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RE-EVALUATION OF THE BACKGROUND TO THE WELLMAN-LORD PROCESS

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Thesis for submission for the degree of MSc by Research

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ABBREVIATIONS USED

S	moles of sulphur dioxide/ 100 moles of water
C	moles of Active sodium/100 moles of water
S/C	moles of sulphur dioxide/moles of active sodium
pp SO_2	Partial pressure of sulphur dioxide
W-L	Wellman Lord
FPD	flame photometric detector
ppmv	parts per million volume
FGD	Flue Gas Desulphurisation
GC	Gas chromatograph
cfm	Cubic feet per minute
w/w	weight-weight
ppmw	parts per million weight
ms^{-1}	metres per second
psia	pounds per square inch absolute

ABSTRACT

This project focuses on the determination of the equilibrium partial pressure of sulphur dioxide above aqueous solutions of sodium sulphite / bisulphite typically found in the absorption section of a Wellman-Lord Flue Gas Desulphurisation (FGD) plant. Data used in the design of the absorption section was that developed by Johnstone in 1938. This study showed that although the general form of his equation describes a method of calculation of the partial pressure, his data was on average 13% lower than that found in this study. Examination of his original data did reveal that a typographical error might have occurred in his paper. Using his **new** equation would result in an increase in the calculated partial pressure of 26% above that determined from his original equation. Given that Johnstone covered a range of conditions that would not be found in the design of a commercial FGD plant, data developed in this study has been used for all future designs.

ACKNOWLEDGEMENTS

I would like to thank the management of Kvaerner Process Technology for the opportunity to be allowed to do this project. Thanks go also to my supervisor Dr Andrew Hughes and his colleagues at Durham University. A special thank you goes to Barrie Scuffham for his encouragement and support and finally to my wife Trish, whose help and understanding has been invaluable.

1. INTRODUCTION

The Wellman-Lord Process (1) is a regenerable Flue Gas Desulphurisation (FGD) process developed in the late sixties by an American design engineering company, Wellman-Lord Inc based in Lakeland, Florida. The chemistry of the process is based on an alkali metal sulphite-bisulphite system. Initially the process was developed using a potassium sulphite-bisulphite system (2), pilot tests were conducted at Tampa Electric Company's Gannon station (3) and indicated a > 90 % removal of sulphur dioxide. A further unit was installed at the Crane station of the Baltimore Gas & Electric Co., (4) the gas treating capacity being 56,500 cfm. Significant problems (5) were encountered with this unit, the major one being the loss of expensive potassium salts.

Consequently the process was modified to use sodium sulphite as the active absorbent; such a cycle was incorporated into a commercial unit installed on an Olin Corporation sulphuric acid plant in Paulsboro, New Jersey. (6 & 7) The chemistry of the sodium cycle is extremely simple and may be represented by the following reaction for both absorption and regeneration

$$Na_2SO_3 + H_2O + SO_2 \longleftrightarrow 2NaHSO_3$$

Following the successful operation of the Paulsboro plant, the Wellman-Lord process was applied to a considerable number of installations in both the USA and Japan. In Japan, Mitsubishi Kakoki (8) and Sumitomo (9) built the units under license, nineteen units operating by the end of 1977.

In the USA in 1977 the first W-L plant installed on a coal fired utility passed its acceptance test; this unit was sponsored by the USA Environmental Protection Agency (10). The installation was on the Dean H Mitchell station in Gary Indiana, a utility (115 MW) owned by the Northern Indiana Public Service Company and operated by Allied Chemicals. (11).

Commercialisation continued on coal fired utilities in the US with the world's largest (1800 MW) regenerable FGD unit (shown in illustration 1) for Public Service Company of New Mexico (12). A further unit using petroleum coke as a fuel feedstock was constructed for the Getty oil refinery in Delaware (13).

Illustration 1 World's largest regenerable FGD unit

The first unit to be installed in Europe was commissioned in 1985 at the OMV Schwechart refinery outside of Vienna. This unit passed all its process guarantees and operated successfully meeting all its process requirements **(14)**. The plant, however had not performed entirely as predicted. The transition of the process from the USA, where energy costs were extremely low compared to Europe had resulted in a firming up of design margins. Consequently, any errors in the data used for design were more evident in this plant than plants in the USA. Extensive studies were carried out on this and an operating unit in the USA. (15) The conclusion drawn from these investigations was that the equilibrium partial pressure of sulphur dioxide above sodium sulphite-bisulphite used for design purposes could be incorrect and should be higher than that used in the design of the absorber. This was evident by higher than design absorber feed rates, resulting in a lower sulphur dioxide loading of the solution exiting the absorber. Also specific types of tests did indicate that greater than 100% stage efficiency could be obtained! The consequence was higher steam usage in the regeneration plant because of the increased amount of water required to be evaporated. The design data used for the partial pressure of SO_2 was from work carried out by Johnstone et al. of the University of Illinois. The equation, which describes the partial pressure of SO_2, and is that used in the design of a Wellman-Lord absorber, is quoted in his paper in Industrial and Engineering Chemistry January 1938 (16), and subsequently in Perry's Chemical Engineer's Handbook (17).

The equation is as follows: -

Johnstone's Equation $$\text{pp } SO_2 \text{ mm Hg} = \frac{M\,(2S-C)^2}{(C-S)}$$

C= Total concentration of base, moles/100 moles of H_2O

S = Total concentration of dissolved SO_2, moles/100 moles of H_2O

M = a constant depending on the temperature

where $\log M = 4.519 - (1987/T\ K)$

The determination of the partial pressure of sulphur dioxide above sodium sulphite-bisulphite under conditions that would exist in a commercial design of an absorber is the subject of this research project.

2. THE WELLMAN-LORD PROCESS

2.1 General

The Wellman-Lord sulphur dioxide recovery process is a regenerable process designed to treat sulphur dioxide containing gases from any of the following sources: -

- Sulphuric acid tail gases.
- Claus plant tail gases.
- Oil, coal, or lignite fired boiler or power plant flue gases.
- Smelter or roaster off-gases.

The incoming gases are conditioned and the sulphur dioxide content reduced to a suitable level before discharge into the atmosphere. The recovered sulphur dioxide can be either returned to the process in the case of sulphuric acid and Claus tail gases, or in other cases be further processed to produce any of the following products (18): -

- Food grade liquid SO_2.
- Sulphuric Acid.
- Sulphur.

The W-L system can be broken up into five-process areas: -

1. Gas pre-treatment.
2. Absorption.
3. Regeneration.
4. SO_2 processing.
5. By-product removal.

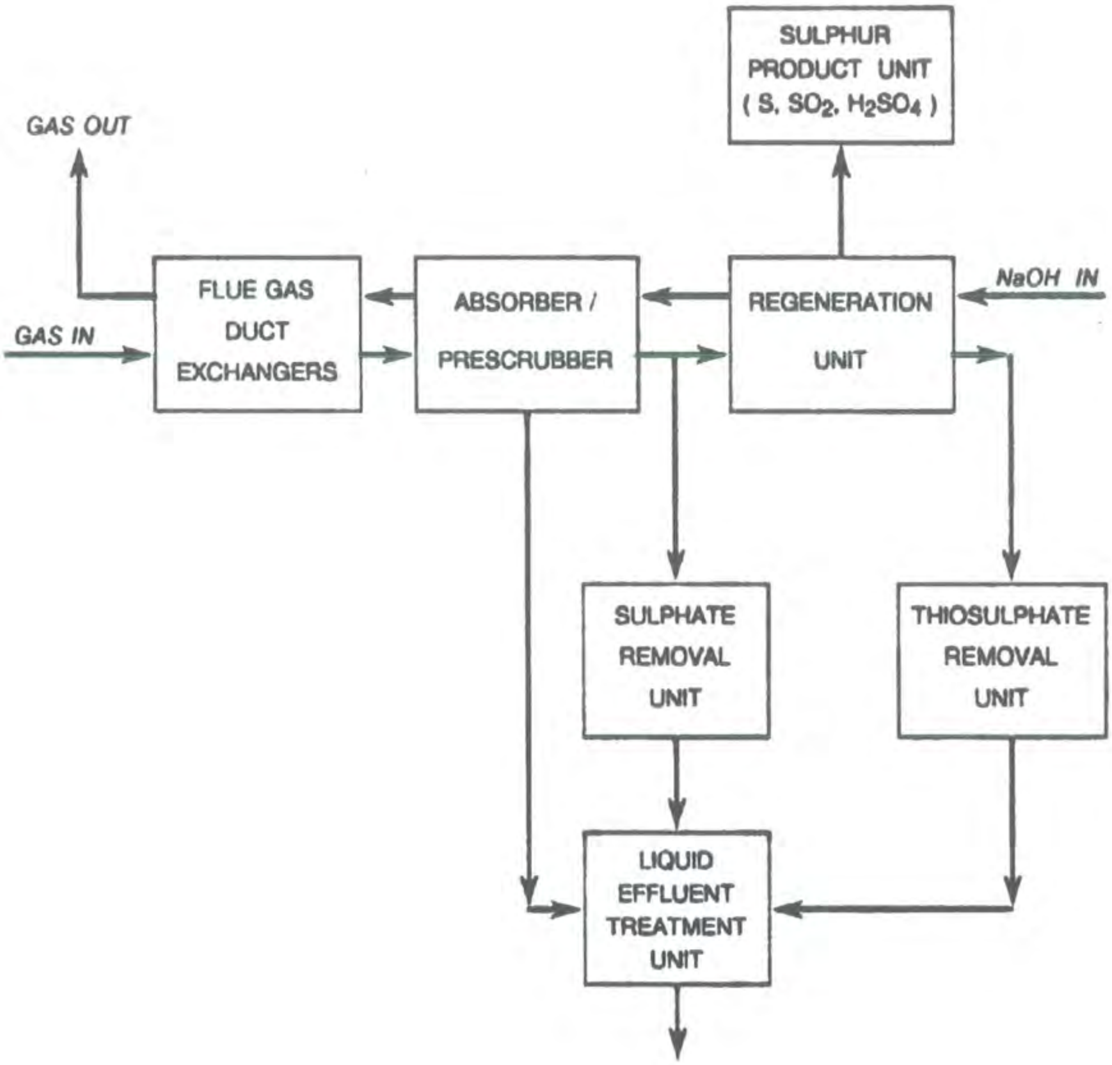
A simplified block diagram is shown in Figure 1

One distinct advantage of the W-L process is that the process areas 1 & 2 can be physically significant distances apart from areas 3 - 5. This is often very important in retrofit applications where a limited amount of space may be available. An example of the distances apart that the regeneration can be from the absorber is a plant in Germany (19) where a single regeneration unit services two power plants seven kilometres apart

The materials of construction are an important aspect of any FGD process (20) because of the corrosive nature of the chemicals involved. Various types of stainless steels, plastics and lining materials have been used or tested (21)

.

Figure 1 Simplified Block Diagram



2.2 Gas pre-treatment

Pre-treatment of the incoming gas is required to achieve some or all of the following: -

- Removal of sulphur trioxide.
- Removal of particulate content.
- Cool and saturate the gas to a temperature below 65°C.

Each individual application does however require different means of treatment. For a specific example, the case of a power plant utility company using brown coal as a fuel source will be used. This is an operating unit, located in Germany, all of the above treatments having to be satisfied.

Gas from the power plant at battery limits enters the W-L system at temperature of 185°C. Removal of SO_3 is accomplished by the addition of an aqueous ammonia solution.

$$2NH_3 + SO_3 + H_2O \longrightarrow (NH_4)_2SO_4$$

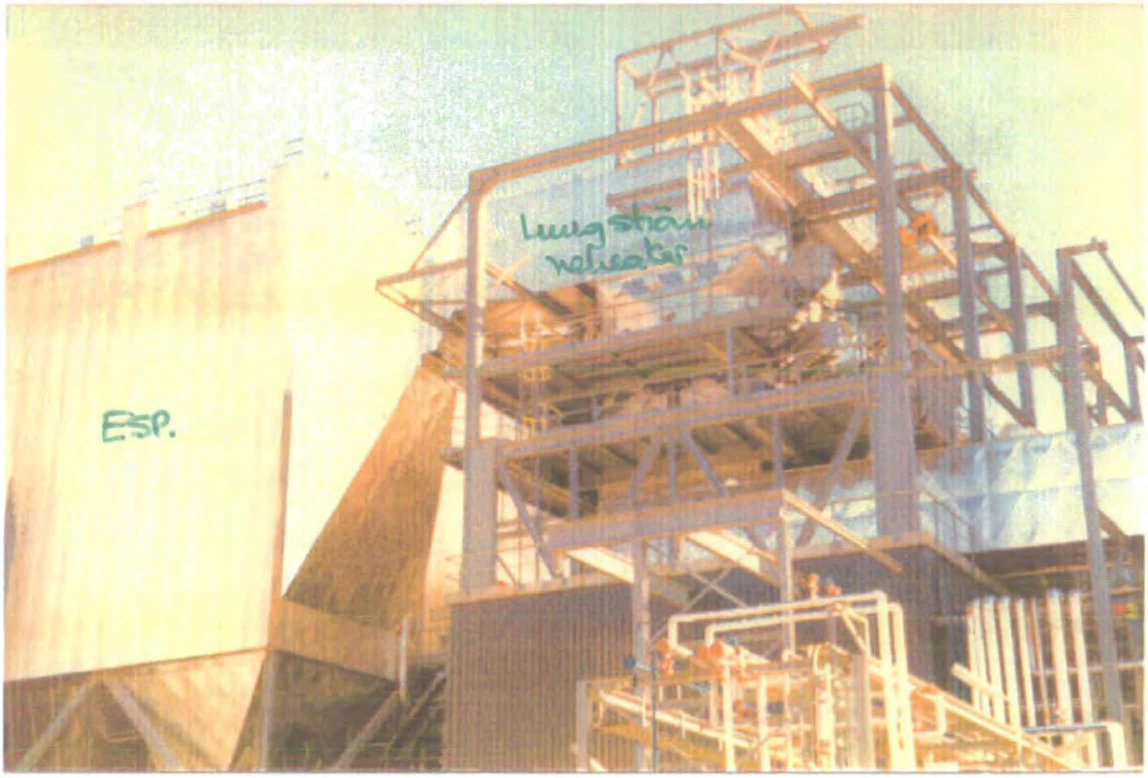
However, this particular gas composition i.e. water and SO_3 content at a temperature of 185°C, is above the acid dew point of sulphuric acid. (22) The reaction with ammonia will not proceed under these conditions. The gas has to be first cooled to 165°C, which is below the acid dew point.

This is achieved by the use of heat exchangers of carbon construction situated in the gas ducting. The heat recovered is used to generate low-pressure steam. An aqueous ammonia solution is injected into the gas stream; excess over stoichiometric is added, in order to prevent the formation of ammonium hydrogen sulphate. This has a tendency to be "sticky" and can cause problems downstream in the removal of the solids.

$$NH_3 + SO_3 + H_2O \longrightarrow NH_4HSO_4$$

The gas then enters an Electrostatic Precipitator (ESP) where the particulate ammonium sulphate is removed as a solid. Shown in illustration 2 is a picture of an ESP together with a Ljungstrom type gas heat exchanger (23). The latter is a rotary device, which acts as a heat sink, interchanging heat from the incoming hot gas to that of the cool exit gas.

Illustration 2 Electrostatic Precipitator for ammonium sulphate removal



The ammonium sulphate is then treated with lime to recover the ammonia as an aqueous solution for subsequent reuse.

$$(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2H_2O + 2NH_3$$

The gas on exiting the ESP in this example is then cooled to 140°C by a further set of carbon heat exchangers. The recovered heat via a cyclic hot water system is used to reheat the treated gas exiting the absorber.

