyses

Analysis of the gypsum and Duff coal samples were done using the ARL 9400XP+ XRF spectrometer. Samples were prepared as pressed powder briquettes and introduced into the spectrometer. Analyses were executed using the UniQuant software that detects and quantifies all elements in the periodic table between Na and U. Only elements present above the detection limits were reported.

5.1.4.2 XRD analyses

An automated Siemens D501 XRD spectrometer was used to analyse the composition of samples. Samples were milled in a swing mill using a WC-milling vessel and prepared for analysis using a back loading preparation method. A PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-K_{α} radiation was used to analyse the samples. Phases were identified using X'Pert Highscore Plus software. Quantification (Rietveld method) was perfomed by Autoquan/BGMN software (GE Inspection Technologies) employing the Fundamental Parameter Approach.

5.2 SOLUBILITY OF CaS

5.2.1 Feedstock

CaS. Calcium sulphide (purity of 90%) was a product obtained from the thermal process (described in 5.1).

5.2.2 Equipment

A 1 ℓ reactor, a magnetic stirrer with temperature controller and a magnetic stirrer bar were used for this study.

5.2.3 Experimental procedure

The study was conducted by adding CaS to water. For the stirring studies, the CaS slurry was stirred for 180 minutes. The slurry was heated from 30 °C to 90 °C when the effect of temperature on solubility was investigated. Samples were taken at different time and temperature intervals and analysed for sulphide and pH (described in 5.3.4).

The influence of the following parameters on the solubility of CaS was investigated:

- Stirring (the CaS slurry was stirred for 180 minutes).
- Temperature (30 °C to 90 °C).

5.3 SULPHIDE STRIPPING AND SULPHUR PRODUCTION

5.3.1 Feedstock

CaS. Calcium sulphide was obtained from the thermal process (described in 5.1).

CO_2. Pure CO_2 was obtained from Air Liquide and used for the stripping of the sulphide gas.

Ferric sulphate solution. A $Fe_2(SO_4)_3$ solution with a concentration of 200 g/ℓ was used for absorption of the H_2S gas. The chemical was obtained from Merck.

Potassium citrate solution. Potassium citrate buffer solution rich in SO_2 was used for the absorption of the stripped H_2S-gas. The potassium citrate solution was prepared from 2 M citric acid (refer to 4.3.4) and 45% KOH added to raise the pH to 6.8.

5.3.2 Equipment

5.3.2.1 *Sulphide stripping using a pressurized reactor*

Figure 5.1 shows a 5 ℓ pressurised reactor, containing a hollow shaft stirrer (Figure 5.2) capable of a maximum pressure of 140 bar and a maximum operating temperature of 300 °C.

Figure 5.1 **The 5 ℓ jacketed, pressurised & continuously stirred reactor used in CaS stripping experiments.**

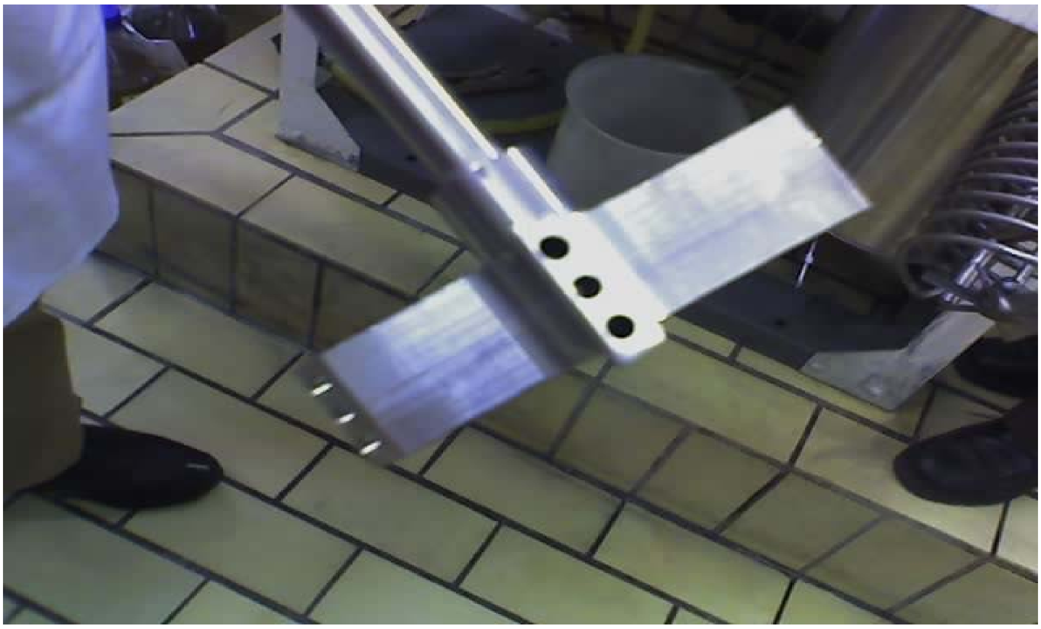

Figure 5.2 **The hollow shaft stirrer used to inject pressurised CO_2 into the CaS slurry**

