CHAPTER 1

INTRODUCTION

1.1 WASTE MATERIALS

Industrial effluents rich in sulphate, acid and metals are produced when sulphuric acid is used as a raw material, and when pyrites is oxidised due to exposure to the atmosphere, e.g. in the mining industry (Jones *et al*., 1988). Acid mine waters contain high concentrations of dissolved metals and sulphate, and can have pH values as low as 2.5 (Barnes and Romberger, 1968). Acidic industrial effluents require treatment prior to discharge into sewage networks or into public watercourses. In water-rich countries the main causes for concern are the low pH and metal content of acidic effluents. Salinity is not a problem due to dilution with surplus capacity of surface water. In water-poor countries, e.g. South Africa, the high salinity associated with acidic industrial effluents is an additional concern (Verhoef, 1982).

Several processes are currently employed for sulphate removal and acid water neutralization, e.g. biological removal (Maree *et al.,* 1987*)* and chemical processes (limestone, SAVMIN (Smit, 1999), reverse osmosis and electrodialysis). Chemical treatment processes are generally the least expensive but produce the largest amounts of waste, e.g. brine, sludge and metal hydroxides.

1.1.1 Brine

Brine is water saturated or nearly saturated with salts such as sodium chloride. It is produced as a waste in membrane processes for sulphate removal (Durham *et al*., 2001). The composition of the brine will vary depending on the composition of the feed water and thus the methods of brine disposal will vary accordingly. In arid climates, the brine can be evaporated, leaving a comparatively small quantity of mixed residue. In cool or wet climates, heating may be required to promote evaporation or alternate disposal options must be considered. Brine disposal strategies are highly site specific but may include other forms of treatment (e.g. lime addition) if metals or sulphate are sufficiently elevated (Lubelli et al, 2004).

1.1.2 Sludge

The metal precipitates resulting from the neutralisation processes of acid mine water with lime and limestone is wastes identified as sludge. The composition of sludge varies due to differences in chemical composition of drainage waters between sites and annual differences at individual sites (Simonyi *et al.,* 1977). Generally the sludge is comprised of hydrated iron and aluminium oxides, phosphate, manganese, copper, magnesium, zinc and large amounts of gypsum.

The amount and consistency of sludge also varies greatly with the chemical composition of acid mine water and the treatment process used. These factors greatly influence disposal and recycling options. Sludge settleability, which is a function of both the settling rate and final sludge volume is influenced by the chemical reagents used to treat acid mine water. Studies have shown that limestone, as opposed to lime, precipitates sludge rapidly. However, lime treatment oxidizes iron completely, and ferric hydroxide is largely responsible for the poor settleability of sludge due to its hydrous nature and electrostatic charge (Ackman, 1982).

Legislation requires that sludge from neutralisation plants be disposed in an environmentally acceptable manner to prevent metals from leaching and entering the environment. Ackman (1982) showed that sludge disposal represents a major fraction of the cost during treatment of mining effluents.

1.2 SLUDGE DISPOSAL PROCESSES

Common methods of sludge disposal are deep mine disposal, permanent retention in a pond, haulage to and disposal at a coal refuse area and on site burial.

1.2.1 Deep mine disposal

This is accomplished by pumping sludge into inactive deep mines or inactive parts of mines in use. Deep mines disposal appears to be the best disposal method environmentally. Since sludge is alkaline, it can neutralize acidity in abandoned mines. The iron hydroxide resulting from the treatment does not readily redissolve and the water portion of the sludge can filter into the groundwater (Ackman, 1982). However, the problem with this method is that surface access to abandoned mines may be prohibited or structures used to retain sludge may fail and sludge enters active mines. This latter situation could inhibit future mining operations or recontaminate the treated water.

1.2.2 Permanent retention in pond

The method requires no transportation. However, large surface areas are required for affected areas, and reclaiming this land can be very difficult (Ackman, 1982). Sludge drying can take several years and the pond may only be covered once the drying is complete. These ponds may also fill up fairly quickly and offer much less disposal volume compared to deep mines. As ponds fill with sludge, washout of pollutants increases due to decreased settling distance. Ponds created by damming a valley are hazardous since in the case of a dam failure, land and streams can be devastated.

1.2.3 Coal refuse area

Sludge disposal at a coal refuse area has some advantages. The areas are already disturbed and the alkaline sludge can reduce seepage. Also, existing runoff collection systems collect all water from these sites for treatment. Disadvantages of this method are the long distances that sludge may need to be transported for disposal. However, if a refuse pile runoff collection site is nearby this may be very viable option.

1.2.4 On site burial

This method requires a dried sludge. If the sludge is disposed of on site through burial, an appropriate cover and capping system should be designed to:

- Provide erosional stability.
- Provide optimum surface water run-off and routing.
- Provide in-place physical stabilization.
- Provide optimum evaporation (use of soil materials, vegetation, engineering design, etc.)
- Minimize infiltration through sludge burial system with geosynthetic liners.

1.3 RECOVERY PROCESS

The enormous volumes of sludge produced, limited disposal sites and the future environmental problems that could be associated with sludge disposal are the major environmental and economic concerns that face acid mine water treatment. Technologies to treat sludge are the only options to solve disposal problems. Sludge rich in gypsum create environmental concerns such as airborne dust as well as effluent problems as gypsum is slightly soluble (2 000 mg/ℓ) in water. Therefore, a need exists to develop methods to convert low quality gypsum into a useful product, namely sulphur.

Sulphur is used in a number of industries and forms, for example:

- Manufacture of sulphuric acid.
- Fertilizers in agriculture.
- Fungicides.
- Vulcanising of rubber.
- Production of matches, gunpowder and fireworks.
- Sewage and waste water treatment.
- Electrodes in alkali metal batteries.
- Corrosion resistant concretes.

As far as the supply and demand for sulphur is concerned, Africa is a major importer of sulphur (Maree *et al.,* 2005). Countries like Zambia and the DRC import large tonnages of sulphur at high cost to manufacture sulphuric acid for the reduction of oxidized ores. These costs are inflated by the cost of transportation whilst sulphur is a cheap product. The South African consumption of sulphur in all forms in 2002 was 1 080 000 tons per annum of which 700 000 tons were imported at a landed cost of about R450/t (Ratlabala, 2003).

Prospects for sulphur recovery are positive with an increasing world-wide demand. In South Africa the fertilizer industry is by far the largest consumer of sulphur. The demand is also expected to increase in line with increased fertilizer usage and exports (Agnello *et al.,* 2003)

In view of serious shortages of foreign exchange, it is becoming increasingly difficult for these African countries to import sulphur. Consequently, industries depending on the use thereof are facing shut–down unless cheaper sources are identified. Most African countries have large amounts of waste gypsum generated by industrial activity. Even the costly sulphuric acid produced from imported sulphur mostly ends up as gypsum once used. Gypsum is a good source for the recovery of sulphur (Wewerka *et al*., 1982).

Thermal decomposition of gypsum was first practised commercially in Germany, during World War II, when the imported sulphur supply was disrupted by the Allied blockade. While numerous process modifications have been proposed and practised since that time, the basic requirements for successfully applying this technology remains unchanged (Lloyd, 1985). All processes require at a minimum:

1) Gypsum: Natural or by-product gypsum can be used.
2) Heating unit: Any heating unit can be used to heat the gypsum to reaction temperature, e.g. a furnace.
3) Reducing agent: This is required for reaction with gypsum at elevated temperature (Reddy *et al*., 1967; Ali *et al.,* 1968), for example, coal or

activated carbon (reaction 1), natural gas (reaction 2), carbon monoxide (reaction 3) and hydrogen (reaction 4).

$$CaSO_4\,(s) + 2C\,(s) \rightarrow CaS\,(s) + 2CO_2\,(s) \qquad (1)$$

$$3CaSO_4\,(s) + 4CS_2\,(g) \rightarrow 3CaS\,(s) + 4COS\,(g) + 4SO_2\,(g) \qquad (2)$$

$$CaSO_4\,(s) + 4CO\,(g) \rightarrow CaS\,(s) + 4CO_2\,(g) \qquad (3)$$

$$CaSO_4\,(s) + 4H_2\,(g) \rightarrow CaS(s) + 4\,H_2O\,(aq) \qquad (4)$$

The CaS produced (reaction 1 to 4) is slurried with water. Next the slurry is reacted with the CO_2 to strip the sulphide and form hydrogen sulphide (H_2S) and limestone ($CaCO_3$) (reaction 5). The H_2S gas formed after stripping is converted to elemental sulphur via the PIPco process (reaction 6) or the iron(III) route (reaction 7),

$$CaS\,(s) + H_2O\,(aq) + CO_2\,(g) \rightarrow CaCO_3\,(s) + H_2S\,(g) \qquad (5)$$

$$2H_2S\,(g) + SO_2\,(g) \rightarrow 3S\,(s) + 2H_2O\,(aq) \qquad (6)$$

$$H_2S\,(g) + 2Fe^{3+}\,(aq) \rightarrow S\,(s) + 2Fe^{2+}\,(aq) + 2H^{+}\,(aq) \qquad (7)$$

The PIPco process, invented and patented by PIPco Inc., is a process wherein elemental liquid sulphur is produced from SO_2 and H_2S gas (Ray *et al.*, 1990). In this process, SO_2 is absorbed in a potassium citrate buffer solution. The H_2S is then bubbled through the SO_2-rich buffer solution to first form $S_2O_3^{2-}$ (reaction 11), then sulphur in reaction 12 (Gryka, 1992).