The gas then enters the prescrubber section, the function of which is to saturate the gas with water, remove chlorides and particulate matter such as fly-ash. This is accomplished by passage of the gas through a dual flow tray with water spray nozzles both below and above it. The gas approaches its adiabatic saturation temperature (24), which in this example is approximately 62°C. A view of both the underside and top of this tray is given in illustrations 3 & 4. A purge of this water stream is taken to prevent a build up of chloride ions and particulate matter; make-up water is added under level control of the sump to replenish both purge and evaporation losses. The gas finally passes through a demister, in order to prevent any highly acidic and corrosive droplet carryover before entering the absorption section; this is shown in illustration 5.

Illustrations 3 and 4 Prescrubber section with dual flow tray

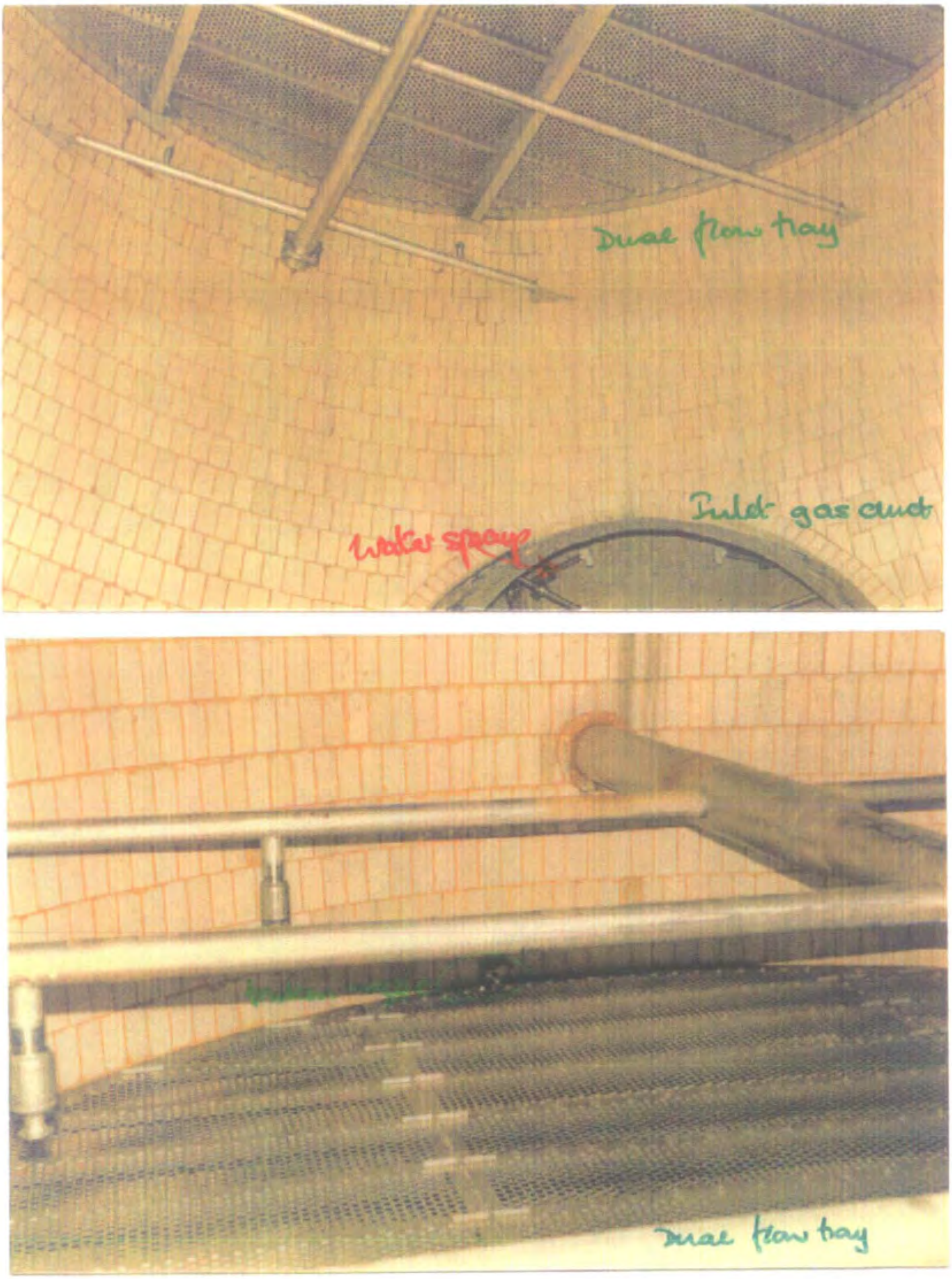


Illustration 5 Mist eliminator downstream of dual flow tray

2.3 Absorption

The W-L absorber is a counter current contacting device designed to reduce the SO_2 content of the incoming gas to less than 250 ppmv in the treated gas. The absorber consists of one lower valve tray and three packed sections; each section having recirculation of liquid. Shown in illustration 6 is a view of two absorbers with the piping associated with the recirculation pumps. The packing used was of Norton manufacture, snowflake in this case, the valve trays being of Koch design and manufacture. (see section 3.)

Illustration 6 Absorbers showing pipe work for recirculation on stages

The regenerated (lean) absorbing solution enters at the top of the absorber the S/C of this solution being in the range of 0.55 - 0.6,

where: -

C= Total concentration of base, moles/100 moles of H_2O and

S = Total concentration of dissolved SO_2, moles/100 moles of H_2O

The reactions occurring in the absorber are as follows: -

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$$

An undesired side reaction also occurs, that being the oxidation of sulphite by the oxygen contained in the flue gas (25).

$$Na_2SO_3 + \frac{1}{2} O_2 \longrightarrow Na_2SO_4$$

The absorbing liquid exiting the absorber is rich in SO_2 and has a S/C approaching 0.85-0.9. The gas exiting the absorption section then passes through a demister, to prevent liquid carryover, into the clean flue gas blower. The blower operates under a slight negative pressure on the suction side, the capacity in this case being in excess of 1×10^6 Nm^3 per hour, and is shown in illustration 7. The gas is then reheated to prevent opacity or dispersion problems (26), the heat being supplied from the interchangers on the incoming gas.

Illustration 7 Clean flue gas blower

2.4 Regeneration

The regeneration of the loaded absorbing solution is accomplished by the action of heat on this solution in a forced circulation evaporator, i.e.by the reverse reaction to that which occurs in the absorber. Water and sulphur dioxide are removed in the overheads of the evaporator.

$$2NaHSO_3 \longrightarrow Na_2SO_3 + H_2O + SO_2$$

The solubility of sodium sulphite in high concentrations of sodium bisulphite is relatively low (27) the result being that sodium sulphite is precipitated. The normal operating concentration of solids being 45% w/w, this slurry is withdrawn continually and is sent to a centrifuge, where the solids, rich in sulphite are discharged into a dissolving tank. The supernatant liquor, which is rich in bisulphite, is recycled back to the evaporator. An undesired side reaction occurs in the evaporator, this being the disproportionation of the bisulphite. (28).

The reaction is as follows: -

$$6NaHSO_3 \longrightarrow 2Na_2SO_4 + Na_2S_2O_3 + 2SO_2 + 3H_2O$$

This reaction is sensitive to temperature; therefore, the evaporator is operated at vacuum sufficient that the temperature does not exceed 98°C. A further complication with this reaction is that it is autocatalytic in thiosulphate concentration (29 & 30). In order to maintain a low concentration of thiosulphate, a purge is taken from the supernatant liquor to maintain a concentration of less than 2% w/w of thiosulphate in this stream. This purge stream is normally sent to the prescrubber sump. The water in the prescrubber is highly acidic from the hydrogen chloride removed from the flue gas. The acidity releases the SO_2 content of this stream from the sulphite and bisulphite components which is then reabsorbed in the absorber.

The design of the evaporators can be multiple-effect or alternatively, mechanical vapour recompression. (31)

- Multiple effect: - These are two or more evaporators in series, each evaporator being called an effect. The first is heated by an indirect steam source, the subsequent effects being heated by the overhead vapours from the previous effect. This does require that the pressure in each effect is different in order to obtain a differing boiling point, shown in illustration 8 is a typical two effect system.
- Mechanical vapour recompression: - This is a system in which the overhead vapours are compressed to such a pressure that these will condense at a temperature high enough to permit it being used as a heating medium in the same evaporator.

The water recovered contains some dissolved SO_2. This is stripped in a packed column with live steam. The resulting water, containing less than 100 ppmw dissolved SO_2, is then used to dissolve the sulphite crystals from the centrifuge, in an agitated tank. The SO_2, which is approximately 98% w/w at this stage is then sent for further processing.

Illustration 8 Two-effect evaporator system

2.5 SO_2 processing

The SO_2 can be processed into one of the following products: -

- Food grade liquid SO_2.
- Sulphuric Acid.
- Sulphur.

In this particular plant, liquid sulphur is the final product; this is achieved in a two step process. The first is the reduction of a portion of the SO_2 with natural gas to form hydrogen sulphide, which is then followed by a conventional Claus plant. (32) The process has been developed by Allied Chemicals and is in operation on several units (33).

The chemical reactions involved are as follows: -

Reduction.

$$3CH_4 + 4SO_2 \longrightarrow 3CO_2 + 2H_2O + 4H_2S$$

Claus reaction.

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

The sulphur is stored as liquid and is transported from site in railcars. This particular unit produces 100,000 metric tonnes per year. The reduction process can be achieved by the use of hydrogen; (34) however a source of hydrogen is generally unavailable in power plant applications.

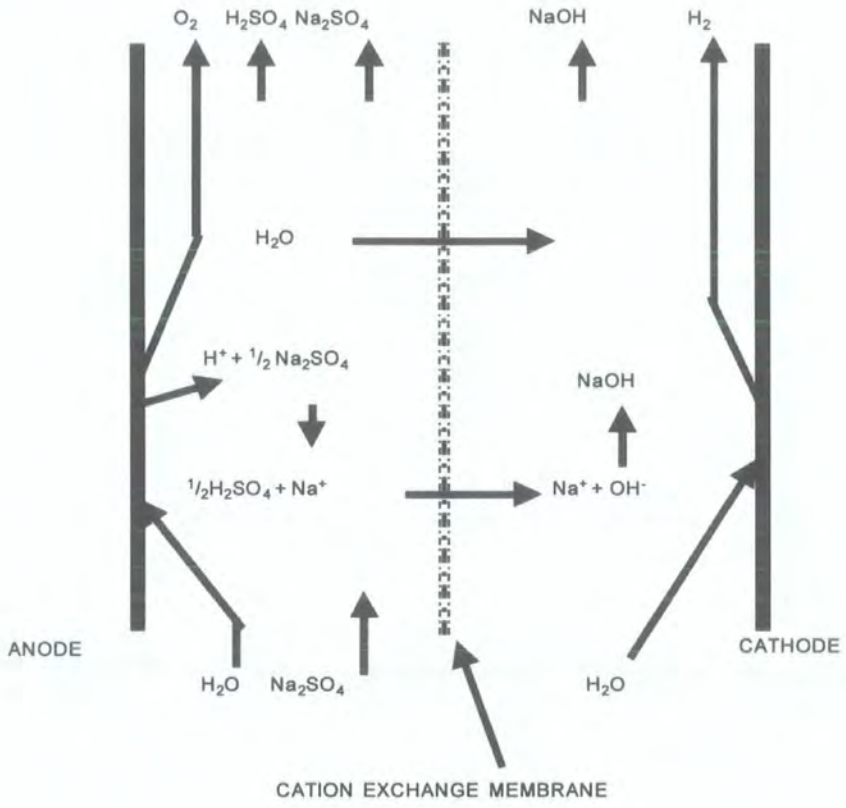
2.6 By-product removal

The by-product sulphate is allowed to build up in the process solution to a level of 6% w/w, whence removal of the sulphate is then effected, as too high a concentration increases the heat duty in the evaporation area.

The sulphate is removed from the system by taking a side stream of the rich absorber solution, which is then processed in an evaporator-crystalliser. This is known as the High Temperature Sulphate Separation (HTSS) (35 & 36) process. It works successfully because the first 3-5% crystals are richer in sulphate than sulphite. Control of such a system is however extremely complex. To overcome this, the crystalliser is equipped with an internal settling zone within the evaporator. The effective solids concentration is 25-30% w/w. This slurry, is continually withdrawn and sent to a centrifuge; the solids (raw sulphate) are dissolved in water in an agitated tank. The supernatant liquor, which is rich in bisulphite, is then returned to the regeneration plant.

The solution from the agitated tank, which is essentially sodium sulphate, does however contain small quantities of both sulphite and bisulphite. This solution is then sent to a batch oxidation tank for removal of these species. Oxidation takes place by passing air through the system for a period of 10-12 hours; via a gas induction stirrer for increased mass transfer. After oxidation, the sulphate solution is transferred to an evaporator. Water removal is such that it operates to produce a 50% w/w slurry. The mixture is centrifuged, and the solids dried in an airlift dryer, the air being heated indirectly with steam. The resulting sodium sulphate has a purity of > 99.6% and can be bagged or shipped by truck, it's major use is in the detergent industry. The price obtained from the sale of the sodium sulphate does not however offset the cost of replacement sodium hydroxide. This is required to compensate for the loss of sodium from the system. In order to find a better economic solution; further treatment routes of the pure/raw sodium sulphate have been investigated one of which includes electrochemical (37) "regeneration". The sodium values are recovered as sodium hydroxide, which is recycled back to the process. Dilute sulphuric acid is a by-product of electrochemical regeneration; which can be recovered as a saleable product especially if the Wellman-Lord process produces sulphuric acid. The reactions occurring during electrochemical treatment are shown in Figure 2

Figure 2 Electrochemical treatment of sodium sulphate



3.1 Absorber configuration

The W-L absorber is a countercurrent-contacting device designed to absorb SO_2 down to < 250 ppmv. Lean solution, rich in sulphite, enters the top of the absorber; the SO_2 loaded gas enters the bottom. A second criterion is that the rich solution (absorber product) should approach the highest possible conversion to bisulphite, i.e. high SO_2 loading to minimise the steam (energy) consumption in the regeneration plant. The ultimate performance limitation of this type of operation is that the outlet gas can never have a SO_2 content less than that in equilibrium with the incoming liquid. Hence, the feed composition is limiting factor on the desired outlet SO_2 content. An alternative performance limitation occurs when the absorber product is in equilibrium with the incoming gas i.e. the highest achievable SO_2 loading of the product solution

The choice of absorber internals depends on a number of variables (38), some of which are listed below: -

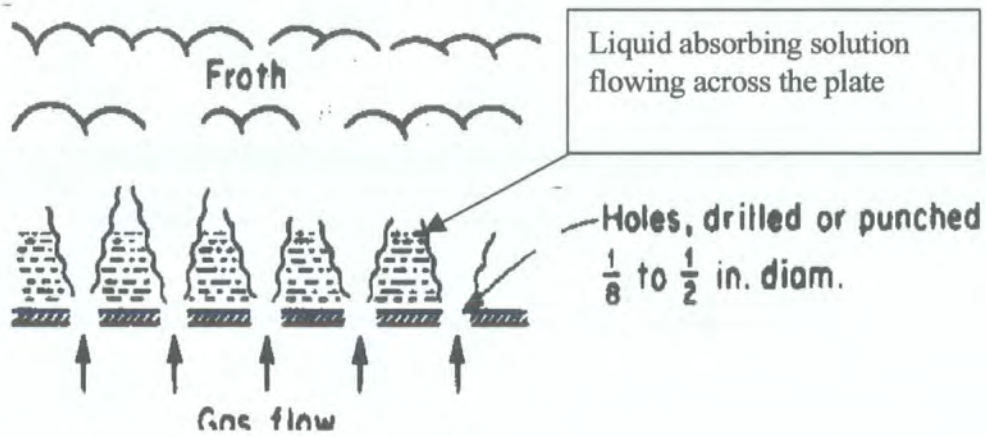
- Inlet SO_2 concentration
- Desired outlet SO_2 concentration
- Volume of gas to be treated
- Pressure drop considerations
- Ability to operate with gas capacities less than normal operation

These internals can be any or a combination of the following: -

Sieve trays,

These are essentially flat plates with perforations of 1/8-1/2 inch in diameter. The liquid enters at one side and flows across the plate and exits to a downcomer, which collects the liquid for distribution onto the next tray. The gas flow through these type of trays can be turned down to a point where liquid starts to drain through the perforations and gas dispersion is inadequate for good efficiency. The action on the tray is illustrated in Figure 3.