5.3.2.2 *Sulphide stripping and sulphur formation*

Figure 5.3 shows the laboratory set-up used for H_2S-stripping and sulphur formation under atmospheric pressure. It consisted of three reactors connected in series and equipped with glass spargers. Reactor 1 (1 ℓ) contained a calcium sulphide slurry from which sulphide was to be stripped. Reactors 2 and 3 (1 ℓ) contained SO_2-rich potassium citrate buffer solution/ Fe (III) solution into which H_2S gas was absorbed and sulphur formed.

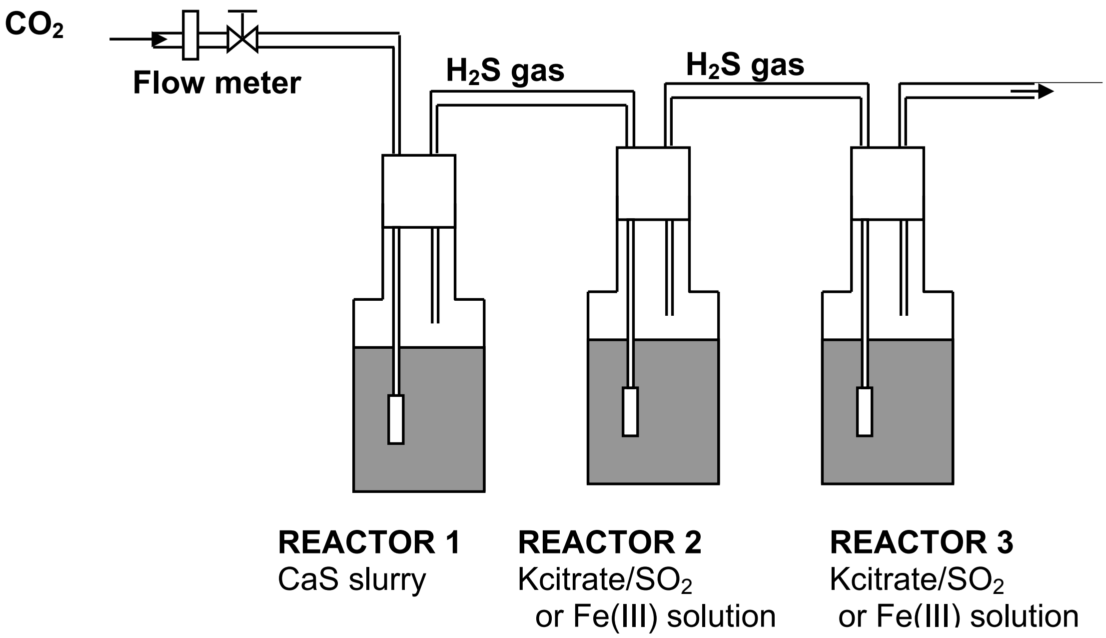

Figure 5.3 Schematic diagram of H_2S-stripping and absorption process.

5.3.2.3 *Solubility of H_2S in Potassium Citrate Buffer*

The experimental setup shown in Figure 5.4 was used for H_2S solubility studies. Two 1 ℓ flasks were connected in series and equipped with glass spargers.