SO_2 absorber: $SO_2\,(g) + H_2O\,(aq) \rightarrow HSO_3^{-}\,(aq) + H^{+}\,(aq)$ (8)

$$Cit^{3-}\,(aq) + H^{+}\,(aq) \rightarrow Cit^{2-}\,(aq) \qquad (9)$$

H_2S reactor: $2H_2S\,(g) \rightarrow 2HS^{-}\,(g) + 2H^{+}\,(aq)$ (10)

$$\tfrac{1}{2}\,HS^{-}\,(aq) + HSO_3^{-}\,(aq) \rightarrow \tfrac{3}{4}\,S_2O_3^{2-}\,(aq) + \tfrac{3}{4}\,H_2O\,(aq) \qquad (11)$$

$$\tfrac{3}{2}\,HS^{-}\,(aq) + \tfrac{3}{4}\,S_2O_3^{2-}\,(aq) \rightarrow 3S\,(s) + \tfrac{9}{4}\,H_2O\,(aq) \qquad (12)$$

Overall: $2H_2S\,(g) + SO_2\,(g) \rightarrow 3S\,(s) + 2H_2O\,(aq)$ (13)

Catalytic and thermal reduction processes (Rameshni and Santo, 2005) for sulphur recovery are expensive, difficult to operate, have high fuel consumption and limited ability to control temperature and side reactions.

CHAPTER 2

LITERATURE REVIEW

2.1 OCCURRENCE OF SULPHATE

Sulphate is a common constituent of water and results from the dissolution of mineral sulphates in soil and rock, particularly calcium sulphate (gypsum) and other partially soluble sulphate minerals (Toerien and Maree, 1987). It is also one of the least toxic anions with a lethal dose for humans of 45 g potassium or zinc salt (WHO, 1996).

Mine waters can contain significant concentrations of sulphuric acid and metal sulphates due to the oxidation of pyritic material in ore bodies and effluents from the uranium leaching process (Jones *et al.,* 1988). The acidity of the water is usually neutralised, but the sulphate content of the water is often in contravention of effluent standards. Sulphates are discharged from acid mine wastes and many other industrial processes such as tanneries, textile mills and processes using sulphuric acid or sulphates (Maree *et al*., 1989). It is estimated that in South Africa, 200 Mℓ/d of mining effluent, saturated with calcium sulphate, is discharged into the public streams of the Pretoria–Witwatersrand–Vereeniging region (Maree, 1988). This represents a sulphate load of 73 000 t/a. Atmospheric sulphur dioxide, discharged on combustion of fossil fuels, can give rise to sulphuric acid in rainwater (acid rain), which in turn results in the return of sulphate to surface waters in the environment.

Typically, the concentration of sulphate in:

- Surface water is 5 mg/ℓ SO_4^{2-}, although concentrations of several hundred mg/ℓ SO_4^{2-} may occur where the dissolution of sulphate minerals or discharge of sulphate rich effluents from acid mine drainage takes place (Maree, 1988).

- Sea water has just over 900 mg/ℓ SO_4^{2-}.
- Run-off water from areas with high mining activities varies between 200 and 2000 mg/ℓ SO_4^{2-}, while in areas of low mining activities it varies between 10 and 55 mg/ℓ SO_4^{2-} (Forster, 1988).

2. 2 EFFECT OF SULPHATE IN THE ENVIRONMENT

Although sulphate is non-toxic, except at very high concentrations, it exerts a purgative effect.

- Precipitation of sulphate can cause damage to equipment through the formation of calcium sulphate scale. (Maree *et al.,* 1990).

- At high concentrations, precipitation of sulphates may affect the efficiency of many industrial processes. The corrosive effect of high sulphate waters, particularly towards concretes, is increasingly becoming a major water quality problem for mining operations (Loewenthal *et al*., 1986).

- Sulphate, especially precipitation of gypsum, may impair the quality of treated water. In many arid environments gypsum becomes the dominant contributor to salinity in the vicinity of the discharge (Verhoef, 1982).

- People consuming drinking water containing sulphate in concentrations exceeding 600 mg/ℓ commonly experience cathartic effects, resulting in purgation of the alimentary canal (WHO 1996). Dehydration has also been reported as a common side effect following the ingestion of large amounts of sulphate.

2.3 TREATMENT OF SULPHATE RICH WATER

Current legislation world-wide places a limit around 400-500 mg/ℓ SO_4^{2-} in groundwater and 2 000 mg/ℓ SO_4^{2-} in industrial effluent (Wagner and Van Niekerk, 1987). Various treatments are available for sulphates involving physical, chemical and biological processes.

Essentially, these processes operate either through separation of salts through a membrane or through precipitation of sulphate as an insoluble salt, or through water evaporation and brine saturation. The selection of the treatment option is dictated by the sulphate and calcium concentration, due to the $CaSO_4$ scaling potential (Loewenthal *et al*., 1986).

2.3.1 Membrane processes

2.3.1.1 Reverse Osmosis

When brines with different salinities are separated by a semi-permeable membrane, pure water from the less concentrated brine will diffuse through the membrane until the salt concentrations on both sides of the membrane are equal (Chamber of Mines Research Organisation, 1988). This process is called *osmosis.* With reverse osmosis, salty feed water on one side of a semi-permeable membrane is typically subjected to pressures of 200-500 lb/sq inches for brackish water, and 800-1 200 lb/sq inches for seawater (AWWA, 1999).

About 10 gallons of water will pass through a square foot of membrane each day. The percentage of incoming feed water that is recovered as product water after one pass through a reverse osmosis module ranges from about 15-80 percent, however, this percentage can be increased if necessary by passing the waste water through sequential membrane elements (Durham *et al*., 2001)

Different osmosis processes have been proposed, for example:

1) The seeded reverse osmosis which uses a suspension of salt crystals to promote precipitation, and
2) The slurry precipitation, recycle and reverse osmosis (SPARRO) which includes the precipitation of metals by increasing effluent pH to 10 as a pre-treatment step, followed by cooling, filtration and readjustment of pH to 5-6 for the protection of the membrane process (Pulles *et al*., 1992; Juby *et al*., 1996).

2.3.1.2 Electrodialysis

Electrodialysis is a process that uses a direct electrical current to remove salt, other inorganic constituents and certain low molecular weight organics from brackish water with concentrations of dissolved solids up to 10 000 ppm (Valerdi-Perez *et al*., 2001). Dialysis tends to be more economical than reverse osmosis at salinities of less than 3 000 ppm but less economical than reverse osmosis at salinities greater than 5 000 ppm (Durham *et al*., 2001).

With this technique several hundred flat, ion permeable membranes and water flow spacers are assembled in a vertical stack. Half of the membranes allow positively charged ions, or cations, to pass through them. The other half-anion-permeable membranes allow negatively charged ions to pass through them (Spiegler, 1966).

2.3.1.3 Filtration Techniques

The process involves the separation of suspended particles from fluids. Different purification schemes are defined on particle size and flow. Any filtration process treatment where coarse particles dominate the suspended load requires pre-treatment (Zeman and Zydney, 1996). Different techniques are available including screening, freezing, elutriation and irradiation.

2.3.1.4 Ion Exchange

Ion exchange occurs between solid and liquid but no change results to the solid's structure. The target ions are removed from the liquid phase and are attached to the solid structure in exchange for another ion (hydrogen or hydroxyl) to immobilise the target ion (Schoeman and Steyn, 2001). For example, sulphate in $CaSO_4$, being an anion, would be exchanged for hydroxyl on an anion exchange resin (positively charged resin) while calcium, being a cation, would be exchanged for hydrogen on a cation exchange resin (negatively charged resin).

Due to the scaling in conventional circuits, GYPCIX (Gypsum Crystallisation Ion Exchange, Chemeffco SA), which is a modified ion exchange technique, was developed. GYPCIX uses low cost reagents such as lime and sulphuric acid. These resins target calcium and sulphate to reduce gypsum levels in effluent and to reduce the total dissolved solids concentration and corrosion problem. It can be used to treat solutions containing sulphate up to 2 000 mg/ℓ and calcium up to 1 000 mg/ℓ.

2.3.2 Precipitation processes

2.3.2.1 Barium salts

Barium sulphate is highly insoluble, thus making it an excellent candidate as a removal phase for sulphate treatment. The barium salts, used to remove sulphate by precipitation, include $BaCO_3$, BaS and $Ba(OH)_2$ according to reactions (14-16):

$$BaCO_3\,(s) + H_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + H_2CO_3\,(aq) \qquad (14)$$
$$Ba(OH)_2\,(s) + H_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + 2H_2O\,(aq) \qquad (15)$$
$$BaS\,(s) + H_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + H_2S\,(g) \qquad (16)$$

All three barium processes can lower high sulphate concentrations down to regulatory standards concentrations. The BaS process was found to be the most attractive process over the $BaCO_3$ and $Ba(OH)_2$ processes (Maree *et al.* , 1990) because:

1) High sulphate concentrations are removed and less gypsum is produced,
2) Acid waters can be treated directly thus eliminating the need for a pre-neutralisation step, and
3) Gypsum sludge disposal are lessened

2.3.2.2 Lime and Limestone

Lime and limestone are traditionally used for the neutralization of Acid Mine Drainage (AMD) but can also be used for the removal of sulphate from AMD through precipitation of gypsum (Bosch, 1990). After the treatment of AMD with lime or limestone, high sulphate levels remain in the treated water. Thus the process may be better suited as a pre-treatment step for AMD waters high in dissolved sulphate concentrations.

Recently, an integrated lime/limestone process was developed at the CSIR that is capable of reducing the sulphate concentration in AMD from 3 000 mg/ℓ to less than 1 200 mg/ℓ (Geldenhuys, 2001). The process consists of the following three stages:

1) Limestone neutralization to raise the pH to circum-neutrality in CO_2 production and gypsum precipitation,
2) Lime treatment to raise the pH to 12 for $Mg(OH)_2$ precipitation and enhanced gypsum precipitation, and
3) pH adjustment with CO_2 recovered from stage 1 with concurrent $CaCO_3$ precipitation.

2.3.3 Biological sulphate reduction process

The biological sulphate removal process is of interest owing to the acceptable cost and low waste production. Maree and Strydom (1985) showed that sulphate can be removed in an anaerobic packed-bed reactor using sucrose, pulp mill effluent or molasses as carbon and energy source. Metals such as nickel, cadmium and lead were completely removed as metal sulphides. Maree and Hill (1989) showed that a three-stage process can be employed for sulphate removal, using molasses as carbon and energy source in an anaerobic packed-bed reactor.