Figure 3 Sieve tray action

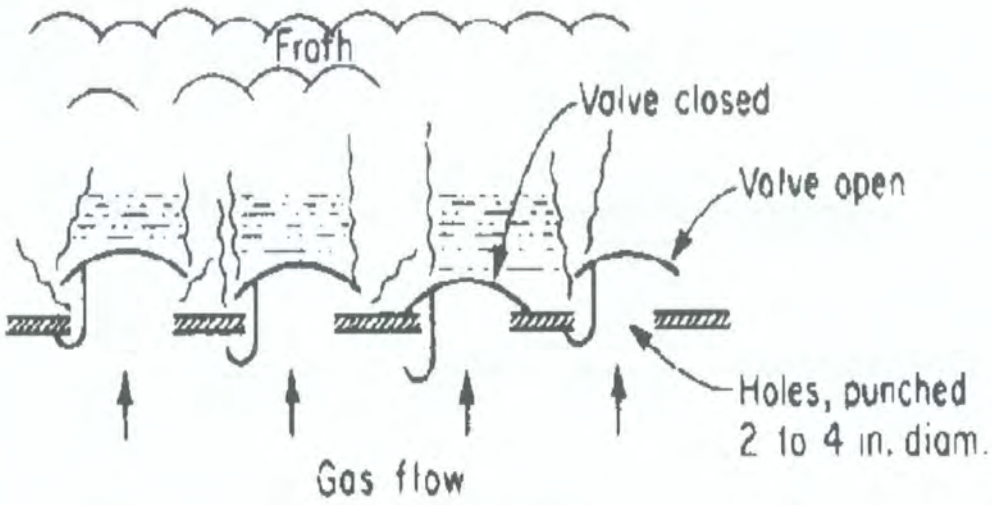


Valve Trays

These are of similar design to sieve trays having valves above the perforations, which are normally 2-4 inches in diameter. Valve trays enable a column to operate effectively at well below its design capacity. The valves can close at low vapour throughput and thus lessen liquid leakage to the tray below.

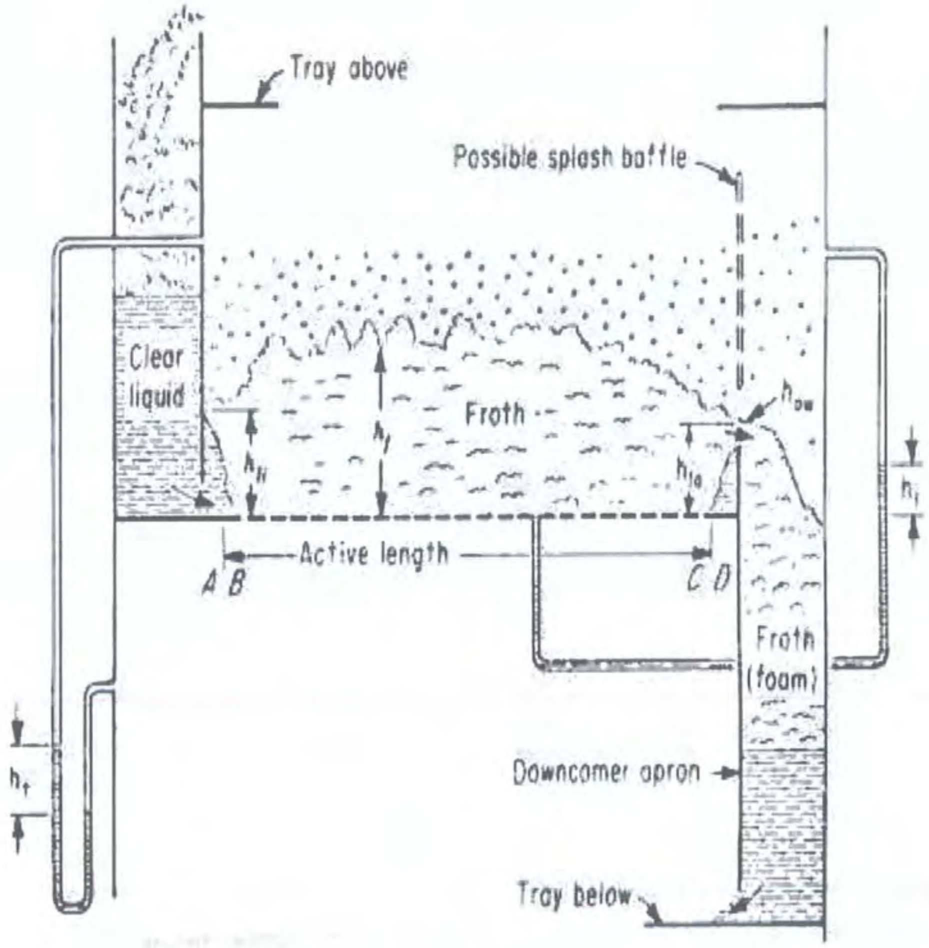
The action on the tray is illustrated in Figure4.

Figure 4 Valve tray action



In both sieve and valve tray designs the liquid has a cross flow pattern, i.e. the liquid flows from one side of the absorber across the tray to the other side. The liquid is collected in a downcomer and is the feed for the tray below. This is illustrated in Figure 5

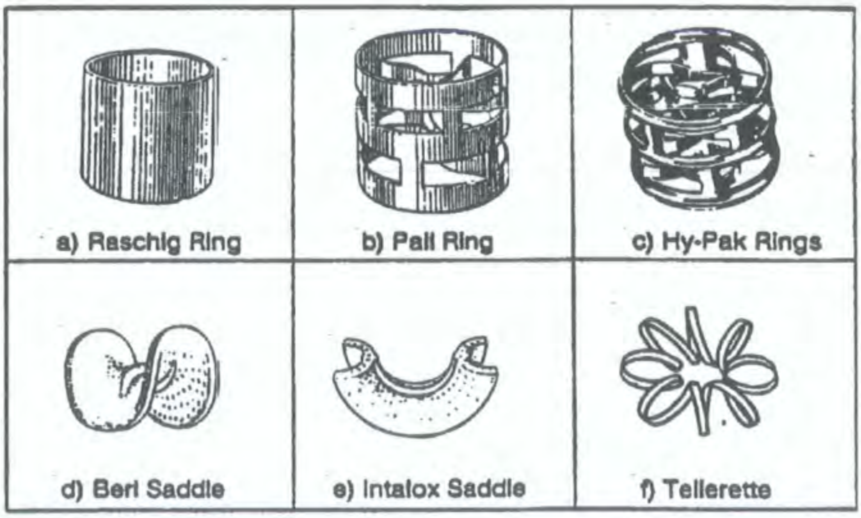
Figure 5 Crossflow action of Sieve and Valve trays.



Random Packing

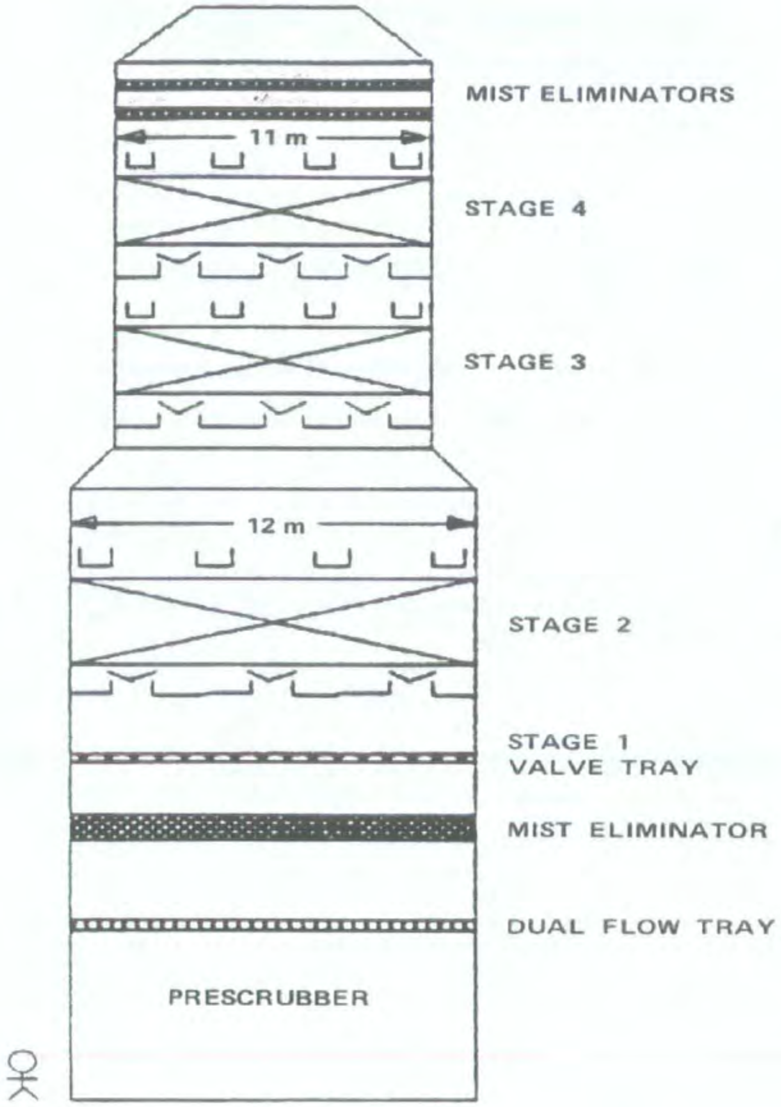
The liquid flows as a film over the surface of solid packing while the gas flows through the interstices. The objective of the packing is to sub-divide and distributes the liquid flow thus providing a high interfacial area and good flow conditions for mass transfer. Ideally, this produces a thin layer of liquid that covers the entire solid surface presented by the packing. In practice, this condition may be closely approximated. However, some degree of "partial" wetting will generally exist and this constitutes one of the potential disadvantages of packed columns. This type of column requires liquid distributors at set intervals down the column. Illustrated in Figures 6 & 7 respectively are types of packing and a sketch of a packed column. Note this does not show liquid recirculation.

Figure 6 Types of Random Packing



a) Raschig Ring
b) Pall Ring
c) Hy-Pak Rings
d) Berl Saddle
e) Intalox Saddle
f) Tellerette

Figure 7. Packed column with liquid distributors



All of the above options or combinations have liquid recirculation on each of the sections typically of the order of $0.1m^3$ of liquid $/1000m^3$ of gas per min. This ensures that both the hydraulics in the case of sieve/valve trays (39) and wetting rates in the case of packing (40) are satisfied. The diameter of the column is dependent on the total gas flow; a superficial gas velocity of approximately three m s^{-1} is typically used for design purposes.

3.2 Mechanism of absorption

The most useful concept of the process of absorption is given by the two-film theory due to Whitman **(41)**. According to this theory, material is transferred in the bulk of the phases by convection currents and concentration differences are regarded as negligible except near the interface between the phases. On the other side of this interface, it is supposed that the currents die out and that there exists a thin film of fluid, through which the transfer is effected by molecular diffusion.

In Figure 8, P_G represents the partial pressure in the bulk of the gas phase and P_i the partial pressure at the interface. C_L is the concentration in the bulk of the liquid phase and C_i the concentration at the interface. According to above theory, the concentrations at the interface are in equilibrium, and resistance to transfer is centred in the thin films on either side.

The two reactions occurring in the absorber, i.e. SO_2 absorption and oxidation of sulphite/ bisulphite to sulphate, both have different restrictions to mass transfer. In the case of SO_2 absorption the restriction to mass transfer is in the gas film. In the case of oxidation, the restriction is in the liquid film. This is illustrated in Figure 9.

Figure 8 Concentration profile for absorbed component

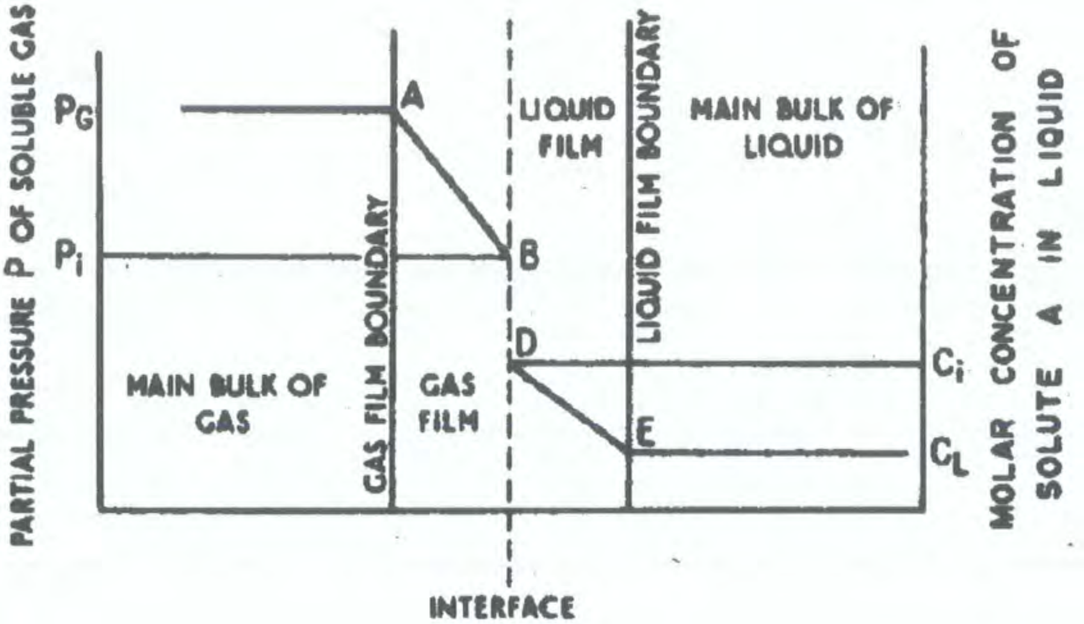
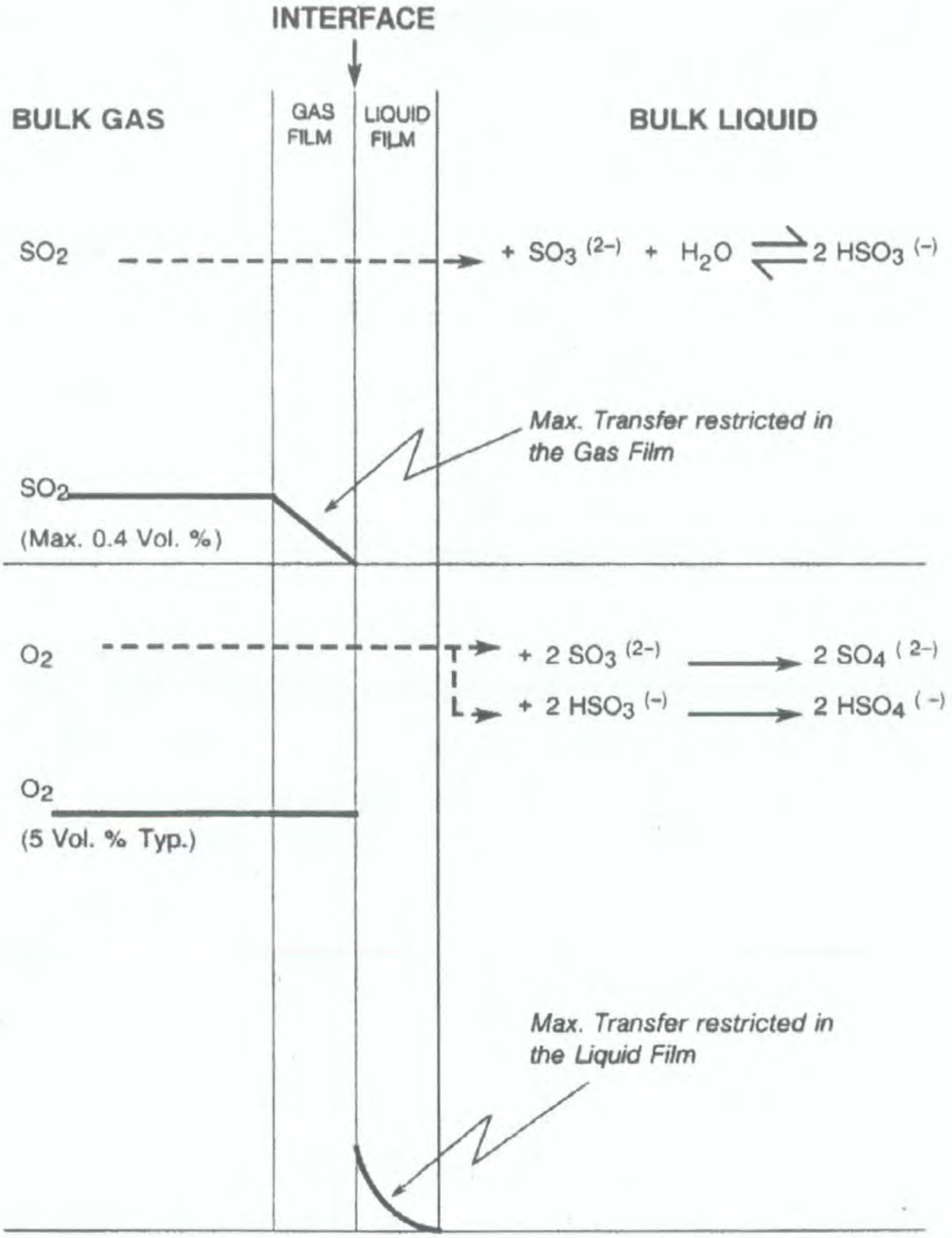