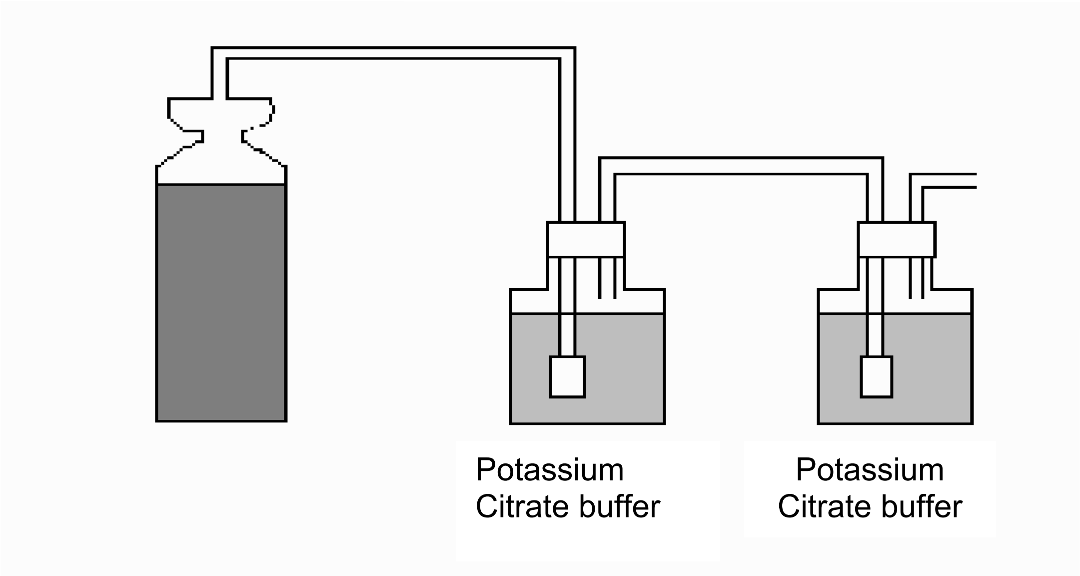

Figure 5.4 Schematic diagram of experimental setup for determining H_2S solubility in potassium citrate buffer solution

5.3.3 Experimental procedure

5.3.3.1 Sulphide stripping using a pressurized reactor

The calcium sulphide product (250 g), obtained from the decomposition of gypsum, was dissolved in water (5 ℓ) and placed in the pressurized reactor. The CO_2 was fed into the reactor. The gas was allowed to flow at pressure through the hollow shaft, finned, mechanical stirrer and mixed with the slurry. The reactor was then pressurized to the desired experimental pressure with CO_2 fed from the cylinder. The stirrer was started and the off-gas valve was opened to the flow-rate specific to each experiment.

At the experimental pressure and stirring rate, the gas in the headspace above the slurry was also re-introduced into the slurry for further reaction.

The effect of the following parameters on the stripping of sulphide using CO_2 was investigated:

- CO_2 flow-rate (2200 mℓ/min and 3300 mℓ/min)
- Temperature of CaS (25 °C and 60 °C)
- CO_2 pressure (atmospheric pressure, 100 kPa and 200 kPa)

- Hydrodynamics (500 rpm and 1000 rpm)

5.3.3.2 Sulphur production

Iron (III) process

The sulphide product from the furnace was dissolved in water and placed in the first reactor. The second and third reactors contained an iron (III) solution (Figure 5.3). The CO_2 used to strip the sulphide gas was introduced into the sulphide solution via a flow meter. The stripped H_2S gas was trapped in the iron (III) solution and converted to sulphur. Samples were taken from the sulphide reactor and iron (III) reactors at different time intervals and analysed for sulphide and iron (II) concentrations, respectively. The relationship between the following parameters, during the stripping process and sulphur formation, were investigated as a function of time:

- The accumulated amount of CO_2 dosed in the reactor for sulphide stripping.
- The amount of sulphide stripped with CO_2.
- The amount of sulphur produced, calculated from the concentration of iron (II).

The residual contents of the iron (III) reactor were analysed using XRD to determine whether compounds other than sulphur had formed.

PIPco process

The process was divided into two stages:

- ***SO_2 absorption***

Pure SO_2 gas was passed through a potassium citrate buffer. The effect of the following parameters on the absorption of SO_2 gas by potassium citrate buffer was studied:

- pH of the citrate solution.
- Potassium citrate concentration (0.5 M, 1 M and 2 M).

- Temperature of potassium citrate solution rich in SO_2 (25 °C-75 °C).

The solubility of H_2S in the potassium citrate buffer solution was also determined by absorbing H_2S gas in a 2 M potassium citrate solution at pH 6.8. H_2S gas was introduced at 600 mℓ/min for 100 min, into Reactor 1 (Figure 5.4) which contained the potassium citrate buffer solution. H_2S gas not absorbed in Reactor 1 was allowed to pass into Reactor 2. The sulphide concentrations in the liquid from both reactors were determined at 20 min intervals. The concentration of H_2S absorbed was then plotted as a function of amount of H_2S fed.

- ***Sulphur production***

The calcium sulphide product (200 g) from the thermal studies was dissolved in water and placed in the first reactor (Figure 5.3). The potassium citrate buffer solution dosed with SO_2 was placed in the second and third reactor. The CO_2 used to strip the H_2S gas was introduced into the sulphide solution via a flow meter. The stripped H_2S gas was trapped in 2 M potassium citrate buffer solution rich in $SO_{2.}$ The reaction between the two gases resulted in the formation of sulphur that was analysed for purity using the LECO Combustion Techniques (paragraph 5.3.4).

The influence of CO_2 flow-rate (520 mℓ/min and 1 112 mℓ/min) on the recovery of sulphur was investigated.