Du Preez *et al.* (1992) were the first to demonstrate that producer gas (mixture of H_2, CO and CO_2) can be used as carbon and energy source for biological sulphate reduction. Visser (1995) investigated the competition between sulphate reducing bacteria (SRB) and methanogenic bacteria (MB) for acetate as energy and carbon source in an upflow anaerobic sludge blanket (UASB) reactor. He found that at pH values less than 7.5, SRB and MB are equally affected by the presence of H_2S, while at higher pH values SRB out-compete MB.

Van Houten (1996) showed that sulphate can be reduced to H_2S at a rate of 30 g SO_4/ℓ.d when H_2/CO_2 is used as carbon and energy source and employing pumice or basalt particles to support bacterial growth in a fluidised-bed reactor. He found the optimum pH to be 6.5-8.0; the optimum temperature between 20-35 °C; the optimum H_2S concentration to be less than 450 mg/ℓ. The system should be completely anaerobic; the biomass immobilized and the retention of the active biomass high. The gas should be in the ratio: $H_2:CO_2$, 80%:20% and the hydrogen mass transfer maximized and there should be a high gas hold-up (through the system recycle) and small bubble diameter.

Eloff *et al*. (2003) showed that a venturi device can be used to introduce hydrogen gas into the system as the energy source, while geotextile (a coarse, fibrous material, used in road construction) can be used as a support material for SRB growth.

2.4 THERMAL ANALYSIS

Thermal analysis is the measurement of certain characteristics of a substance as a function of temperature or time. The technique has a wide range of applications, of which some are:

- Structural changes e.g. glass transition, melting/crystallization, solid and liquid phase transitions.
- Mechanical properties e.g. elastic behaviour and expansion/shrinkage.
- Thermal properties e.g. specific heat, melting point and expansion coefficient.
- Chemical reactions e.g. decomposition and stability in various gaseous atmospheres, reaction in solution, reaction in liquid phase, reaction with purge gas and dehydration (humidity, water of crystallization).

Figure 2.1 shows the schematic diagram of a Thermal Analysis instrument.

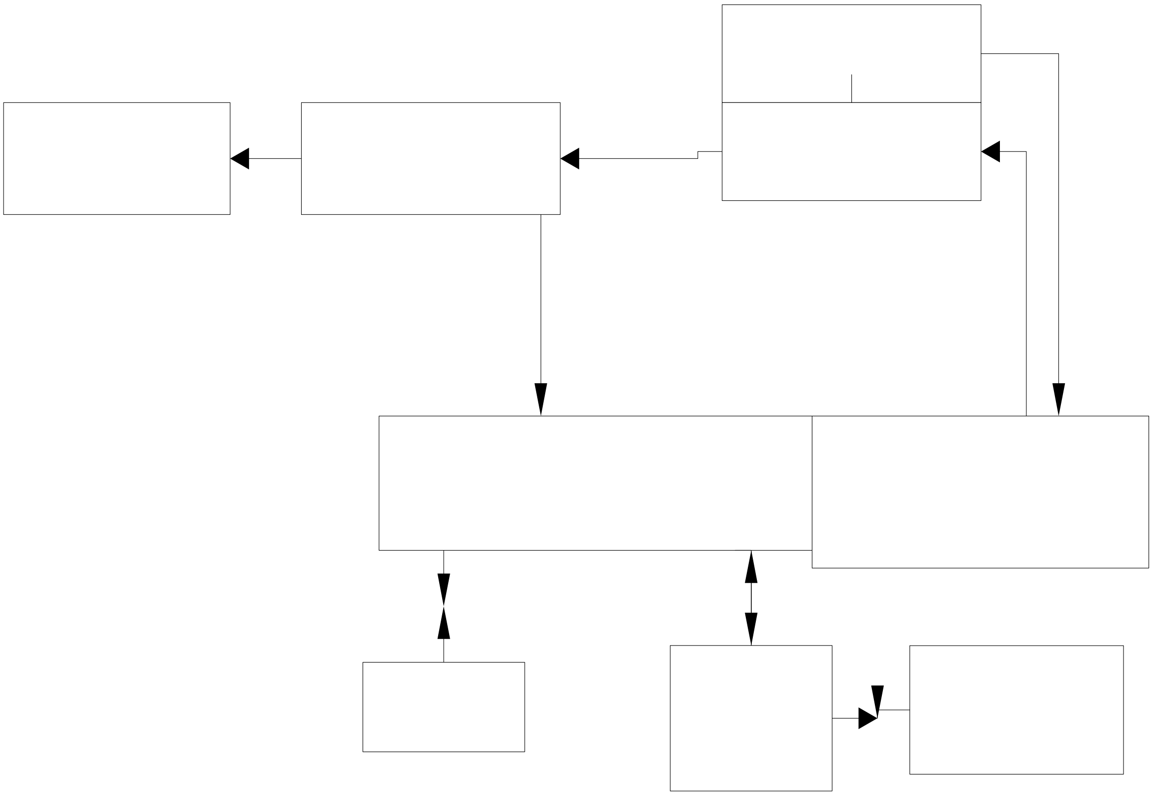

Figure 2.1 Schematic diagram of a Thermal Analysis instrument

Most important thermal analysis techniques are:

1. Thermogravimetry (TG) for measuring mass changes.
2. Differential Thermal Analysis (DTA) for measuring temperature differences.
3. Differential Scanning Calorimetry (DSC) for measuring heat flow.
4. Thermochemical Analysis (TMA) for measuring deformation.
5. Dynamic Mechanical Thermal Analysis (DMA) for measuring storage and loss moduli (Brown,1988).

2.4.1 Thermogravimetry

Thermogravimetry is the most widely used thermal technique to study heterogeneous processes. It is a limited technique, however, in that a gas-solid system must be involved in which the gaseous component is either a reactant or product of the reaction. Phase transitions such as solid to gas may also be investigated by this technique.

Three modes of thermogravimetry are:

a) isothermal or static thermogravimetry, in which the sample mass is recorded as a function of time at constant temperature,
b) quasistatic thermogravimetry or non-isothermal in which the sample is heated to constant mass at each of a series of increasing temperatures, and
c) dynamic thermogravimetry, in which the sample is heated in an environment whose temperature is changing in a predetermined manner preferably at a linear rate (Garner, 1955 and Sestak *et al.*, 1973).

In the thermogravimetric curve of a single non-isothermal reaction, there are two characteristic temperatures, the initial temperature, T_i and the final temperature T_f. T_i is the lowest temperature where the cumulative weight change reaches a magnitude that a particular thermobalance can detect. T_f is the temperature where the cumulative weight change first reaches its maximum value (Bamford and Tipper, 1980).

The development and ready availability of reliable and accurate electronic microbalances in thermogravimetry have led to their wide application in kinetic studies of the decomposition of solids (Garn, 1965).

2.4.2 Thermal decomposition reactions of solids

Thermal decomposition of solids means the breakdown of one or more constituents of the reactants into simpler atomic groupings upon heating. The thermal decomposition of a solid may be associated with physical transformations, such as melting, sublimation and recrystallization. The recrystallization of a solid may result in the production of a higher temperature lattice modification, which permits increased freedom of motion of one or more lattice constituents. The reactivity and chemical properties of solids are strongly influenced by the relative immobility of the constituent ions or molecules in the lattice of the reactant phase. The reactivity of identical chemical groupings in a solid reactant may vary with their position in the solid, as the structure may contain imperfections.

In regions of local distortion, the forces of lattice stabilization may be relatively diminished, with a consequent increase in the probability of reaction. This contrasts with the homogeneous behaviour of similar groups in the liquid or gaseous phase. In rate processes of solids it is often observed that there are localized regions or sites of preferred onset of reaction. Such initiation usually occurs at a surface, leading to the development of a zone of preferred chemical transformation, which thereafter progressively advances into adjoining volumes of unreacted material. This restricted zone of the solid is called the reaction interface (Bamford and Tipper, 1980).

The occurrence of reaction is usually regarded as being exclusively restricted to the reactant-product interface, at which local conditions markedly enhance the ease of the chemical transformation. The kinetic characteristics of the overall process are determined by the velocity of the advance of this interface into unchanged reactant and the variation of its effective area with time (Bamford and Tipper, 1980).

The following general kinetic tenets have been used as a widely accepted basis for the interpretation of the kinetic behaviour of the decomposition reactions of solids (Bamford and Tipper, 1980):

1) the rate of reaction of a solid is proportional to the aggregate effective area of the reactant product interface,
2) the rate of interface advance is constant through an isotropic reactant under isothermal conditions and
3) the temperature dependence of the rate coefficient obeys the Arrhenius equation.

These tenets are applicable only where the reactant undergoes no melting. If no melting occurs, the shape of the fraction decomposed (α) against time (t) curve for an isothermal reaction can be related to the geometry of formation and advance of the reaction interface.

2.4.3 Kinetic rate laws for the decomposition of solids

The number of potential nucleus forming sites (N_o) and the number of molecules having the energy at least equal to the activation energy for nucleus formation determines the rate at which nuclei are formed. The laws describing the decomposition rate in decomposition reactions (Note: all these reactions are valid at constant temperature) are divided into three groups depending on the location of the maximum rate of decomposition, $(\frac{d\alpha}{dt})_{\max}$, where α is the degree of conversion and t is the time (Keattch and Dollimore, 1975):

1) α against t relationships obeyed up to $(\frac{d\alpha}{dt})_{\max}$, and concerned with nuclei growth,
2) α against t relationships obeyed on both sides of $(\frac{d\alpha}{dt})_{\max}$ and thus concerned with both nuclei growth and interference and
3) α against t relationships obeyed beyond $(\frac{d\alpha}{dt})_{\max}$, i.e. relationships concerned with either nuclei interference or a decreasing reaction interface.