Figure 9 Mass transfer limitations for SO_2 and O_2



3.3 The Theoretical Stage Concept

Given the nature of stagewise contactors, a convenient approach to design would be to estimate the number of stages required and then to design the stages themselves according to the mass transfer requirements. In order to be able to do this, a rational basis for mass transfer assumed to be occurring in a given stage is required. If the conditions for mass transfer and the phase residence times are favourable, then the concentrations of the effluent phases will tend towards those of equilibrium. Equilibrium represents a well-defined real and theoretical end-point for a single stage, and this is therefore assumed the case.

A theoretical STAGE is thus defined as a contacting stage where the effluent phases are in equilibrium (42) The first and most important step in the design of a stagewise contactor is the evaluation of the number of theoretical stages (NTS) required obtaining the desired separation. Subsequently, the stages themselves should be designed and the degree to which equilibrium is approached (stage efficiency) can then be estimated for each stage. Thus, the number of real or actual stages can be calculated. The methods for stage design and efficiency calculation vary from one type of equipment to another (and from one unit operation to another). The general method for NTS evaluation varies little and this value will always be required.

With plate columns, the generic term "Theoretical Plate" is normally used in preference to theoretical stage. There is no difference between them: it is simply a question of nomenclature.

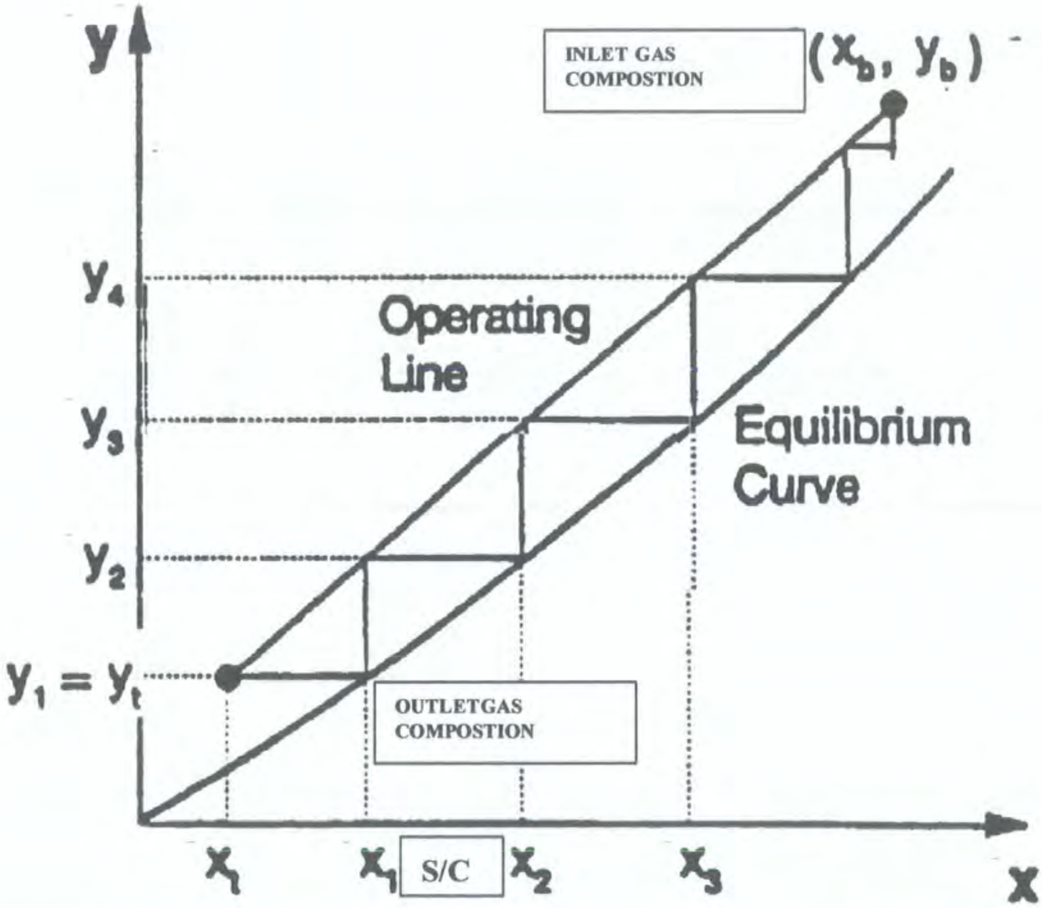
The number of theoretical plates required is a direct indication of the difficulty of the separation. A high NTP value infers a difficult separation and conversely, a low NTP value indicates a relatively easy separation.

3.3.1 Determination of the NTP required for a Given Separation

The graphical construction shown in Figure.10 may readily be used to provide a method for determining the NTPs required performing a specified separation. (43) The X-axis is the S/C of the absorbing solution with X_b being the feed composition and X_t the desired product composition. The Y-axis represents the SO_2 content of the gas with Y_b being the inlet gas concentration and Y_t being the desired outlet composition. The line drawn between the points (X_b, Y_b) and (X_t, Y_t) is called the operating line. The equilibrium line is then drawn on the same graph under the conditions expected in the absorber i.e. temperature and pressure. Then at the point (X_t, Y_t) a horizontal line is drawn until it meets the equilibrium line, at this point of intersection a vertical line is drawn to the operating line. This step on the diagram corresponding to a theoretical plate, which corresponds to the theoretical change in gas composition for a given change in liquid composition. This is repeated until

(X_b, Y_b) is reached thus giving the total number of theoretical stages required. Whilst described as a graphical method; the technique could obviously be carried out numerically using the operating line equation and an analytical expression for the equilibrium relationship. The equilibrium relationship used in the design of the W-L process being the Johnstone equation.

Figure 10 Graphical method for determining the Number of stages



4. EXPERIMENTAL PARAMETERS INVESTIGATED

4.1 Introduction

The experimental work carried out by Johnstone, Read and Blankmeyer as reported in their paper in Industrial and Engineering Chemistry Vol. 30, No.1 1938 determined the partial pressure of SO_2 using a dynamic method. This involved passing nitrogen through the sodium sulphite-bisulphite solution and determining the SO_2 of the carrier gas stream Iodometrically. Further details are given in an earlier paper (44) published in 1935.

Although this is a perfectly acceptable method of determining the partial pressure of a gas above solvents, at very low concentrations of SO_2 this can involve large errors. Given also that instrumental analytical techniques have advanced tremendously since Johnstone did his work it was decided to use a static method for this work. This type of method has previously been used for determination of the partial pressure of hydrogen sulphide above amine absorbents. (45)

4.2 Description of static determination of partial pressure

A solution of sodium sulphite-bisulphite is charged to an autoclave, the headspace is purged with nitrogen and pressurised to a known pressure. The stirrer, a gas induction impeller, which recirculates the headspace gas through the solution, is operated at > 1000 rpm, at which speed it has been shown that no mass transfer limitations are likely to occur under these conditions. The system is allowed to operate under these conditions for a minimum of 12 hours, it having been shown that no change in gas composition could be observed after this period and that equilibrium had been attained. The gas headspace is analysed for SO_2 content and the liquid sampled and analysed for sulphite-bisulphite. The volumes of both the liquid and gas phases in the autoclave are such that the samples taken for analysis do not have any significant effect on the overall composition of the liquid or gas.

The water vapour pressure under the conditions of the tests (50-65°C) is between 100 -200 mm Hg. (46). Under these conditions, the gas sample line and GC sample loop would have to be heated to prevent condensation of water. To avoid this complication and the possible errors involved in the SO_2 measurements should water condense, which condensate would contain SO_2, the autoclave was operated at such a pressure that the gas composition above liquid under all test conditions was always above the dew point of water when the gas was sampled at ambient temperature and pressure. Typically, the autoclave operated at pressures in excess of 100 psia.

4.3 Experimental conditions.

The temperature range used by Johnstone was 35-90°C and an active sodium ion concentration (C value) in the range 4-8. Another significant difference is that the W-L process operates with 6% w/w sodium sulphate in solution. Johnstone did not have any significant quantity of sulphate and took meticulous care to avoid any oxidation of the sulphite. This study will therefore examine only the range of variables, as applicable to the commercial design of a Wellman-Lord process.

4.3.1 Solution Concentration

The most practical and economic solution concentration is as close to saturation as possible. With the correct design of equipment, a feed solution containing 2-3% undissolved solids i.e. sodium sulphite in the feed solution is the best option. The conversion of the sulphite to the bisulphite results in a clear, almost saturated solution exiting the absorber.

Using dilute solutions has two major consequences: -

- The first is the quantity of water that has to be removed in the regeneration of the solution, which impacts on the energy requirements and hence the operating costs.
- The second is the oxidation of sulphite to sulphate, which is considerably higher in dilute solutions. (47) This is directly due to the increased solubility of oxygen from the flue gas in the solution (48&49)

The range of solution concentrations to be investigated will therefore be only in the range of a C value of 7.5-8.

4.3.2 Temperature

The temperatures that are normally observed in commercial FGD plants are 50-65°C. Cooling below these temperatures, although advantageous from an absorption perspective, would be economically impractical. Large surface area heat exchangers would be required without the recovery of any sensible heat. Operation with higher temperatures would reduce the absorption capability of the solution for SO_2 removal; it would also increase the rate of the oxidation of sulphite to sulphate.

5. EXPERIMENTAL EQUIPMENT

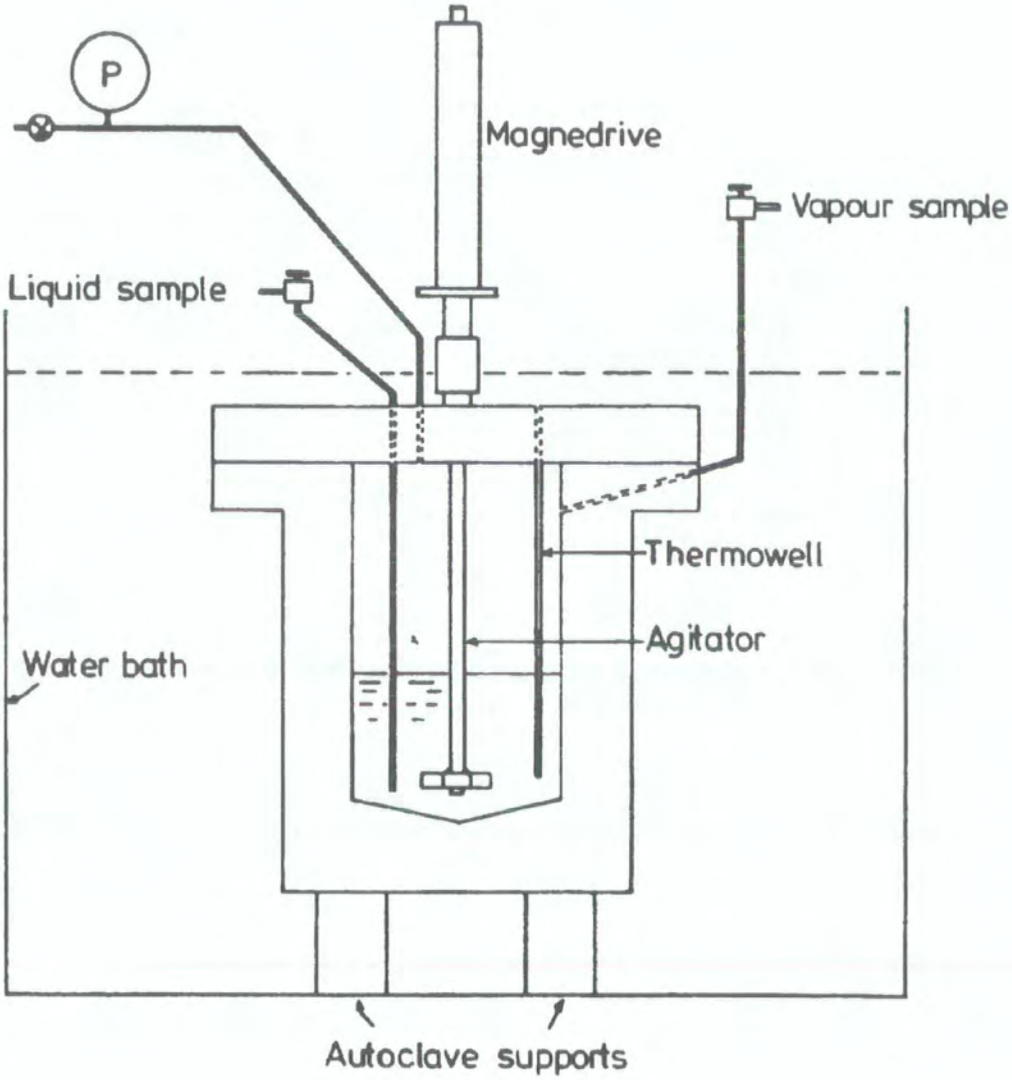
The experimental equipment used to measure the partial pressure of SO_2 above a W-L type solution is described as follows. The equipment consisted of a 4.5 litre capacity autoclave equipped with a Magnedrive gas induction impeller. The principle of this impeller is to draw gas from the vapour space via holes in the hollow shaft; this gas is then dispersed through the liquid. This continual recirculation of the headspace gas throughout the liquid ensures a rapid approach to equilibrium.

To ensure that liquid and vapour were at the same temperatures, the autoclave was totally immersed in an electrically heated fully mixed, thermostatically controlled water bath, the temperature of which was controlled to +/- 0.1°C. Temperature measurements of the liquid and vapour phases in the autoclave were made by means of Pt resistance thermocouples, which had been calibrated before use.

Three sample points were attached to the autoclave. The first was used to either introduce gaseous SO_2 to adjust the solution composition or to vent the headspace and re-pressurise with nitrogen. The second was used to sample the gas headspace. The line (1/8-inch OD) into the autoclave, the valve seat and to the line to the GC was constructed in PTFE. This was to ensure that no absorption of the SO_2 occurred in the pipework. The third was used to sample the liquid phase. This sample line consisted of 1/16 inch OD stainless steel dip tube situated just above the bottom of the autoclave. The small diameter ensured that the hold up in this line was minimal and that large qualities of solution did not have to be removed for purging. The autoclave was fitted with a previously calibrated absolute pressure gauge accurate to 0.05 psia. A pressure relief valve was also fitted with a relief set pressure of 750 psig, 150 psig above anticipated maximum pressure for the testwork. The autoclave at the temperatures to be used had a maximum working pressure of 2750 psig.