5.3.4 Analytical Procedure

The pH determinations (Metrohm 691) were carried out manually. Iron (II) and sulphide analyses were carried out manually according to standard procedures (APHA, 1985).

5.3.4.1 Sulphide titration method

A sample volume (10-50 mℓ) was placed in a beaker, 10 mℓ of 0.05 M iodine, 6 drops of 50% HCl and 6 drops of starch were added to the sample. The mixture was titrated with sodium thiosulphate to a clear endpoint. The titration value obtained was substituted into the following equation to obtain the concentration of sulphide stripped:

mg/ℓ S^{2-} = 16 x ((volume I_2 x $[I_2]$) – (titration volume x $[Na_2S_2O_7]$)) x
1 000/volume of sample (76)

5.3.4.2 Iron (II) titration method

A filtered sample volume (10-25 mℓ) was taken. 1 N H_2SO_4 (10 mℓ) and Zimmerman Reinhardt reagent (10 mℓ) were added. The mixture was titrated with 0.1 N $KMnO_4$ until the first indication of a pink colour appeared. The concentration of iron (II) was calculated as follows:

Iron(II) (mg/ℓ Fe) = 55.85 g/mol x 0.1 N x Titration volume x 1 000 / sample volume (77)

5.3.4.3 SO_3^{2-} and $S_2O_3^{2-}$ titration

The titration procedure to determine the concentration of sulphite (SO_3^{2-}) and thiosulphate ($S_2O_3^{2-}$) was developed by Pfizer and is accurate to ± 0.1 mol/ℓ (Gryka, 2005). The following method was used to analyse for SO_3^{2-} and $S_2O_3^{2-}$:

Combined SO_3^{2-} and $S_2O_3^{2-}$ titration: Sample (0.5 mℓ) was pipetted into a beaker containing water (50 mℓ) and starch indicator (1 mℓ). The solution was titrated with 0.05 M iodine solution to a yellow end point. Beginning and end titration readings were recorded (Gryka, 2005).

$S_2O_3^{2-}$ titration: Sample (0.5 mℓ) was pipetted into a beaker containing water (50 mℓ), starch indicator (1 mℓ). and formaldehyde (50 mℓ). The solution was titrated with 0.05 M iodine solution to a yellow end point. Beginning and end titration readings were recorded (Gryka, 2005).

$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2I^- + 2H^+ \qquad (78)$$

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \qquad (79)$$

The following calculations were done: 0.05 M iodine was used to oxidize SO_3^{2-} to SO_4^{2-} (Reaction 78) and $S_2O_3^{2-}$ to $S_4O_6^{2-}$ (Reaction 79) to give a combined titration value A. The concentration of $S_2O_3^{2-}$ was determined by adding formaldehyde to precipitate SO_3^{2-} to give a titration value B. The difference between A and B (C) is equivalent to the SO_3^{2-} concentration.

$S_2O_3^{2-}$ is calculated from

$$(V * 2M)_{S_2O_3^{2-}} = (B * M)_{I_2} \qquad (80)$$

$$M_{S_2O_3^{2-}} = \frac{(B * M)_{I_2}}{2V_{S_2O_3^{2-}}} \qquad (81)$$

where V – volume of solution

B – I_2 titration volume

M – concentration in moles/ℓ

and SO_3^{2-} from

$$M_{SO_3^{2-}} = \frac{(C * M)I_2}{V_{SO_3^{2-}}} \qquad (82)$$

5.3.4.4 Preparation of 2 M Potassium Citrate Buffer Solution

- **5 ℓ of 2M potassium citrate buffer solution:**

192 g/mol x 2 M x 5 ℓ = 1 920 g or 1.920 kg anhydrous citric acid

- **45 % KOH to raise the pH of the citrate solution**

56 g/mol x 2.8 mol/mol of acid x 2 M x 5 ℓ = 1.568 kg pure KOH

Citric acid is trivalent. To achieve the target pH approximately 2.8 mol (as determined experimentally) of KOH per mole of citric acid are required (Gryka, 2005).

5.3.4.5 LECO Combustion Techniques

A CS200 LECO Combustion Analyser was used for sulphur purity analysis. The instrument was calibrated using a certified reference material, and the analysis verified by analysing a different reference material of similar sulphur concentration to the sample and the calibration standard.

A portion of sample is weighed into a ceramic crucible, and an appropriate flux/accelerator mix is added (a combination of copper and tungsten). The crucible is placed in the instrument, where it is moved into the induction furnace. The crucible is heated, and the sample/flux mixture melted. Any sulphur in the sample is released and converted to SO_2. The SO_2 is carried in a stream of high-purity oxygen to the detector. The SO_2 is detected quantitatively by an infrared detector, and converted to equivalent sulphur concentration.