The measured thermogravimetric scan is transformed into the degree of conversion as follows:

$$\alpha_i = \frac{M_0 - M_i}{M_0 - M_f} \qquad (17)$$

where M_i = mass at time t
M_o = initial mass
M_f = final mass

The kinetics of many solid-state reactions can be represented by the general equation $f(\alpha) = kt$, where the function $f(\alpha)$ depends on the reaction mechanism and geometry of the reacting particles. Sharp *et al.* (1966) have shown that an approach based on a reduced time scale facilities comparison of experimental data with theoretical models; some theoretical equations were expressed in the form $f(\alpha) = A(t/t_{0.5})$, where $t_{0.5}$ is the time at which α = 0.5 and A is a calculable constant which depends on the form of $f(\alpha)$. Experimental data can be tabulated as α vs t for a variety of experimental conditions. Rate constants can be then be determined from linear plots of $f(\alpha)$ vs t.

The equations can be divided into groups to differentiate among equations within a group requires considerable experimental accuracy to high values of α. The groups and their equations are:

1) Diffusion-controlled reactions (Jander, 1927):

$$f(\alpha) = \alpha^2 = kt \tag{18}$$

$$(1-\alpha)\ln(1-\alpha) + \alpha = kt \tag{19}$$

$$[1-(1-\alpha)^{1/3}]^2 = kt \tag{20}$$

$$1 - 2\alpha/3 - (1-\alpha)^{2/3} = kt \tag{21}$$

2) Phase-boundary-controlled (Keattch and Dollimore, 1975): $f(\alpha) =$

$$1-(1-\alpha)^{1/2} = kt \tag{22}$$

$$1-(1-\alpha)^{1/3} = kt \tag{23}$$

3) Avrami-Erofe'ev equations (Erofe'ev, 1946): $f(\alpha) =$

$$[-\ln(1-\alpha)^{1/2}] = kt \tag{24}$$

$$[-\ln(1-\alpha)^{1/3}] = kt \tag{25}$$

2.4.4 Kinetic parameters

The temperature dependence of chemical processes can be expressed in terms of the Arrhenius equation,

$$k = Ae^{-E_a/RT} \tag{26}$$

where k is the rate constant, R is the gas constant and T is the thermodynamic temperature. The Arrhenius parameters (E_a and A) provide measures of the magnitude of the energy barrier to reaction (the activation energy, E_a) and the frequency of the occurrence of a condition that may lead to a reaction (the frequency factor, A) (Blaine and Hahn, 1998).

There is no discrete activated state in the solid state, so activation energy values need to be evaluated critically before conclusions regarding the stability of the solid reactants can be drawn (Garn, 1978). The activation energy value (E) is expressed as an energy quantity per mole (kJ.mol^{-1}), since the measured slope of the Arrhenius plot (lnk vs 1/T) is divided by the gas constant, R (R=8.314 J.K^{-1}.mol^{-1}). For the initial stages of the reaction

($\alpha < 0.1$), the relationship between the rate constants, k, and the reaction time, t, can be given as

$$\frac{d\alpha}{dt} = kt \qquad (27)$$

Using the k values at different temperatures and applying them to the Arrhenius equation, an activation energy value for the nucleation process of a reaction can be obtained.

2.4.5 Determination of kinetic parameters

Any approach to the analysis of both complex (those whose kinetics cannot be described as an overall single stage process (single rate constant)) and simple (overall single- stage) processes must rely on the methods relating to complementary techniques (Vyazovkin and Lesnikovich, 1987), in other words, using generalised descriptions of the process instead of discriminating separate elementary models.

The quasi isoconversional methods can be used for determination of activation energy of the single-stage process. Among methods that are used to analyse complex processes are the isoconversional method (Flynn, 1983), method of invariant kinetic parameters (Lesnikovich and Levchik, 1983), Sestak-Berggren method (Sestak and Berggren, 1971) and Piloyan method (Piloyan *et al.,* 1966).

It has been shown by Vyazovkin and Lesnikovich, (1990) that reliable information about the mechanism and kinetics of complex processes can be obtained by isoconversional methods. One attribute to such methods is that the effective activation energy specific for a given extent of conversion can be determined if several thermal analysis experiments are performed at different heating rates.

The well known isoconversional methods used for the determination of activation energy is the Ozawa-Flynn Wall method (Dowdy, 1987). The method provides a model free approximation of the activation energy by using multiple scan analysis. It is suited for use in systems where many reactions are occurring. It does not require any assumptions concerning the form of the kinetic equation, other than that there is Arrhenius-type temperature dependence (Dowdy, 1987).

The differential methods for the calculation of the kinetic parameters are based on the use of the well known reaction rate equation:

$$\beta \frac{d\alpha}{dt} = f(\alpha) A \exp\left(\frac{-E}{RT}\right) \tag{28}$$

where β is the heating rate, T is the temperature, A is the pre-exponential factor and f(α) is the differential conversion function.

As far as the isoconversional integral methods are concerned, the above equation at constant heating can be expressed as follows:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f\alpha} = \frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT \tag{29}$$

$$g(\alpha) = \frac{AE}{R\beta} p\left(\frac{E}{RT}\right) \tag{30}$$

where $g(\alpha)$ is the integral conversion function.

Assuming that T_0 is below the temperature at which the reaction becomes noticeable, the lower limit, T_0, can be set to zero. Then equation 30 expressed in logarithmic form is:

$$\log g(\alpha) = \log\left(\frac{AE}{R}\right) - \log\beta + \log p\left(\frac{E}{RT}\right) \tag{31}$$

Doyle, (1962) has found that for E/RT≥20, log p$\frac{E}{RT}$ may be approximated by equation 32,

$$\log p\left(\frac{E}{RT_i}\right) = -2.315 - 0.4567\left(\frac{E}{RT_i}\right) \qquad (32)$$

Therefore equation 31 becomes,

$$\log g(\alpha) = \log\left(\frac{AE}{R}\right) - \log\beta - 2.315 - 0.4567\frac{E}{RT} \qquad (33)$$

“Differentiating” equation 33 at constant degree of conversion results in

$$\frac{d\log\beta}{d1/T} \cong \left(\frac{0.457}{R}\right)E \qquad (34)$$

For R = 1.987 cal.mole^{-1}.K^{-1}

$$E = -4.35\frac{d\log\beta}{d\frac{1}{T}} \qquad (35)$$

Therefore, if a series of experiments are performed at different heating rates, this equation can be used to obtain the activation energy. A specific degree of conversion is considered, and the temperature required for this degree of conversion is determined for each heating rate. If log β is plotted against 1/T the gradient is -0.4567E/R, and so the activation energy can be determined for the particular degree of conversion (α) being considered.

2.4.6 Identifying the type of reaction/process

According to Vyazovkin and Lesnikovich, (1990) and Dowdy (1987), it was stated that for the isoconversional method, a complex process/reaction is identified by the changes in activation energy for different α, while on a single stage reaction, the activation energy does not change with α. The high sensitivity of the degree of conversion dependence of the activation energy provides a higher efficiency of its application as a criterion of a complex process. Therefore, the analysis of a complex reaction is based on the dependence of the α on the activation energy.

Vyazovkin and Lesnikovich, (1990) further showed that the increase in dependencies of activation energy on the degree of conversion occur when simultaneous/parallel reactions occur. Decreasing dependencies are typical of complex reactions with a change in limiting stage. Among these are, in particular processes containing a reversible intermediate stage or those proceeding with a change over from kinetic to the diffusion regime.

The IKP (Invariant Kinetic Parameters) method can also be used to determine the complex character of a model process based on the shape of the Arrhenius dependence. The rate of such a process is determined by the equation,

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = (k_1 + k_2)(1-\alpha) \tag{36}$$

where β is the heating rate, T is the temperature , t is the time, k_1 and k_2 are the rate constant. Integrating equation 36, we obtain the temperature dependence of the degree of conversion.

$$\alpha = 1 - \exp\left[-\left(\frac{1}{\beta}\right)\int_0^T (k_1 + k_2)dT\right] \tag{37}$$

Taking into account the Arrhenius shape of the temperature dependence of the rate constants, the integral can easily be calculated as Senum-Yang approximation (Senum and Yang, 1979). If the plot of lnk vs 1000/T (Arrhenius dependence) gives a concave shape then that particular process involves parallel reactions while the convex shape shows a process with a change in the limiting stage.

2.5 THERMAL DECOMPOSITION OF GYPSUM TO CALCIUM SULPHIDE

The process of converting gypsum to calcium sulphide is normally effected by passing reducing gases at elevated temperatures over gypsum and cooling the calcium sulphide produced in a non-oxidising atmosphere.

Calcium sulphide is a white powder if pure, but crude calcium sulphide called sulphurated lime, can be yellowish to pale grey (Anthony *et al.*, 1990). It has an odour of H_2S in moist air and an unpleasant alkaline taste. CaS has a very low solubility of 0.2 g/ℓ.

Calcium sulphide can be prepared in the laboratory by heating pure calcium carbonate in a stream of H_2S and H_2 at 1000 °C (Brauer, 1963). It can be used as a lubricant additive in phosphorus. Luminous CaS can be used for making luminous paints or varnishes. Pure CaS is used in electron emitters (Budavari, 1989). In industries it is used in the production of sulphur by the Chance-Claus process and as an insecticide in the treatment of waste liquor from paper mills (Ali *et al.,* 1968). It is also used in cement to achieve an increase in mechanical strength with time.

2.5.1 Description of gypsum

Gypsum can be colourless, white, grey, yellow, red or brown in colour. The crystals are prisms or flat plates, and can grow up to 1 metre (Figure 2.2). It can appear as transparent crystals (selenite); fibrous, elongated crystals (satin spar); granular and compact masses (alabaster); and in rosette-shaped aggregates called desert roses (Follner *et al.*, 2002).