A simplified diagram of the autoclave assembly is shown in Figure 11.

Figure 11 Autoclave Assembly



6. ANALYTICAL METHODS

Analytical methods used in this experimental work included the following methods: -

1.The determination of sodium sulphite.(50)

(Wet chemical method)

2. The determination of sodium bisulphite. (50)

(Wet chemical method)

3. The determination of sodium thiosulphate. (50)

(Wet chemical method)

4. The determination of sodium sulphate. (51)

(Instrumental method -Ion chromatography)

5. The determination of gaseous sulphur dioxide. (52)

(Instrumental method -GC/ FPD detector)

6.1 The determination of sodium sulphite.

6.1.1 Outline of method.

Formaldehyde in the form of a 36% solution in methanol is added to a sample of the test mixture; to react with the bisulphite and sulphite in the mixture. The reaction product with bisulphite is the neutral hydroxysulphonate (53) $HOCH_2SO_3Na$. However, in the case of the sulphite one mole of free caustic is produced per mole of sulphite. The free caustic can then be titrated using classical methods.

$$NaHSO_3 + CH_2O \longrightarrow HOCH_2SO_3Na$$

$$Na_2SO_3 + CH_2O + H_2O \longrightarrow HOCH_2SO_3Na + NaOH$$

6.1.2 Procedure

Reagents required:

~ 0.1 M sodium hydroxide (standardised)
~ 0.1 M hydrochloric acid (standardised)
phenolphthalein indicator (0.5% w/v in iso-propanol)
36% formaldehyde in methanol

Method:

To a 20 cm ^{3} of a 36% formaldehyde solution in a 250 cm ^{3} conical flask, 0.1 cm ^{3} of phenolphthalein indicator was added. This was then titrated to the pink end-point with 0.1-M sodium hydroxide as this solution is acidic by nature. Then by means of a pipette, 5 cm^3 of the test sample was added to the standardised formaldehyde solution. The solution was then titrated with 0.1 M hydrochloric acid until the pink colour begins to fade, then drop-wise, whilst swirling continuously, until only a very faint colour persists. The volume of 0.1-M hydrochloric acid was recorded.

6.1.3 Calculation

The specific gravity of the sample was previously determined by accurately weighing a known volume of the sample.

The molecular wt of Na_2SO_3 is 126.05 g mol^{-1}

The sample volume is V cm^3

The volume of hydrochloric acid used is V_1 cm^3

The molarity of the hydrochloric acid is M_1 mol l^{-1}

Hence, the sodium sulphite content expressed as percentage w/w

$$= \frac{V_1\,(M_1 x 0.12605) x 100}{V \text{ x sp. gr.}}$$

6.2 The determination of sodium bisulphite

6.2.1 Outline of method.

The sample was oxidised using a 30% w/v solution of hydrogen peroxide. This action destroys the buffering capacity of the sulphite by conversion to the sulphate and converting the weakly acidic bisulphite to the highly ionised bisulphate. This can be titrated to a sharp end-point with almost any indicator suitable for strong acid-strong base titrations. A potentiometric titration to pH 4.3 averts the necessity for destruction of the excess peroxide.

6.2.2 Procedure

Reagents required:

~ 0.1 M sodium hydroxide (standardised)
30 % w/v solution of hydrogen peroxide
Buffer solutions for pH meter

Method:

15 cm ^{3} of hydrogen peroxide was added to a 250 cm ^{3} beaker containing a magnetic follower, this was made up a volume of 50 cm ^{3} with dimineralised water. The beaker was then placed on a magnetic stirrer together with a pH electrode. Whist stirring, the peroxide was neutralised to pH 4.3 by the addition of 0.1 M sodium hydroxide. Then by means of a pipette, 5 cm ^{3} of the sample was added to the neutralised peroxide, the solution is stirred for 3

minutes in order to allow to reaction to come to completion The solution was then titrated with 0.1 M sodium hydroxide back to a pH 4.3, the volume of sodium hydroxide used was recorded.

6.2.3 Calculation

The specific gravity of the sample was previously determined by accurately weighing a known volume of the sample.

The molecular wt of $NaHSO_3$ is 104.07 g mol^{-1}

The sample volume is V cm^3

The volume of sodium hydroxide used is V_1 cm^3

The molarity of the sodium hydroxide is M_1 mol l^{-1}

Hence, the sodium bisulphite content expressed as

$$\% \text{ w/w} = \frac{V_1 \text{ x}(M_1\text{x}0.10407)\text{x}100}{V \text{ x sp. gr.}}$$

6.3 The determination of sodium thiosulphate

6.3.1 Outline of method.

The thiosulphate is determined by iodimetric titration. The sulphite and bisulphite, which would react with iodine solution, are masked by the addition of a 36% solution of formaldehyde in methanol as described in the method for the determination of sodium sulphite.

6.3.2 Procedure

Reagents required:

36% formaldehyde in methanol

Concentrated hydrochloric acid

starch indicator solution 1% w/v aqueous solution

methyl orange indicator solution

~ 0.01 N iodine solution (standardised)

Method:

By means of a pipette, 10 cm ^{3} of the sample was added into a 500 cm ^{3} conical flask, 20 cm ^{3} of 36% formaldehyde in methanol is added to the sample. Three drops of methyl orange indicator was then added to the mixture, the solution was then made acid to methyl orange by the addition hydrochloric acid from a dropping bottle. The volume was then made up to 300 cm ^{3} with dimineralised water and allowed to stand for seven minutes. The solution is then titrated with 0.01 N iodine solution using starch indicator until the dark violet colour persists for 13 seconds, the volume of iodine used was recorded.

6.3.3 Calculation

The specific gravity of the sample is previously determined by weighing accurately a known volume of the sample.

The molecular wt of $Na_2S_2O_3$ is 158.11 g mol^{-1}

The sample volume is V cm^3

The volume of sodium hydroxide used is V_1 cm^3

The normality of the iodine is N_1

Hence, the sodium thiosulphate content expressed

$$\text{as \% w/w} = \frac{V_1 x (N_1 x 0.15811) x 100}{V \text{ x sp. gr.}}$$

6.4 The determination of sodium sulphate

6.4.1 Outline of method.

A suitable aliquot of the sample was mixed with a 36% solution of formaldehyde, diluted and a known quantity introduced into an Ion Chromatograph.(54) The formaldehyde masks the sulphite, which would not be separated satisfactory from the sulphate. The peak height is then compared to the peak height of a previously injected standard of known concentration.

6.4.2 Procedure

Reagents - equipment required:

36% formaldehyde in methanol;

Ion Chromatograph Dionex 2000 i/sp, fitted with conductivity detector;

50 micro litre sample loop;

AS3 guard column and AS3 analysis column;

Computing integrator;

The instrument was set up according to the manufacturers instructions.

Calibration of the instrument used standards prepared from Analar anhydrous sodium sulphate.

Method:

By means of a pipette, 5 cm^3 of the sample was added into a 250 cm^3 volumetric flask containing 10 cm^3 of a solution of 36% formaldehyde in methanol.

The flask was stoppered and allowed to stand for 10 minutes; the mixture was then diluted to 250 cm^3 using dimineralised water. By means of a pipette, 10 cm^3 of the diluted sample was added to another 250 cm^3 volumetric flask, diluted to 250 cm^3 with dimineralised water, and mixed. Using a 5 cm^3 plastic syringe, a sample was injected into the ion chromatograph, the integrator then quantifying the sodium sulphate in the sample.

6.4.3 Calculation

The specific gravity of the sample is previously determined by weighing accurately a known volume of the sample.

Hence, the sodium sulphate content expressed as percentage w/w

= mg/l of sample (from integrator calibration) x dilution (1250)

6.5 The determination of sulphur dioxide

6.5.1 Outline of method.

A constant gas volume of approximately 5 cm^3 was introduced via a gas sample loop into a gas chromatograph equipped with flame photometric detector. The analysis column consists of six foot x ¼ inch diameter Teflon coil packed with acetone washed Poropak QS. A computing integrator using the signal from the FPD detector determines the concentration of the sulphur species. The output from the FPD detector is a power response to sulphur concentration; (55) a calibration graph was prepared by injecting standards of known concentration, then plotting concentration vs. peak area on log-log graph paper.

6.5.2 Preparation of SO_2 gas standards

Calibration gas standards were prepared by injecting via a gas syringe a known volume of SO_2 into an evacuated aluminium cylinder of known volume. Typically the cylinders were approximately 5 litres in capacity; the exact volume being determined by weighing the cylinder empty; then filling with water and re-weighing, hence the capacity of the cylinder could be calculated. The cylinder was then pressured with nitrogen to 100 psia using a pressure gauge accurate to +/- 0.05 psia. The exact value of the standard (ppmv SO_2) can then be calculated from these volumes. Five different standards were prepared using this technique. As there is a tendency for SO_2 to be adsorbed onto the walls of the aluminium cylinder each cylinder was designated a particular concentration. Additionally, each standard was let down to atmospheric pressure and re-prepared by the same procedure.

This let down and repreparation was repeated until all five standards gave a straight line calibration when peak height was plotted against concentration on log/log graph paper. The range of standards used was in the range 10-70 ppmv, two of the higher standards as a cross check, were analysed using a classical wet analytical method, in this case iodometrically

6.5.3 Procedure

Equipment

Gas Chromatograph Pye Unicam 304 fitted with flame photometric detector, and narrow band passes filter, wavelength 394 nanometre

All sample lines and the sample loop on the GC up to the detector were P.T.F.E. The reason for the P.T.F.E lines is that sulphur dioxide can be absorbed on stainless steel; at low concentrations this can lead to significant errors.

Computing integrator.

SO_2 Standard mixtures were prepared in aluminium cylinders.

Method:

The instrument was calibrated using standards prepared in aluminium cylinders. A sample of the headspace gas from the autoclave was purged through the sample line connected to the GC sample loop. When sufficient gas had been purged, the sample was injected into the GC.

6.5.4 Calculation

The sample gas sulphur dioxide content was then determined by comparing the peak height with the calibration graph. A reading in ppmv is then obtained

In order to express the sulphur dioxide content in terms of a partial pressure the following calculation was performed:

Partial pressure in mm Hg

$$= \frac{(\text{ppmv x Total system pressure in mm Hg})}{1\text{x}10^{6}}$$

7. EXPERIMENTAL AND RESULTS

Nine series of tests were carried out during this investigation. The conditions for each series are given in this section.

7.1 Series 1 Test conditions investigated

The parameters for first series of tests were chosen as follows: -

- Fixed C value approximately 8
- Fixed temperature 54.4°C (130°F)
- Fixed total pressure 110 psia
- Variable S/C

7.1.1 Test procedure

The procedure used for this series of tests was as follows: -

A synthetic solution of W-L solution was prepared from Analar grade chemicals, i.e. sodium bisulphite, sulphite, thiosulphate and sulphate the volume being 1.5 litres. The target C value i.e. active sodium that does not include that from sulphate or thiosulphate was approximately 8 and a S/C of 0.65. This was charged by applying a vacuum to the autoclave and sucking the solution in via the liquid sample line. The system was then purged with oxygen free nitrogen and pressurised to 110 psia, the stirrer having been switched on at this time. A sample of the liquid was taken and a complete analysis carried out in order to determine the exact C value.

The autoclave was then allowed to equilibrate for a period of 12 hours, the exact pressure of the system being recorded. Gas samples were then taken and analysed in triplicate on the GC. After suitable purging, a liquid sample was taken, the volume being 20 ml, which was sufficient to do duplicate analysis for the sulphite and bisulphite contents.

From the total pressure and the SO_2 analysis, the partial pressure of SO_2 could be calculated in mm Hg as follows: -

$$= \frac{\text{ppmv of } SO_2 \text{ x Total pressure in Psia x } 51.715}{1 \text{ x} 10^{4}}$$

Where 51.715 is conversion factor for psia to mm Hg

The S/C of the solution can be calculated as follows: -

w/w % $Na_2\,SO_3$ =A　　　w/w % $NaHSO_3$ =B

Molecular wt of sodium sulphite =126.05 g mol^{-1}

Molecular wt of sodium bisulphite =104.07 g mol^{-1}

Moles of Na = (2xA/126.5) + (B/104.07)

Moles of SO_2 = (A/126.5) + (B/104.07)

Hence, S/C is the ratio of the moles of SO_2/ moles of "active" Na^+

On completion of the first test the autoclave was slowly depressurised via the vent valve, the discharged gas being passed through a caustic scrubber to prevent releasing SO_2 into the atmosphere. The solution S/C was then increased by the introduction of pure SO_2 via a canister of liquid SO_2 connected to the vent valve. The canister was placed on a balance so that the adjustment could be achieved within the desired range. Downward adjustment was made by a series of depressurisation-pressurisation operations in order to reduce the overall SO_2 content of the solution. A total of fourteen data points were obtained for the first series.

7.1.2 Series 1 Results

The calculation of C value requires that the total water content of the solution be taken into account i.e. Free and combined. For this reason, sodium bisulphite will be expressed as sodium metabisulphite i.e. $NaHSO_3$ will be expressed as $Na_2S_2O_5$

$$2NaHSO_3 \longrightarrow Na_2S_2O_5 + H_2O$$

The initial solution composition is given in Table 1.

Table 1 Series 1 initial solution composition

Component	amount % w/w	Moles of SO_2	Moles of Active Na	moles of H_2O
Na_2SO_3	13.79	0.109	0.219	
$Na_2S_2O_5$	9.08	0.096	0.096	
Na_2SO_4	6.19			
$Na_2S_2O_3$	0.30			
H_2O	70.64			3.920
Total		0.205	0.314	3.920

The C value of this solution is 8.018

The experimental results for series 1 are given in table 2 below, the calculated partial pressure SO_2 using Johnstone's equation is also given for comparison together with the percentage difference. These results are illustrated graphically in Appendix 1.

Table 2 Experimental results series 1

Test No	S/C	$ppSO_2$ Experimental	$ppSO_2$ Calculated Johnstone's equation	Percentage difference
1.1	0.651	0.060	0.059	2.1
1.2	0.726	0.179	0.169	5.7
1.3	0.741	0.213	0.203	4.9
1.4	0.771	0.329	0.290	13.4
1.5	0.776	0.382	0.308	23.9
1.6	0.797	0.455	0.394	15.7
1.7	0.817	0.633	0.497	27.4
1.8	0.820	0.638	0.515	23.8
1.9	0.833	0.762	0.601	26.7
1.1	0.853	0.878	0.768	14.3
1.11	0.856	0.897	0.797	12.5
1.12	0.861	0.958	0.849	12.8
1.13	0.877	1.183	1.046	13.1
1.14	0.898	1.720	1.406	22.3

7.2 Series 2 & 3 Test conditions investigated

The parameters for series two and three of tests were chosen as follows: -

- Fixed C value approximately 7.4
- Two temperatures 48.9°C (120°F) and 54.4°C (130°F)

- Fixed total pressure 110 psia
- Variable S/C

7.2.1 Test procedure

The procedure used for this series of tests was as described previously, the exception being that on completion of the first test at 48.9°C (series 2), the temperature of the autoclave was increased to 54.4°C (Series 3) and allowed to equilibrate for a period of 12 hours. A gas sample was then taken and analysed for SO_2. A liquid sample was not taken at this point, the analysis from the first temperature measurement being used. The volume of liquid in the autoclave is sufficient that insignificant differences in the analysis would occur.

7.2.2 Series 2&3 Results

The initial solution composition for series 2 & 3 is given in Table 3 with the results in Tables 4 & 5. The results are shown graphically in Appendices 2 & 3.