Figure 2.2 Crystals of natural gypsum

2.5.2 Occurrence of gypsum

Natural gypsum deposits were formed millions of years ago when salt water oceans covered most of the earth, and as they receded, many inland “dead” seas were formed which, as evaporation continued, became more salty. As those salts precipitated, they formed various compounds in turn, one of which was gypsum (natural gypsum).

Gypsum can also be produced as a waste product by various industries, e.g.

- fertilizer industry, when sulphuric acid is reacted with calcium phosphate rock, resulting in a solution of phosphoric acid and a solid calcium sulphate called phosphogypsum (Benstedt, 1979; Roode, 1996).

$$Ca_5(PO_4)_3.F(s) + 5H_2SO_4(aq) + 5x\ H_2O\ (l) \rightarrow 5CaSO_4.xH_2O(s) + 3H_3PO_4(aq) + HF(aq) \qquad (38)$$

where x depends on the temperature and acid concentration and can be either 0 (anhydrite), ½ (hemihydrate) or 2 (dihydrate).

- mining industry, when acid mine water is neutralized with limestone or lime (reaction 39) .

$$CaCO_3\ (s) + H_2SO_4\ (aq) \rightarrow CaSO_4\ (s) + CO_2\ (g) + H_2O\ (aq) \qquad (39)$$

- power stations, when powdered calcium carbonate is fed to the combustion chamber to react with SO_2 gas (reaction 40).

$$SO_2\ (g) + CaCO_3\ (s) + \tfrac{1}{2}\ O_2\ (g) + 2H_2O \rightarrow CaSO_4.2H_2O(s) + CO_2\ (g) \qquad (40)$$

Furthermore, at PPC Cleveland’s Jupiter cement plant, gypsum is prepared by mixing $CaCO_3$ with diluted H_2SO_4 (Mantel and Liddell, 1988).

2.5.3 Uses of gypsum

Gypsum is used in the building and agricultural industries. As a building material, it is used

- in the manufacture of plaster walls, ceramic tiles, tombstones and partitions,
- to adjust time of setting of Portland cement, and in ceramic tiles (Mantel, 1991).

In agriculture, it is used

- as a fertilizer and soil conditioner to reduce salinity of soils,
- as an animal–food additive (Bye, 1983).

Gypsum is also used as a source for Plaster of Paris in treatment of fractured bones and as a dental plaster mold to cast the dental. It can also be sprayed in coal mines to prevent gas explosion (Mantel, 1991).

Gypsum can be ground up and calcined at a comparatively low temperature (110-120 °C) until 75% of its moisture content has evaporated. When that happens, the rock becomes a fine powder (Plaster of Paris). By returning the water to the powder, a pliable mortar can be made that can be formed into any shape and hardened. Heat treated gypsum is the only natural substance that can be restored to its original rock-like state by the addition of water alone (Murat, 1987).

2.5.4 Effect of gypsum

Gypsum wastes, not only occupy thousands of acres of land but create serious problems such as air borne dust and water pollution problems due to the release of hazardous substances such as heavy metals and acid as a result of weathering and chemical decomposition (Savostianoff, 1990).

2.5.5 Dehydration of gypsum

Waste gypsum is a mixture of calcium sulphate dihydrate ($CaSO_4\,.2H_2O$), calcium sulphate hemihydrate ($CaSO_4.0.5\ H_2O$), anhydrous calcium sulphate ($CaSO_4$) and some impurities (Taylor, 1990). Dihydrate and insoluble anhydrite are stable materials found in nature, while hemihydrate and soluble anhydrite are highly unstable, and readily react with water. When the dihydrate is heated, it dehydrates in two steps to the hemihydrate and soluble anhydrite (reaction 41 and 42),

$$CaSO_4.2H_2O\ (s) \xrightarrow{>95°C} CaSO_4.0.5H_2O(s) + 1.5\ H_2O\ ((g) \quad (41)$$

$$CaSO_4.0.5H_2O\ (s) \xrightarrow{>120°C} CaSO_4\ (s) + 0.5\ H_2O\ (g) \quad (42)$$

The degree of gypsum dehydration is strongly influenced by the structure and the impurities in the material, as well as by the conditions under which the process takes place, such as temperature, heating rate, vapour pressure, humidity and particle size (Molony and Ridge, 1968). Dehydration increases with exposure time to elevated temperatures. The dehydration of the gypsum present in cement will proceed at a higher rate than dehydration of gypsum by itself as the humidity increases. Mantel and Liddell, (1988) described the kinetics differences between naturally occurring South African gypsum (used in Port Elizabeth cement companies), synthetic gypsum (which is prepared from the reaction of limestone with sulphuric acid and used in Johannesburg cement companies) and pure calcium sulphate dehydrate in different atmospheres.

2.5.5.1 Hemihydrate ($CaSO_4.0.5H_2O$)

Hemihydrate (partially dried calcium sulphate) is a fine, odourless and tasteless powder which occurs in nature as a mineral bassanite. When mixed with water, it sets to a hard mass. It is used for wall plasters, wallboard and blocks for the building industry (Ball and Norwood, 1969).

The hemihydrate exists in two forms, termed α and β. These two forms are the limiting states of this phase and are distinguished from each other by their properties, energy relationships and methods of preparation. The α-hemihydrate is produced under pressure in a humid atmosphere and consists of large primary particles. The β-hemihydrate forms flaky, irregular secondary particles which consist of small individual crystals. The solubility of the α-hemihydrate in water at 20 °C is 0.88 g/100g solution and that of the β-hemihydrate is 0.67 g/100mℓ solution. Figure 2.4 showed the crystal structure, (Bezou *et al.,* 1995).

2.5.5.2 Anhydrite ($CaSO_4$)

The anhydrite (dead burned gypsum) exists in three phases (Hand, 1997):

a. soluble calcium sulphate anhydrite (γ-$CaSO_4$) (crystal structure for γ-$CaSO_4$ is given in figure 2.3, Bezou *et al*, 1995),
b. insoluble calcium sulphate anhydrite (β-$CaSO_4$)
c. high temperature calcium sulphate anhydrite phase (α-$CaSO_4$).

Insoluble anhydrite has the same crystal structure as the mineral and is obtained upon complete dehydration of the calcium sulphate dihydrate above 200 °C. It is used in cement formulations and as a paper filter (Ball and Norwood, 1969).

Soluble anhydrite is obtained in granular or powder form by complete dehydration of the calcium sulphate dihydrate above 120 °C. Because of its strong tendency to absorb moisture, soluble anhydrite is useful as a drying agent for solids, organic liquids and gases (Ball and Norwood, 1969).

The high temperature calcium sulphate anhydrite is insoluble in water and exists at temperatures above 1 180 °C (Wirsching 1978).

2.5.5.3 Dihydrate ($CaSO_4.2H_2O$)

The dihydrate occurs in nature as a fine grained, compact mass of small crystals (crystal structure is indicated in Figure 2.5, Atoji and Rundle, 1958). It is used in the manufacturing of Portland cement, in soil treatment to neutralise alkali carbonates and to prevent loss of volatile compounds and for the manufacturing of Plaster of Paris as a white pigment (Ball and Norwood, 1969). The dihydrate is soluble in water and practically insoluble in most organic solvents. Its solubility in water is 0.21g/100g solution.

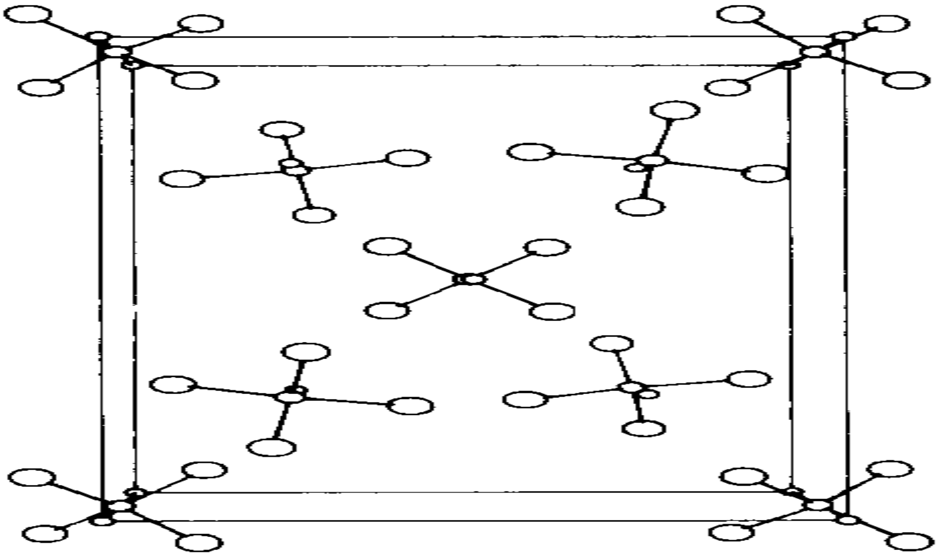

Figure 2.3 Crystal structure of γ-$CaSO_4$ (Bezou *et al*, 1995)

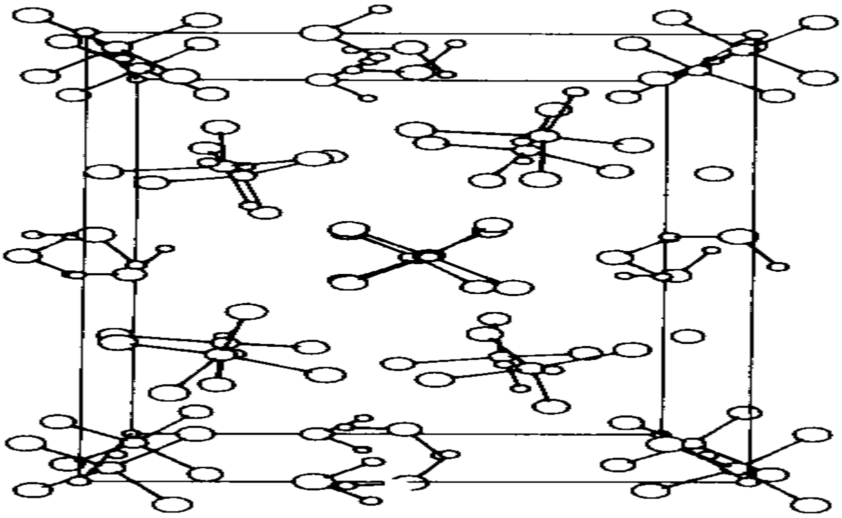

Figure 2.4 Crystal structure of $CaSO_4.0.5H_2O$ (Bezou *et al*, 1995)

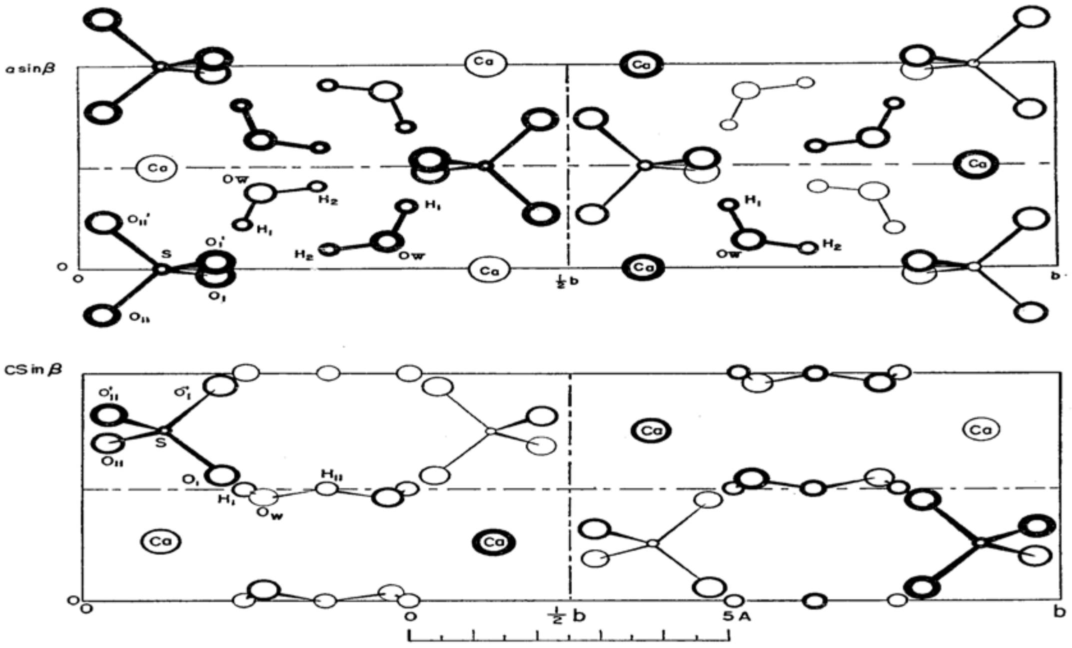

Figure 2.5 Crystal structure of $CaSO_4.2H_2O$ (Atoji and Rundle, 1958)

2.6 SULPHUR PRODUCTION PROCESS USING HYDROGEN GAS

Hydrogen sulphide (H_2S) is a highly toxic, corrosive and malodorous gas. Besides its other bad habits, it also deactivates industrial catalysts. H_2S is commonly found in natural gas and is also a by-product at oil refineries.

If water comes into contact with gas streams containing hydrogen sulphide it turns sour (Cadena and Peters, 1988). In water, sulphide (S^{2-}) has an oxygen demand of 2 mol O_2/mol S^{2-} and thus would consume oxygen and have an adverse effect on aquatic life if discharged into surface water (Kobayashi *et al*., 1983). Because H_2S is such an obnoxious substance, it is converted to non-toxic and useful elemental sulphur at most locations that produce it.

Removal of H_2S from gas streams is a familiar industrial requirement, whose economic importance will grow with the increasing utilization of fuels with higher sulphur content. Among the removal processes for H_2S, conversion to elemental sulphur is advantageous because sulphur can be used for the treatment of gases in an environmentally permissible procedure (Astarita *et al*., 1983; Kohl and Riesenfeld, 1985). It can also be applied to the treatment of gases with relatively low concentrations of H_2S in the presence of CO_2.

The conventional chemical processes for H_2S abatement and sulphur recovery (e.g. the Claus process) have some drawbacks, such as deactivation, loss of absorbent or catalyst poisoning or side reactions, unfavourable selectivity, corrosiveness, toxicity and the need to operate at a high pressure or temperature (Cork *et al*., 1986).

2.6.1 Description of the Claus process

The Claus reaction consists of H_2S and sulfur dioxide (SO_2) reacting in the vapour phase to produce sulphur and water. The H_2S is first separated from the host gas stream using amine extraction. Then it is fed to the Claus unit, where it is converted in two steps (Chandler and Isbell, 1976). The first step is the thermal step (reaction 43), where one-third of the H_2S is oxidized, producing the H_2S and SO_2 in a 2:1 ratio. This is done in a reaction furnace at high temperatures (1 000-1 400 °C).

Some sulphur is formed, but the remaining unreacted H_2S proceeds to the next step, the catalytic step. The thermal step reaction and a schematic drawing of the process are as follows:

$2H_2S\ (g) + 3O_2\ (g) \rightarrow 2SO_2\ (g) + 2H_2O\ (aq)$ (43)

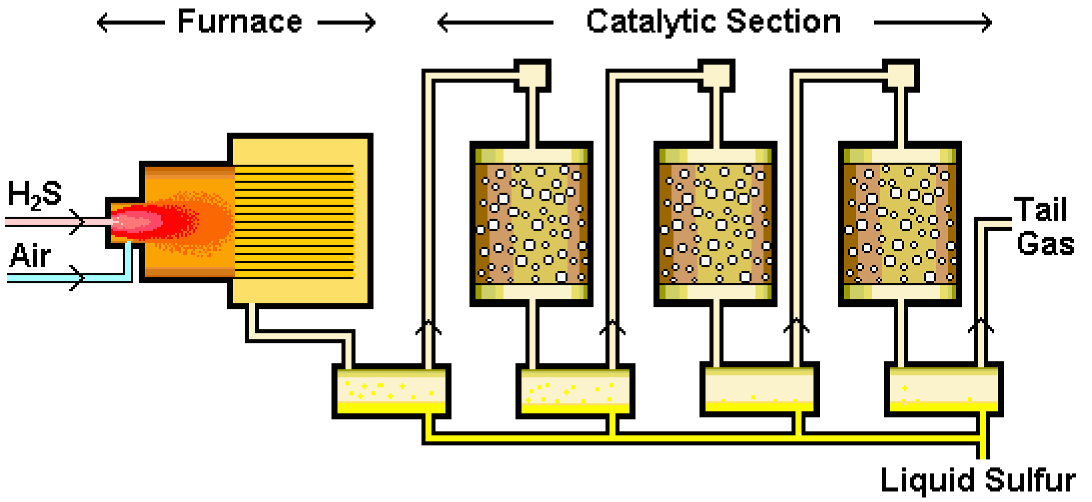

Figure 2.6 Schematic representation of the Claus technology (www.nelliott.demon.co.uk)

The liquid sulphur produced can be reused in the plant. The effluent tailgas contains SO_2, carbon disulphide (CS_2) and carbonyl sulphide (COS), which are byproducts produced in the Claus reactors.

2.6.1.1 Catalytic step

The Claus reaction continues in the catalytic step with activated alumina or titanium dioxide, and serves to boost the sulphur yield. The remaining H_2S is reacted with the SO_2 formed in the thermal step (reaction 44) at lower temperatures (200-350 °C) over a catalyst bed to make more sulphur (Shimin, *et al.,* 1997).

$2H_2S\ (g) + SO_2\ (g) \rightarrow 1.5\ S_2\ (s) + 2H_2O\ (aq)$ (44)

The catalytic recovery of sulphur consists of three substeps: heating, catalytic reaction and cooling plus condensation. The first process step in the catalytic stage is the process gas heating. It is necessary to prevent sulphur condensation in the catalyst bed, which can lead to catalyst fouling. The required bed operating temperature in the individual catalytic stages is achieved by heating the process gas in a reheater until the desired operating bed temperature is reached (Nagl, 1997).

The typically recommended operating temperature of the first catalyst stage is 315-330 °C (bottom bed temperature). The catalytic conversion is maximized at lower temperatures, but care must be taken to ensure that each bed is operated above the dewpoint of sulphur. The operating temperatures of the subsequent catalytic stages are typically 240 °C for the second stage and 200 C for the third stage (bottom bed temperatures).

In the sulphur condenser, the process gas coming from the catalytic reactor is cooled to between 150-130 °C. The condensation heat is used to generate steam at the shell side of the condenser. Before storage and downstream processing, liquid sulphur streams from the process gas cooler, the sulphur condensers and from the final sulphur separator are routed to the degassing unit, where the gases (primarily H_2S) dissolved in the sulphur are removed (Larraz, 1999).

The tail gas from the Claus process still containing combustible components and sulphur compounds (H_2S, H_2 and CO) is either burned in an incineration unit or further desulphurized in a downstream tail gas treatment unit.