Table 3 Series 2 & 3 initial solution composition

Component	amount % w/w	Moles of SO_2	Moles of Active Na	moles of H_2O
Na_2SO_3	12.89	0.102	0.205	
$Na_2S_2O_5$	8.69	0.091	0.091	
Na_2SO_4	6.09			
$Na_2S_2O_3$	0.30			
H_2O	72.03			4.000
Total		0.194	0.296	4.000

Table 4 Experimental results series 2

Test No	S/C	ppSO_2 Experimental	ppSO_2 Calculated	Percentage higher
2.1	0.654	0.058	0.049	18.2
2.2	0.723	0.157	0.128	22.6
2.3	0.766	0.251	0.215	16.6
2.4	0.798	0.386	0.313	23.4
2.5	0.832	0.559	0.467	19.7
2.6	0.846	0.600	0.553	8.6
2.7	0.874	0.850	0.790	7.6
2.8	0.905	1.395	1.229	13.5

Table 5 Experimental results series 3

Test No	S/C	$ppSO_2$ Experimental	$ppSO_2$ Calculated Johnstone's equation	Percentage higher
3.1	0.654	0.061	0.062	-2.1
3.2	0.723	0.185	0.163	14
3.3	0.766	0.312	0.274	13.8
3.4	0.798	0.436	0.398	9.6
3.5	0.832	0.688	0.594	15.8
3.6	0.846	0.752	0.704	6.9
3.7	0.874	1.108	1.005	10.2
3.8	0.905	1.721	1.564	10.1

7.3 Series 4 & 5 Test conditions investigated

The parameters for series 4 & 5 of tests were similar to that of 2 & 3, with the exception that the C value was increased to 8.4 and the temperatures chosen were the standard of 54.4°C (130°F) and 65.6 ° (150°F). The pressure was increased for these tests to 150 psia to accommodate the higher temperature being used, thus ensuring no water dew point problems.

7.3.1 Series 4 & 5 Results

The initial solution composition for series 4 & 5 is given in Table 6 with the results given in tables 7 & 8, and shown graphically in appendices 4 & 5.

Table 6 Series 4 & 5 initial solution composition

Component	amount % w/w	Moles of SO_2	Moles of Active Na	moles of H_2O
Na_2SO_3	14.21	0.113	0.226	
$Na_2S_2O_5$	9.64	0.101	0.101	
Na_2SO_4	6.11			
$Na_2S_2O_3$	0.30			
H_2O	69.74			3.870
Total		0.214	0.327	3.870

Table 7 Experimental results series 4

Test No	S/C	ppSO$_2$ Experimental	ppSO$_2$ Calculated Johnstone's equation	Percentage higher
4.1	0.650	0.063	0.058	8.6
4.2	0.724	0.192	0.165	16.8
4.3	0.753	0.296	0.235	26.3
4.4	0.780	0.395	0.323	22.5
4.5	0.818	0.612	0.503	21.6
4.6	0.841	0.794	0.662	19.9

Table 8 Experimental results series 5

Test No	S/C	ppSO$_2$ Experimental	ppSO$_2$ Calculated Johnstone's equation	Percentage higher
5.1	0.650	0.106	0.092	15.5
5.2	0.724	0.315	0.260	21.1
5.3	0.753	0.437	0.371	17.7
5.4	0.780	0.638	0.511	25.1
5.5	0.818	0.958	0.796	20.3
5.6	0.841	1.307	1.048	24.8

7.4 Series 6 Test conditions investigated

In order to investigate the effect of not having sodium sulphate in the solution, this being the condition that Johnstone used in his investigation, a short series of tests were carried out without the addition of either sulphate or thiosulphate.

The parameters used for series six tests were as follows: -

- Fixed C value approximately 7.8
- Standard temperature 54.4°C (130°F)
- Fixed total pressure 110 psia
- Variable S/C

The test procedure being as previously described

7.4.1 Results series 6

The initial solution composition for series 6 is given in Table 9 with the results in table 10; the results are shown graphically in Appendix 6.

Table 9 Series 6 initial solution composition

Component	amount % w/w	Moles of SO_2	Moles of Active Na	moles of H_2O
Na_2SO_3	10.32	0.082	0.164	
$Na_2S_2O_5$	15.05	0.158	0.158	
Na_2SO_4	0.38			
$Na_2S_2O_3$	0.00			
H_2O	74.25			4.120
Total		0.240	0.322	4.120

The C value of this solution is 7.820

Table 10 Experimental results series 6

Test No	S/C	ppSO_2 Experimental	ppSO_2 Calculated using Johnstone's equation	Percentage higher
6.1	0.746	0.249	0.216	15.2
6.2	0.772	0.362	0.294	23.1
6.3	0.808	0.494	0.447	10.4
6.4	0.832	0.673	0.594	13.2

7.5 Series 7 test conditions investigated

The design of this series of tests was to investigate the effect of total system pressure on the pp SO_2.

- Fixed C value 8.013
- Standard temperature 54.4°C (130°F)
- Variable total pressure 100-600 psia
- Fixed S/C 0.820

7.5.1 Test procedure

The procedure used for this series of tests was to analyse the liquid and gas composition after the first test at 100 psia. The pressure was then increased using nitrogen in 100-psi increments, the system was allowed to equilibrate, then the gas was analysed, and the liquid composition was taken as that determined at the first point. This procedure was repeated to cover the range 100- 600 psia.

7.5.2 Results of series 7

The results obtained for the effect of total pressure are given in table 11 and are shown graphically in appendix. 7

Table 10 Experimental results series 6 effect of total pressure

Total System Pressure psia	pp. SO_2 mm Hg
100.0	0.638
200.0	0.637
300.0	0.638
400.0	0.639
500.0	0.641
600.0	0.646

7.6 Series 8 & 9 test conditions investigated

The objective of these series of tests was to investigate the effect of temperature on the pp SO_2 and hence derive the log M function in the Johnstone equation.

The conditions used were as follows: -

Series 8

- Fixed C value 7.4
- Variable temperature range 37.8-54.4°C
- Fixed total pressure 110 psia
- Fixed S/C 0.846

Series 9

- Fixed C value 8.44
- Variable temperature range 48.9-65.6°C
- Fixed total pressure 150 psia
- Fixed S/C 0.818

7.6.1 Test procedure

The procedure used for this series of tests was to analyse the liquid and gas composition after the first test. The temperature was then increased in 5.5°C (10°F) intervals.

The system was allowed to equilibrate.

Then a gas analysis was carried out; this procedure was repeated until all the data points had been examined.

7.6.2 Results of series 8 & 9

The effect of temperature on the partial pressure of SO_2 as described by Johnstone is said to follow the Young Equation (56).

$$\log (\text{pp } SO_2) = a + b/T$$

Where a and b are constants T is the temperature K.

Given Johnstone's formula that that pp SO_2 is given by

$$\text{pp } SO_2 \text{ mm Hg} = \frac{M \times (2S-C)^2}{(C-S)}$$

C= Total concentration of base, moles/100 moles of H_2O.

S = Total concentration of dissolved SO_2, moles/100 moles of H_2O.

M = a constant depending on the temperature.

where log M in the Johnstone equation = 4.519 - 1987/T

From the results of series, 8 & 9 the value of M can be calculated.

If log M is plotted against 1/TK, the equation can be calculated by least squares regression of the slope.

The raw results of series 8 & 9 and 1/TK vs. calculated log M are given in Tables 11 and 12.These are shown graphically in Appendices 8-11 together with the calculated equation

Appendix 12 gives the combined data and the overall equation.

Table 11 Experimental results series 8 & 9 effect of temperature

Test No	Temperature °C	pp. SO_2 mm Hg
8.1	37.8	0.363
8.2	43.3	0.464
8.3	48.9	0.600
8.4	54.4	0.752
9.1	48.9	0.484
9.2	54.4	0.612
9.3	60.0	0.769
9.4	65.6	0.958

Table 12 1/TemperatureK vs. log M series 8 & 9

Test No	1/Temperature K	log M
8.1	0.00311	-1.5844
8.2	0.00305	-1.4866
8.3	0.00300	-1.3872
8.4	0.00295	-1.2917
9.1	0.00322	-1.8017
9.2	0.00316	-1.6950
9.3	0.00311	-1.5835
9.4	0.00305	-1.4855

8. EVALUATION AND DISCUSSION OF EXPERIMENTAL DATA

8.1 Temperature coefficient log M

The temperature coefficient log M determined in the tests specifically designed to evaluate the effect of temperature i.e. series 8 & 9 gave the following: -

Log M = 4.412 - (1931.1/T K)

In order to have a direct comparison with the difference between this value of M and Johnstone's value of M, the function can be calculated using a fixed temperature for this example e.g. 323K.

For this work **M= 0.0270** and for Johnstone's work **M = 0.0233**

This difference in the value of the M function means that the average calculated partial pressure of SO_2 in this work is 13.6% higher than that calculated using Johnstone's equation.

8.2 Experimental results vs. calculated results

Using the M function derived in this work and the basic model as described by Johnstone for the calculation of partial pressure of SO_2, the theoretical results for all the series can be made, and the data then compared to the experimental data. A graphical plot of calculated and determined values of the partial pressure of SO_2 for each of the series is given in Appendix 13. It can be seen from this plot that the correlation between experimental and calculated values is extremely close and is within +/-1%

8.3 Review of Johnstone's original data

A review was made of Johnstone's original data given in his paper in 1938 to possibly account for the variation between the two sets of data. Given in Table 13 are data as presented in his paper, which gives the experimental and calculated partial pressure SO_2 over a range of experimental conditions. This is also shown graphically in Appendix 14. A discriminating review of the data did reveal that the equation used for the calculated values of the partial pressure of SO_2 used the temperature exponent for log M as the following: -

log M = **4.619**-(1987/T)

This being in conflict with his reported equation of: -

log M = **4.519**-(1987/T)

This may have been a typographical error in his original paper, recalculation of his original data using his "quoted equation" does shows a great deal more scatter in his results. This is illustrated graphically in Appendix 15.

In order to determine the impact of this typographical error, the value of M for the example given in section 8.1 was calculated using the "Revised Johnstone" log M function.

Then the value obtained is: **M=0.0293**

This now gives a value for the partial pressure SO_2 to be of 26% higher than that calculated using "Johnstone's as quoted" equation and is 9% higher than that derived in this work. Given the fact that Johnstone examined a range of sodium ion concentrations i.e. C values, which would not be economically viable in a commercial absorption system, a regression analysis was carried out using only his data which had a C value of approximately eight, that which would be found in a W-L plant, i.e. solutions K3, K5 and K6.

A plot of log M vs.1/T°K as shown in Appendix 16 gave the following function: log M=4.4521-(1952/T°K) using 323°K to calculate M.

Then the value obtained is **M= 0.0256**.

This would result in a value of the partial pressure of SO_2 being approximately 5% lower than determined in this project.

Table 13 Johnstone's original data

Test solution	**S**	**C**	**Temperature °C**	**90**	**70**	**50**	**35**
K-3	7.22	7.77	Experimental mm Hg	8.5	3.6	1.61	0.85
			Calculated mm Hg	11.3	5.4	2.35	1.18
K-5	7.5	7.78	Experimental mm Hg	25	11.5	5.1	2.6
			Calculated mm Hg	38	18.2	8	4
K-6	6.8	7.75	Experimental mm Hg	4.7	2.2	1.1	0.57
			Calculated mm Hg	5	2.4	1.1	0.53
KB-1	5.38	5.87	Experimental mm Hg	8.8	4.1	1.8	0.91
			Calculated mm Hg	6.8	3.3	1.4	0.71
KB-4	5.06	5.85	Experimental mm Hg	3.2	1.5	0.71	0.34
			Calculated mm Hg	3.2	1.5	0.68	0.34
KB-5	4.4	5.87	Experimental mm Hg	0.94	0.51	0.3	0.16
			Calculated mm Hg	0.82	0.39	0.17	0.09
KB-6	5.61	5.88	Experimental mm Hg	17.8	9	4	1.78
			Calculated mm Hg	14.7	7.1	3.1	1.54
KC-2	3.54	3.98	Experimental mm Hg	3.3	1.4	0.84	0.51
			Calculated mm Hg	3.1	1.5	0.64	0.32
KC-3	3.61	4	Experimental mm Hg	4	2	-	0.47
			Calculated mm Hg	3.7	1.6	0.78	0.39
KC-4	3.3	4.01	Experimental mm Hg	1.02	0.46	-	-
			Calculated mm Hg	1.32	0.63	0.28	0.14
KC-5	3.74	3.99	Experimental mm Hg	6.8	3.7	1.7	0.76
			Calculated mm Hg	6.8	3.7	1.4	0.71

9 CONCLUSIONS

The original form of Johnstone's equation has been found more than adequate in describing the partial pressure of sulphur dioxide above solutions of sodium sulphite-bisulphite solutions at concentrations that would exist in a commercial W-L FGD plant. The major shortcoming when trying to apply the findings of his work and that of other workers (57&58) who have examined the partial pressure of sulphur dioxide above solutions of sodium sulphite-bisulphite solutions *is being the very narrow range of parameters studied that can be applied to the design of a commercial FGD process*. Although a more rigorous mathematical equation to cover the range of concentrations and temperatures of interest would be valuable, data obtained in this project, particularly the good correlation of experimental and theoretical results, are adequate for the design of the absorption section of a W-L plant.

A critical examination of Johnstone's original data should have been undertaken when the process was first being developed. The equation as quoted in Perry and generally accepted as describing the partial pressure does not, without reference to the original work, give details of the range of parameters, which this equation applies. It has been shown in this project that the use of Johnstone's data restricted to the concentration ranges applicable to a W-L plant would have given a modified equation, which from a design standpoint, would have been more accurate.

An area which warrants further investigation, is the measurement of the partial pressure of sulphur dioxide as applied in the regeneration section. The conditions existing here are completely different in nature to those existing in the absorption section, some of these being: -

temperature, (a very narrow range 92-98 °C), S/C in the 0.9 –0.93 region and the presence of undissolved sodium sulphite.

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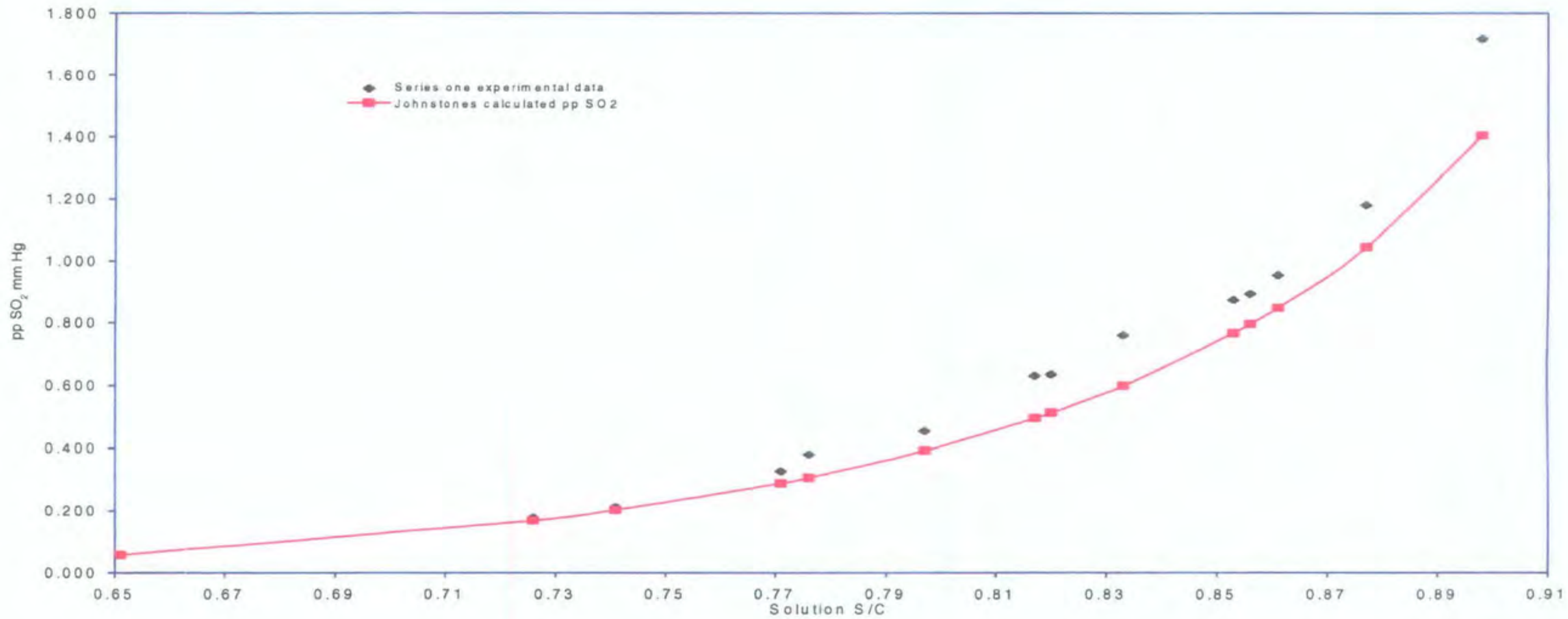
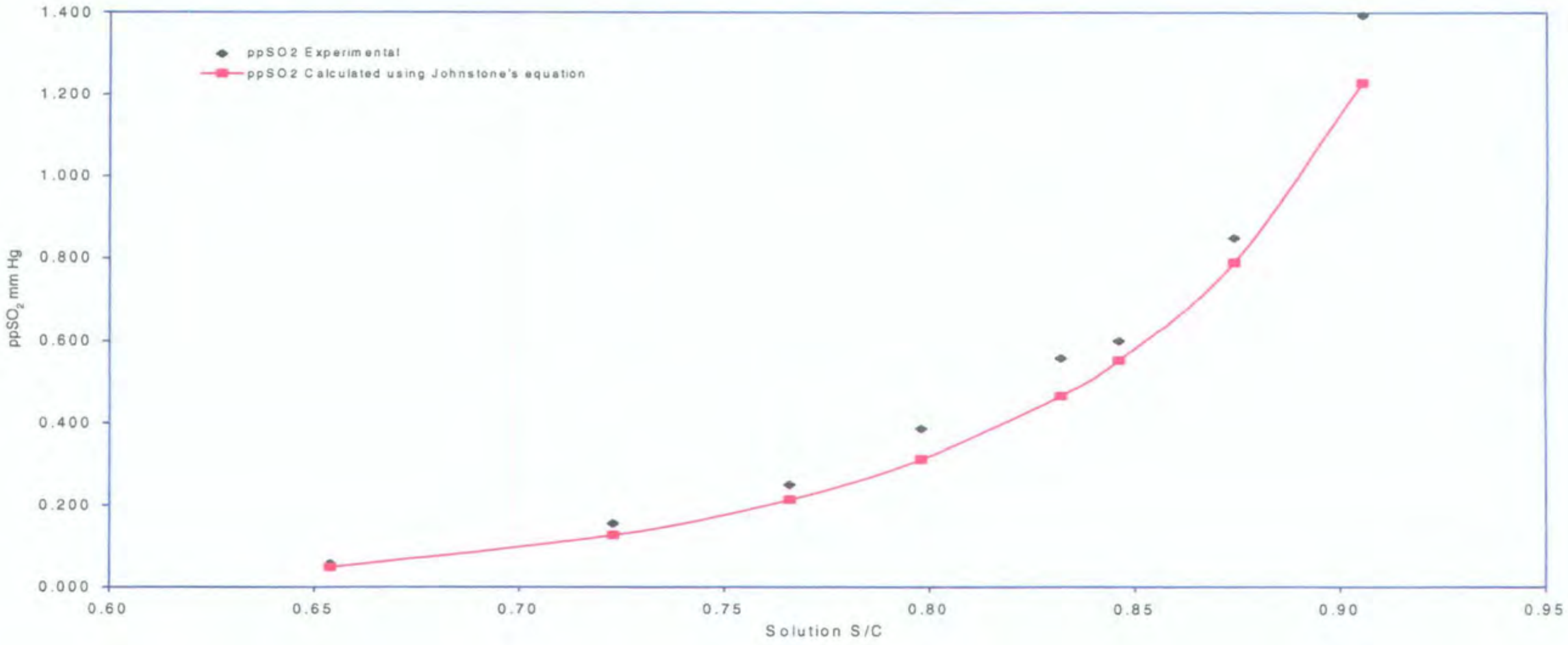
Appendix 1 Experimental results series 1



Appendix 2 Experimental results series 2



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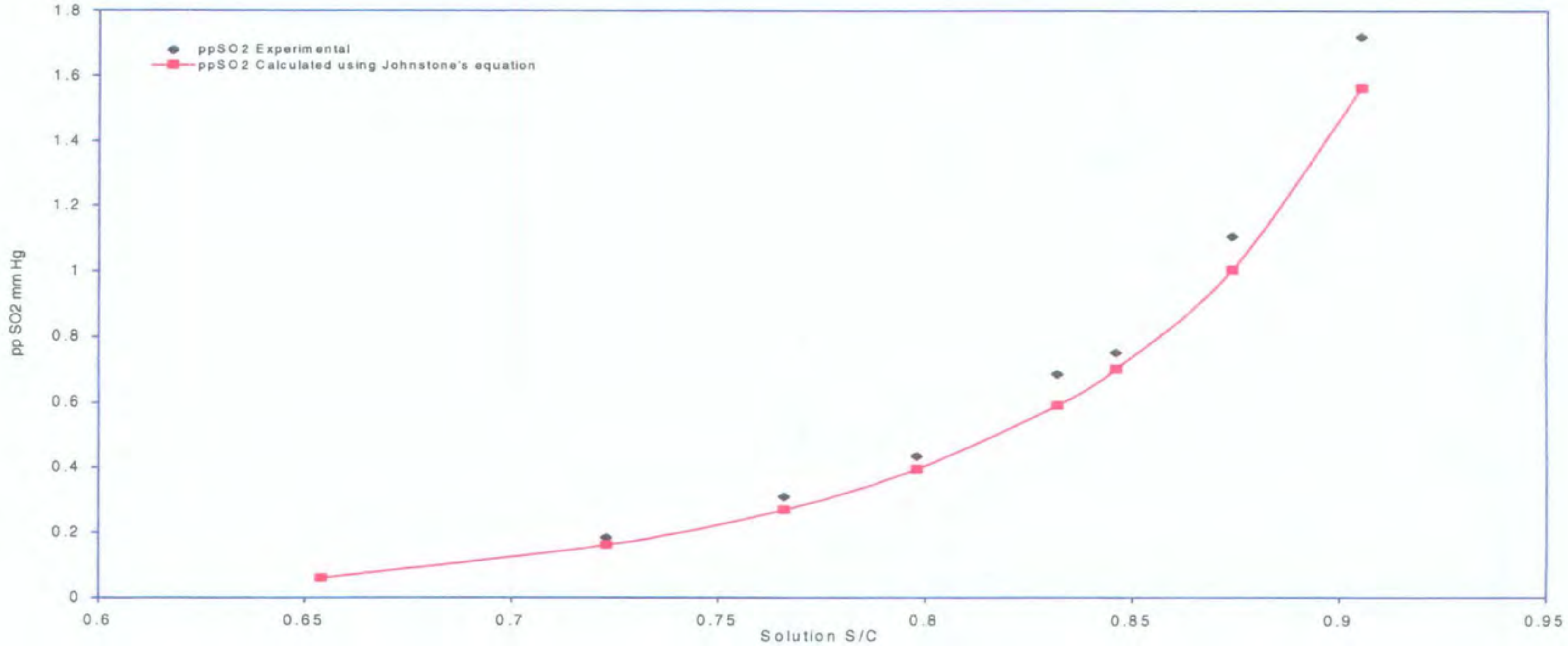

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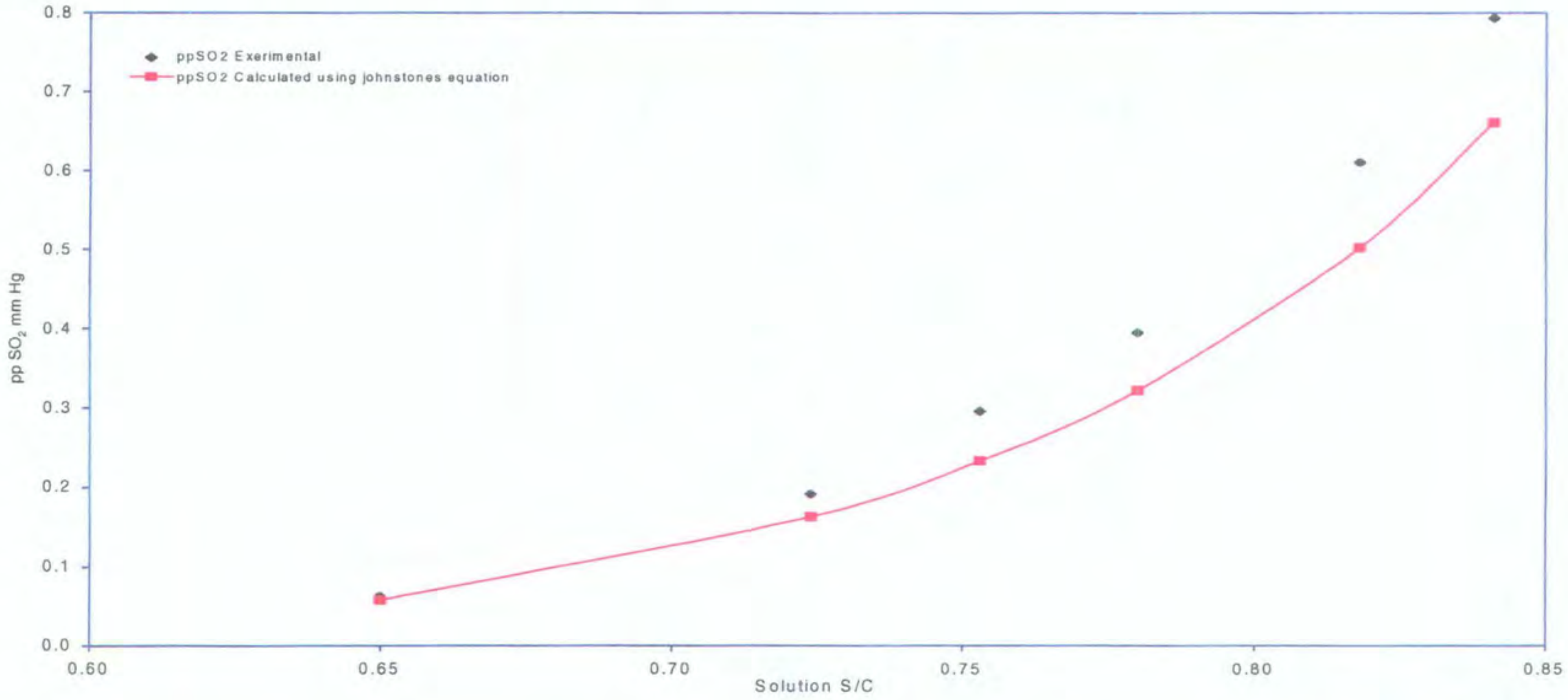

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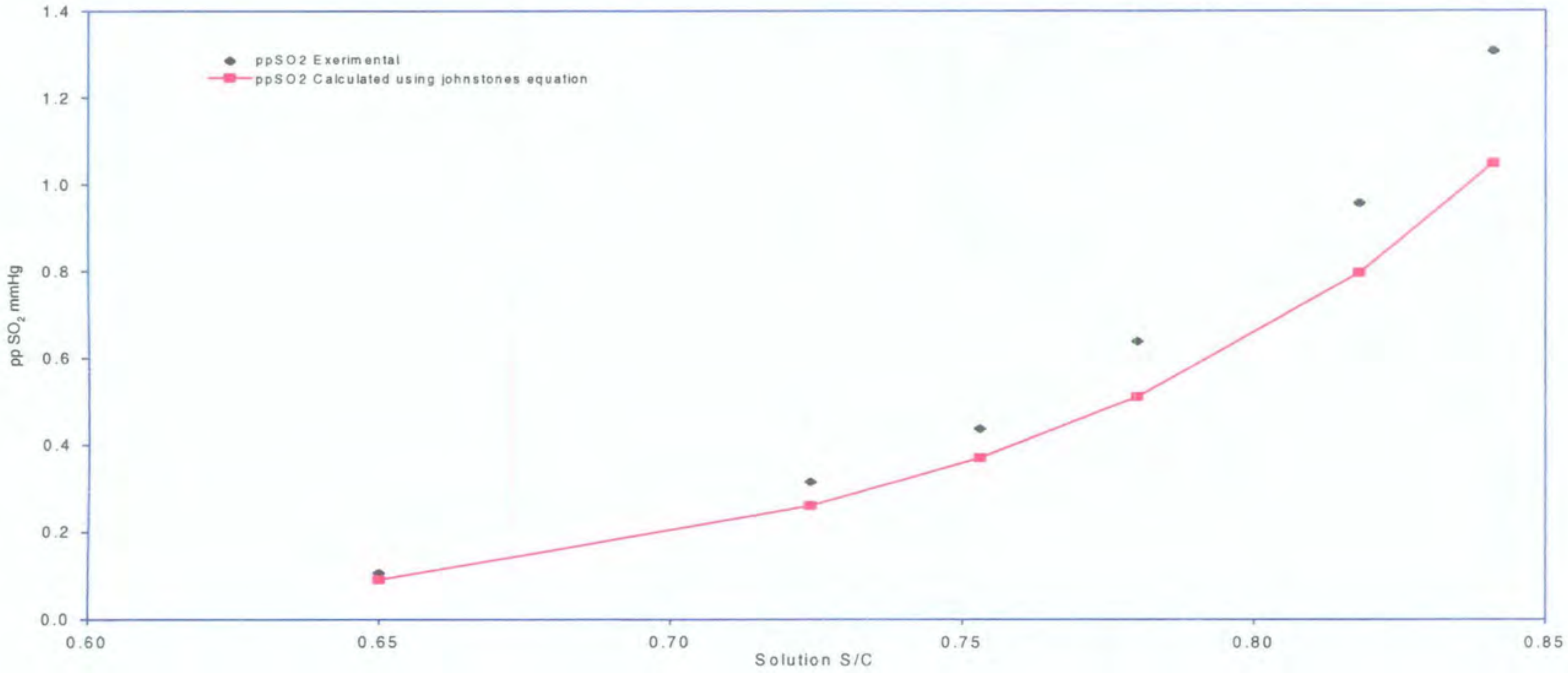