2.6.2 Fe(III) process

Dowa Mining Co. in Japan have developed a process of H_2S removal (Imaizumi, 1986). In this process, aqueous $Fe_2(SO_4)_3$ solution is used as an absorbent. H_2S is oxidized to elemental sulphur and $Fe_2(SO_4)_3$ is reduced to $FeSO_4$. The reaction is:

$$H_2S\ (g) + Fe_2(SO_4)_3\ (aq) \rightarrow S\ (s) + 2FeSO_4\ (aq) + H_2SO_4\ (aq) \tag{45}$$

The sulphur formed is separated with a filter and the reactant $Fe_2(SO_4)_3$ is regenerated from the products $FeSO_4$ and H_2SO_4 by biological oxidation using the iron oxidising bacterium, *Thiobacillus ferrooxidans*:

$2FeSO_4 (aq) + H_2SO_4 (aq) + ½O_2 (g) \rightarrow Fe_2(SO_4)_3 (aq) + H_2O(aq)$ (46)

Then the overall reaction is:

$H_2S (g) + ½ O_2 (g) \rightarrow S (s) + H_2O (aq)$ (47)

In 1999, Pagella and Faveri developed a process of H_2S gas treatment by an iron bioprocess. The process is based on two steps corresponding to absorption with chemical reaction of the gas in a ferric solution (where the ferric ion is converted to a ferrous ion), and biological oxidation of ferrous ions in the solution to produce ferric ions again. The reactions (Satoh *et al*., 1988) are:

$H_2S (g) + 2Fe^{3+} (aq) \rightarrow S^o (s) + 2Fe^{2+} (aq) + 2H^+ (aq)$ (48)

$Fe^{2+} (aq) \rightarrow Fe^{3+} (aq) + e^-$ (49)

The electron produced in equation 49 is transferred, through the biochemical paths of the cell, to the dissolved oxygen, which acts as the final electron acceptor:

$2H^+ (aq) + ½ O_2 (g) + 2e^- \rightarrow H_2O (aq)$ (50)

The following overall reaction is performed:

$H_2S (g) + ½ O_2 (g) \rightarrow S (s) + H_2O (aq)$ (51)

Advantages of this process for H_2S abatement are mild pressure and temperature conditions, lower costs and closed loop operation without input of chemicals or output of wastes (Pagella and Faveri, 1999).

Asai *et al*., (1990) proposed the reaction where H_2S is absorbed with ferric monohydrate as follows:

$H_2S (g) + 2FeOH^{2+} (aq) \rightarrow S (s) + 2Fe^{2+} (aq) + 2H_2O (aq)$ (52)

Reaction (52) is made up out of the following steps:

H_2S (g) + $FeOH^{2+}$ (aq) → $H_2S.FeOH^{2+}$ (aq) (53)

$H_2S.FeOH^{2+}$ (aq) + $FeOH^{2+}$ (aq) → S (s) + $2Fe^{2+}$ (aq) + $2H_2O$ (aq) (54)

2.6.3 PIPco process

The PIPco process is a patented process and offers a great potential to convert H_2S gas into uncontaminated liquid sulphur in an environmental friendly and economical way. The black box description of the process is given in Figure 2.7.

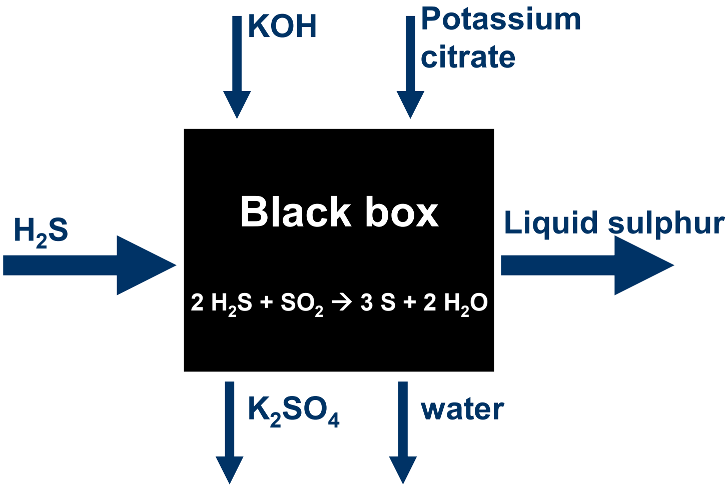

Figure 2.7 Black box description of the PIPco process

The only feedstock of the PIPco process is H_2S gas. During operation KOH and potassium citrate are added as make-up chemicals. The main by-products are potassium sulphate (which can be used as a fertilizer) and the process also produces water. The core of the process is a potassium citrate solution which is used to selectively absorb SO_2 in water. This solution is contacted with H_2S to form elemental liquid sulphur. Note that SO_2 is not added to the process from an external source but is generated within the process.

This process is closely related to processes developed by others. Comparable processes are the Sodium Phosphate Process and the Sodium Citrate Process (Bekassy-Molnar *et al.*, 2005). Both processes use a buffer (sodium phosphate and sodium citrate, respectively) to absorb SO_2 which is then used as an oxidizing agent to convert H_2S to elemental sulphur. However, in contrast to the PIPco process, these processes take place at a low temperature and produce solid elemental sulphur instead of liquid sulphur.

The advantages of the PIPco process compared to similar processes are as follows (Gryka, 1992):

- Mild conditions - the temperatures and pressures are, although slightly elevated, not very high. The temperature of the potassium citrate buffer in the absorption reactor must be as low as possible, preferable below 50 °C. The reaction is carried out at a temperature above the melting point of sulphur and below the temperature where sulphur becomes very viscous. The preferred reaction temperature is about 125 °C. A maximum of 4 bar pressure is recommended.

- Favourable economics - an engineering study carried out showed that the PIPco process costs 50% of today's preferred technology to remove H_2S from natural gas. Flexible feed is possible - the process is very flexible towards impurities in the feed. Other components besides H_2S or SO_2 are either burned in the furnace or leave the process through the vent of the absorption column as potassium citrate is a selective absorbent for SO_2.

- No liquid or solid wastes - the process does not produce any liquid or solid wastes (a big disadvantage of throwaway processes which might produce, for example, gypsum).

- Uncontaminated liquid sulphur is produced: If the PIPco process is used in a brine treatment plant, brine is converted into a very valuable feedstock for the chemical industry in general. Moreover, this enhances the economic potential of the process as industry might consider sulphur as a co-product of their activities.

The description of the PIPco process is detailed in US patent 5057298 (Ray *et al.,* 1990) and a report prepared by PIPco Inc. (Gryka, 1992) for the Gas Research Institute. Also processes that are developed by earlier workers serve as a foundation of knowledge which can be applied to the PIPco process. A schematic diagram of the PIPco process is given in Figure 2.8.

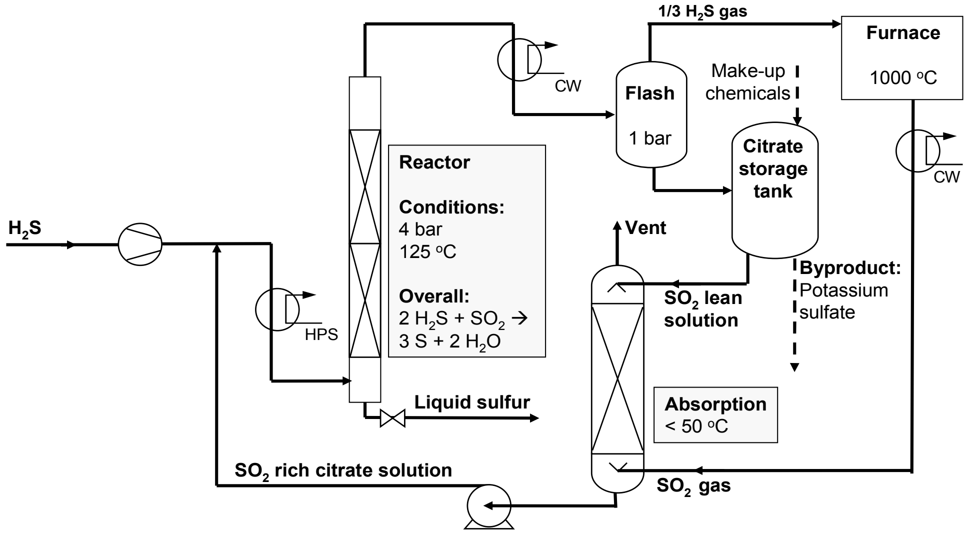

Figure 2.8 Process flow sheet for the PIPco process (Gryka, 1992)

The pressure of the H_2S feed gas is elevated to approximately 4 bar (reaction conditions) and mixed with a SO_2 rich potassium citrate solution. This gas liquid mixture is then heated to 125 °C and fed to the reactor. The H_2S gas reacts with the absorbed SO_2 to form sulphur. The network of reactions taking place in the liquid phase is very complex, but the overall (exothermic) reaction can be given as follows:

$$2H_2S\ (g) + SO_2\ (g) \rightarrow 3S\ (s) + 2H_2O\ (aq) \qquad (55)$$

The formation of sulphur proceeds through reactions of several intermediate compounds. The reaction is carried out at an elevated pressure to prevent the potassium citrate solution from boiling. In the reactor ideally 2/3 of the H_2S that enters the reactor reacts with SO_2 to form sulphur. Within the reactor, sulphur is coalesced and separated by decantation. The reaction is favoured by a low pH.

At the top of the reactor a gas liquid mixture leaves the reactor. The gas and the liquid phase are separated in a flash vessel at atmospheric pressure. The gas phase is introduced to a furnace where the unreacted H_2S is converted to SO_2 according to the following reaction:

$$2H_2S\ (g) + 3O_2\ (g) \rightarrow 2H_2O\ (g) + 2SO_2\ (g) \quad (56)$$

The SO_2 gas is introduced into the bottom of an absorption column as shown in Figure 2.8. The liquid phase is first introduced to a citrate storage tank, where make-up chemicals can be added and by-products can be removed, before it is added to the top of the absorption column. In the absorption column the potassium citrate solution is again enriched with SO_2 gas and can be used for the reaction.

The unique aspect of a buffered process such as the PIPco process is illustrated by the following: SO_2 solubility in water at 50 °C is only 0.17 g/ℓ (with 1000 ppm SO_2 in the feed gas), while a solution buffered with citrate has a solubility of 8.7 g/ℓ (at pH = 4.5), which is a fifty-fold increase (Vasan, 1975). The task of a buffering agent like citric acid is to shift the equilibrium to the right as shown below:

$$SO_2\ (g) + H_2O\ (aq) \rightarrow HSO_3^-\ (aq) + H^+\ (aq) \quad (57)$$

$$Cit^{3-}\ (aq) + H^+\ (aq) \rightarrow HCit^{2-}\ (aq) \quad (58)$$

$$HCit^{2-}\ (aq) + H^+\ (aq) \rightarrow H_2Cit^-\ (aq) \quad (59)$$

The concentration of potassium citrate in the solution should preferably be as high as possible to increase the buffering capacity, but should be below the concentration at which potassium citrate would crystallize from the solution at the coldest or most concentrated part of the process. Generally, a concentration in the range of 1 M to about 3.5 M is suitable and about 2 M is preferred.

Sulphur plugging may be a problem for continuous operation of the PIPco process. This could be caused by two mechanisms. As mentioned previously, temperature control is important. The temperature must be above the melting point of sulphur at every part of the reactor. If the temperature is low somewhere, sulphur precipitates and may cause plugging of the equipment. Also sulphur post-formation (sulphur that is formed after the reaction mixture has left the reactor) may cause plugging of equipment. To prevent the first eventuality, careful insulation should be applied everywhere where liquid sulphur is present. To prevent the second type of plugging a different process flow sheet might be applied. The post-formation of sulphur is prevented by the introduction of some SO_2 rich solution into the SO_2 lean solution that exits the reactor.

The mechanism is described in the literature (Vasan, 1975; Rochelle and King, 1979; Korosy *et al*, 1974) and by PIPco Inc (Gryka, 1992). The most important reactions that take place in the liquid phase are given below (Gryka, 1992):

$$H_2S\ (g) \rightarrow HS^-\ (aq) + H^+\ (aq) \tag{60}$$

$$HS^-\ (aq) + 3HSO_3^-\ (aq) + 2H^+\ (aq) \rightarrow S_4O_6^{2-}(aq) + 3\ H_2O\ (aq) \tag{61}$$

$$2HS^-\ (aq) + 4HSO_3^-\ (aq) \rightarrow 3\ S_2O_3^{2-}\ (aq) + 3H_2O\ (aq) \tag{62}$$

$$HSO_3^-\ (aq) + S_4O_6^{2-}\ (aq) \rightarrow S_3O_6^{2-}\ (aq) + S_2O_3^{2-}\ (aq) + H^+\ (aq) \tag{63}$$

$$3HS^-\ (aq) + S_3O_6^{2-}\ (aq) + 3H^+\ (aq) \rightarrow S_2O_3^{2-}\ (aq) + 4S\ (s) + 3H_2O\ (aq) \tag{64}$$

$$2HS^-\ (aq) + S_2O_3^{2-}\ (aq) + 4H^+\ (aq) \rightarrow 4S\ (s) + 3H_2O\ (aq) \tag{65}$$

Under the operating conditions of the reactor, reaction 65 is the slowest and is therefore the overall reaction-rate controlling step (Gryka, 1992; Rochelle and King, 1979). The rate of reaction 65 is favoured by a low pH. Different equations that describe the rate of this reaction are given in the literature (Rochelle and King, 1979). Keller (1956) found that the rate of H_2S

consumption in concentrated buffered solutions is a function of pH and thiosulphate concentration but independent of H_2S partial pressure, as given below:

rate of H_2S consumption = $k\left[S_2O_3^{2-}\right]^{3/2}\left[H^+\right]^{1/2}$ (66)

$k = 3 \cdot 10^{11} \exp(-16500/RT)$ [mol^{-1} min^{-1}] (67)

Typical conditions for the experiments were, pH = 4.5, [$S_2O_3^{2-}$] = 0.4 M and T = 25 °C. Keller's results corresponded closely with those of Johnston and McAmish (1973) on the acid decomposition of thiosulphate. They found that the rate of sulphur production in dilute solutions was given by

$$\frac{dS}{dt} = k \cdot \left[H^+\right] \cdot \left[S_2O_3^{2-}\right]^2 \quad (68)$$

$k = 1.6 \cdot 10^{11} \exp(-16500/RT)$ [mol^{-1} s^{-1}] (69)

The literature source does not specify for which temperature range equations 66 to 69 are valid.

To understand the network of reactions better, a schematic overview of the reaction path that leads to the formation of sulphur is given in Figure 2.9.

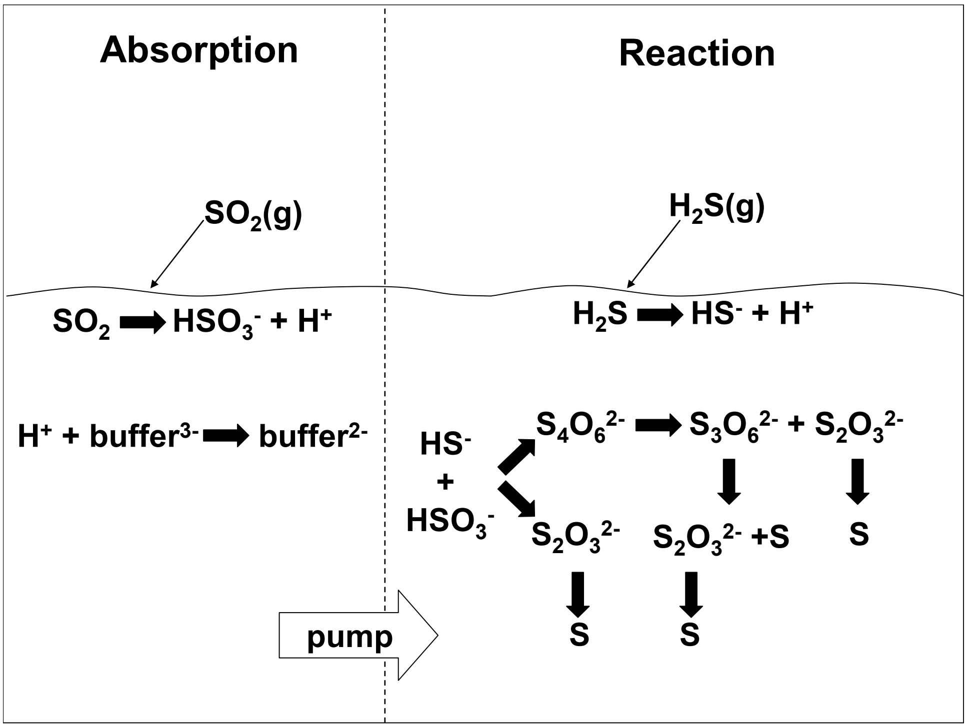

Figure 2.9 **Reaction pathways of absorption and reaction leading to the formation of sulphur in the PIPco process (Gryka, 1992)**

For completeness the absorption step is also included in Figure 2.9, showing why the thiosulphate concentration is important. It is the end of each pathway and leads to the formation of sulphur. Moreover, as mentioned before, this final reaction is the rate limiting step in the experiments as carried out by PIPco Inc (Gryka, 1992). Furthermore, it is mentioned that both absorption steps are favoured by a high pH, but the reaction is favoured by a low pH. A pH from 4.5 to 6.5 is recommended for the lean solution (Gryka, 1992).

Several investigators have followed the batch reaction of H_2S sparged into buffered solutions for low temperature systems. Typical results are presented in Figure 2.10.

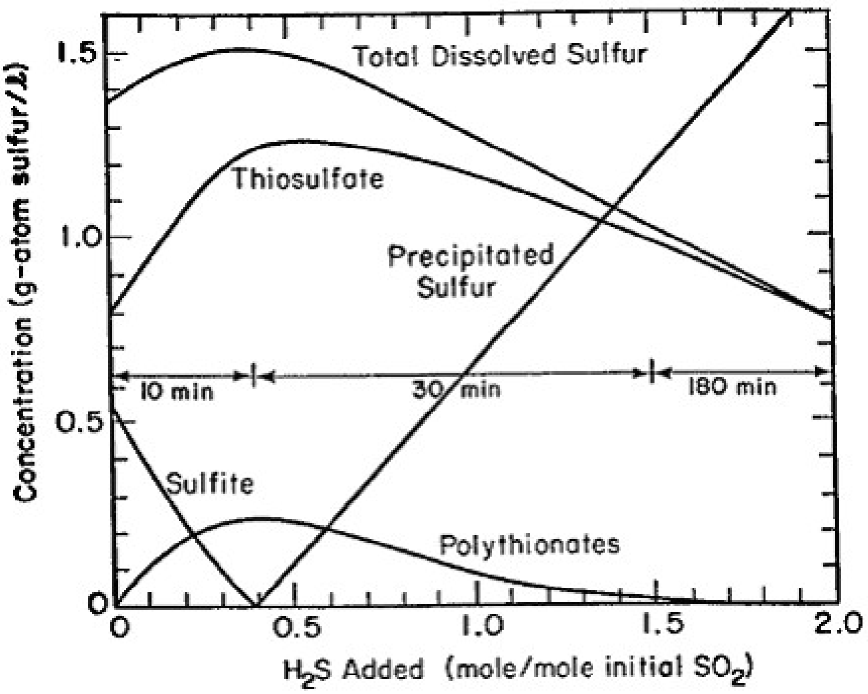

Figure 2.10 Course of H_2S/SO_2 reaction in pH = 4.4 at 25 °C .

Although the temperature is much lower than the PIPco temperature, Figure 2.10 can give some clarification of the reaction mechanisms. Three reaction phases are apparent. In the first phase there is a net consumption of bisulphite and a net production of polythionate and thiosulphate. In the second phase polythionate and some thiosulphate are consumed, with the production of sulphur. In the third and longest phase, residual thiosulphate is converted to sulphur. The sulphite is quickly converted to thiosulphate and polythionate.

The polythionate is also quickly converted to thiosulphate and finally thiosulphate is almost the only sulphur species present and is slowly converted to sulphur.