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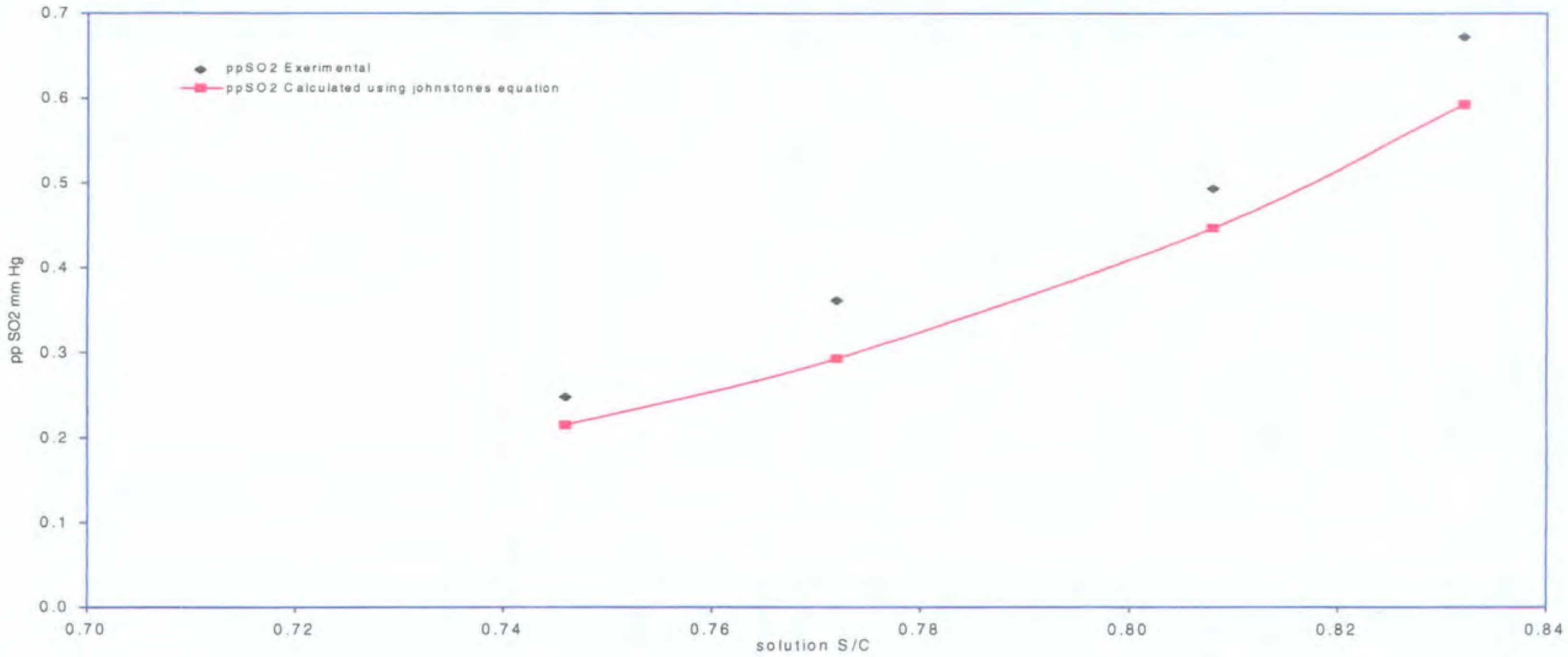
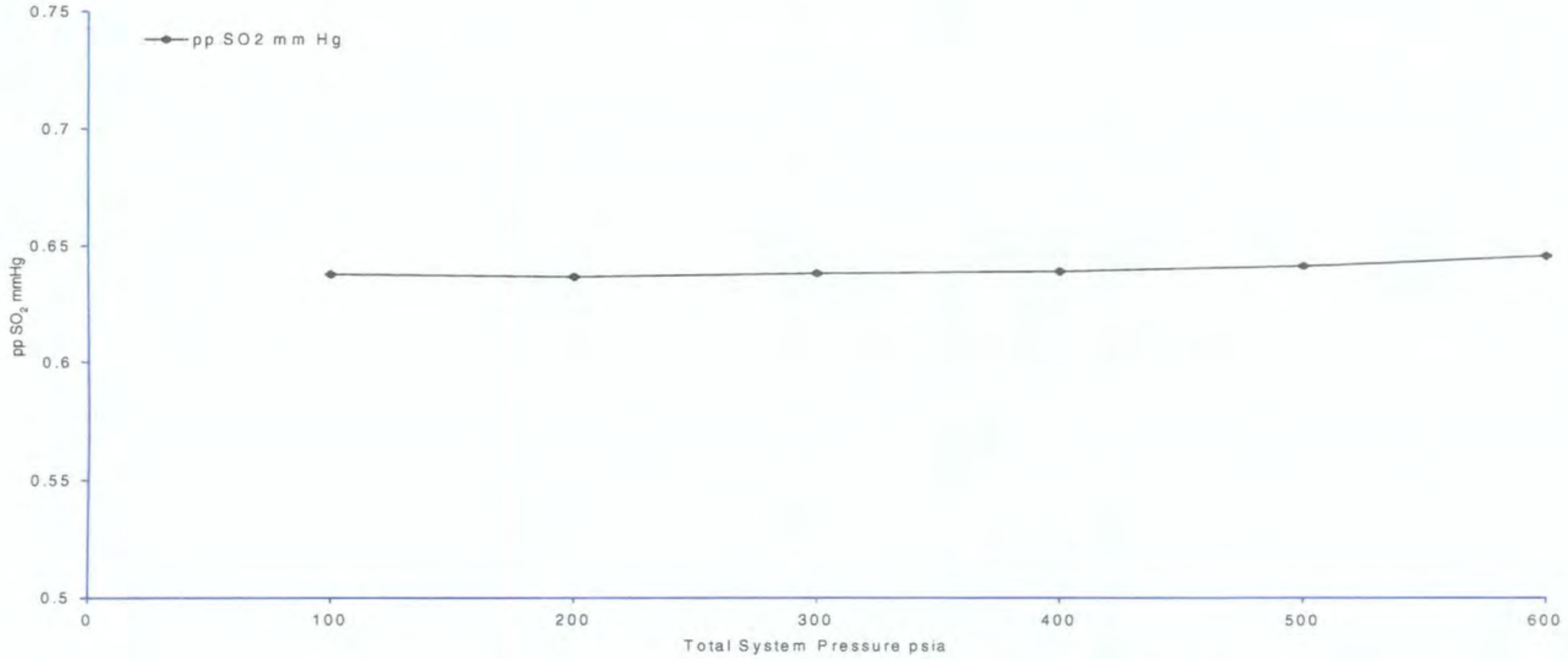
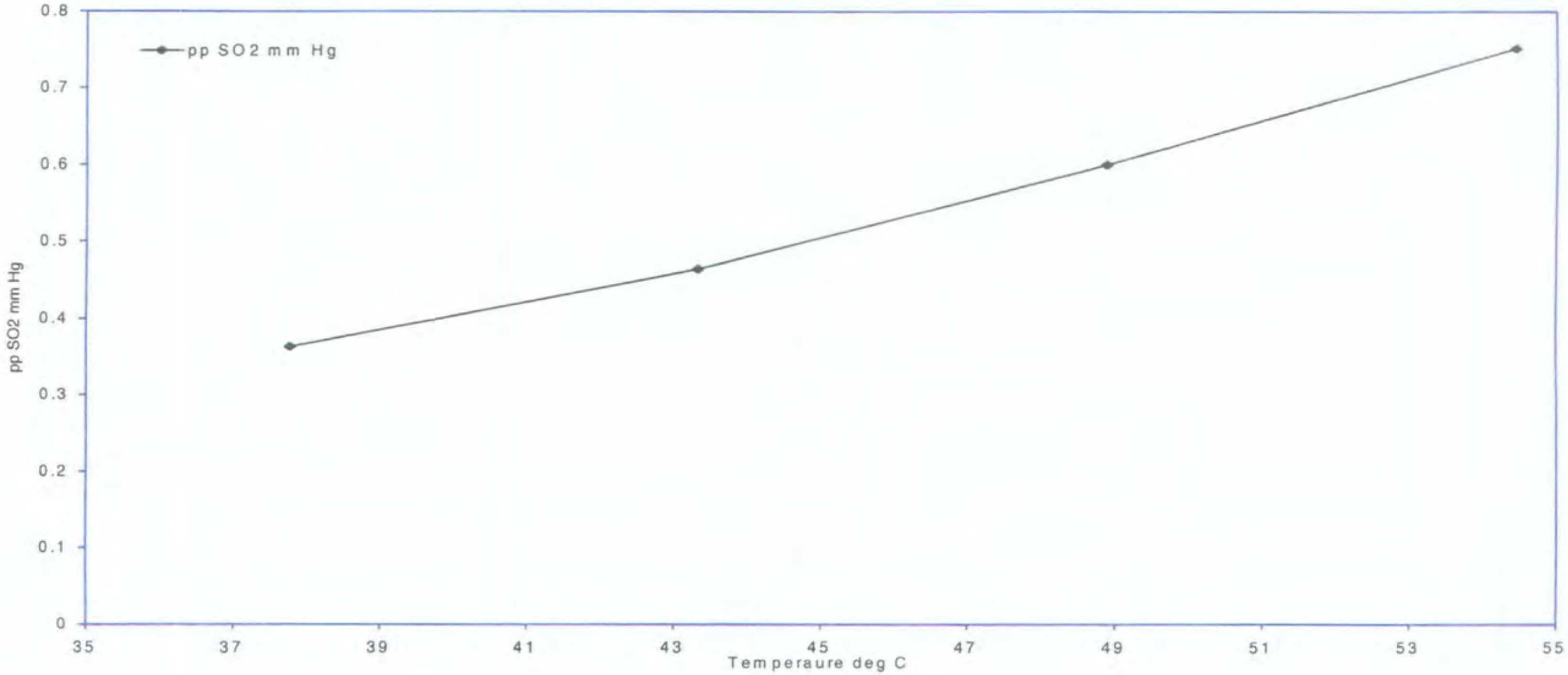


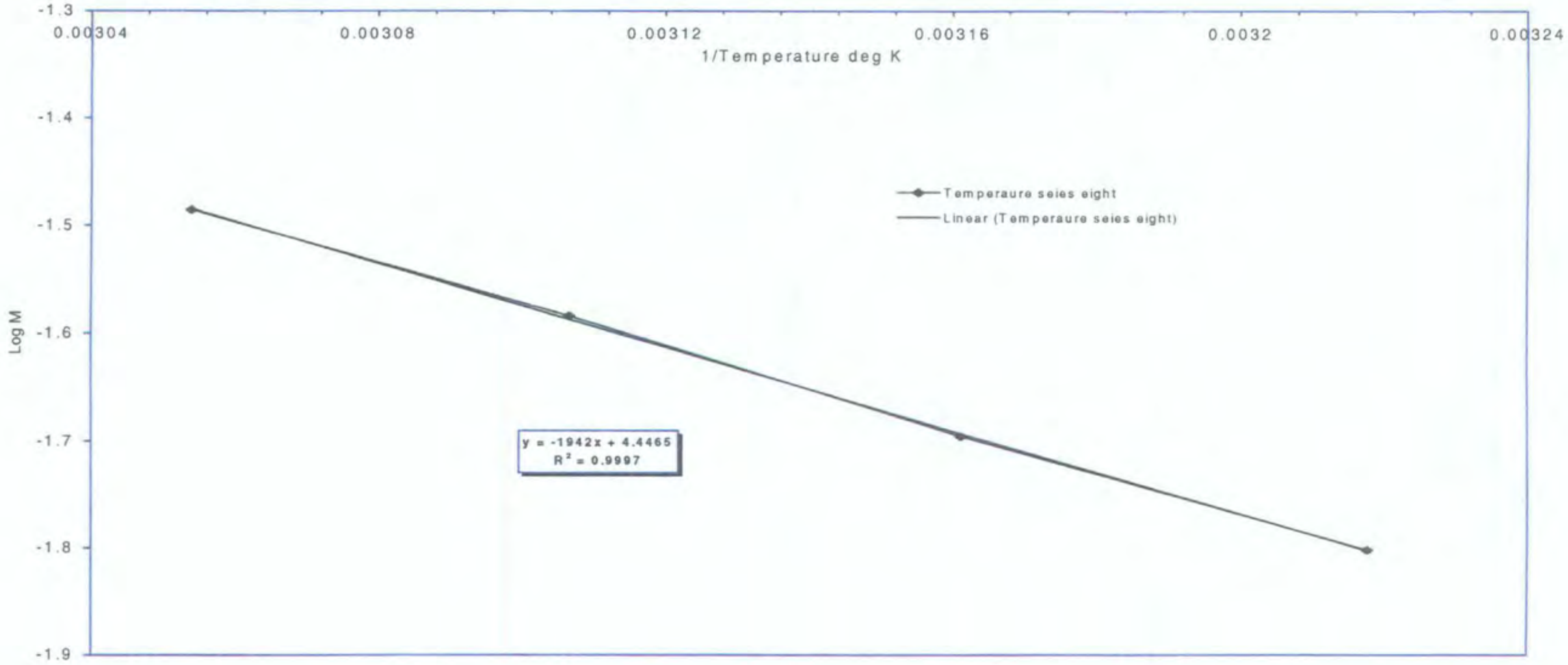
Appendix 7 Experimental results series 7 effect of total pressure



Appendix 8 Experimental results series 8 effect of temperature



Appendix 9 1/Temperature K vs. log M series 8



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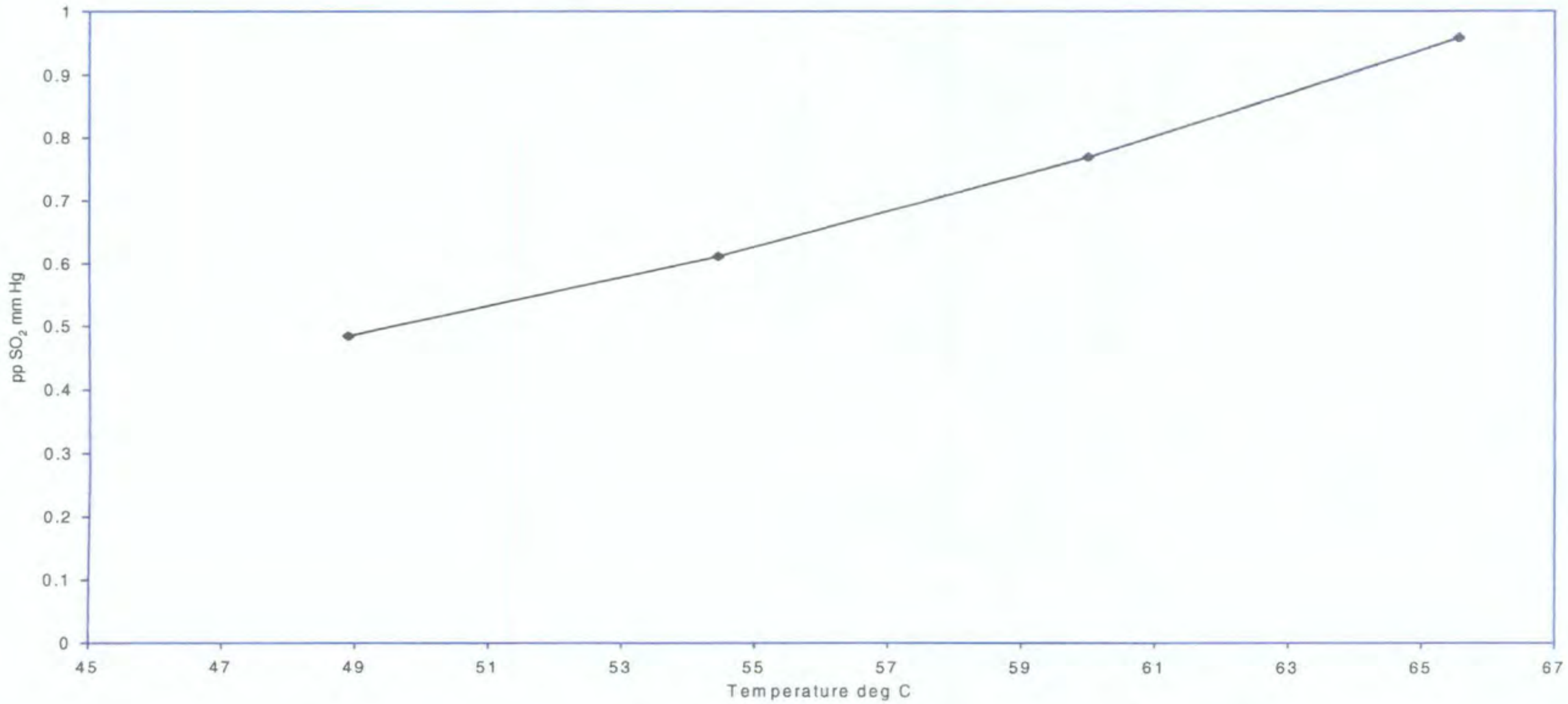

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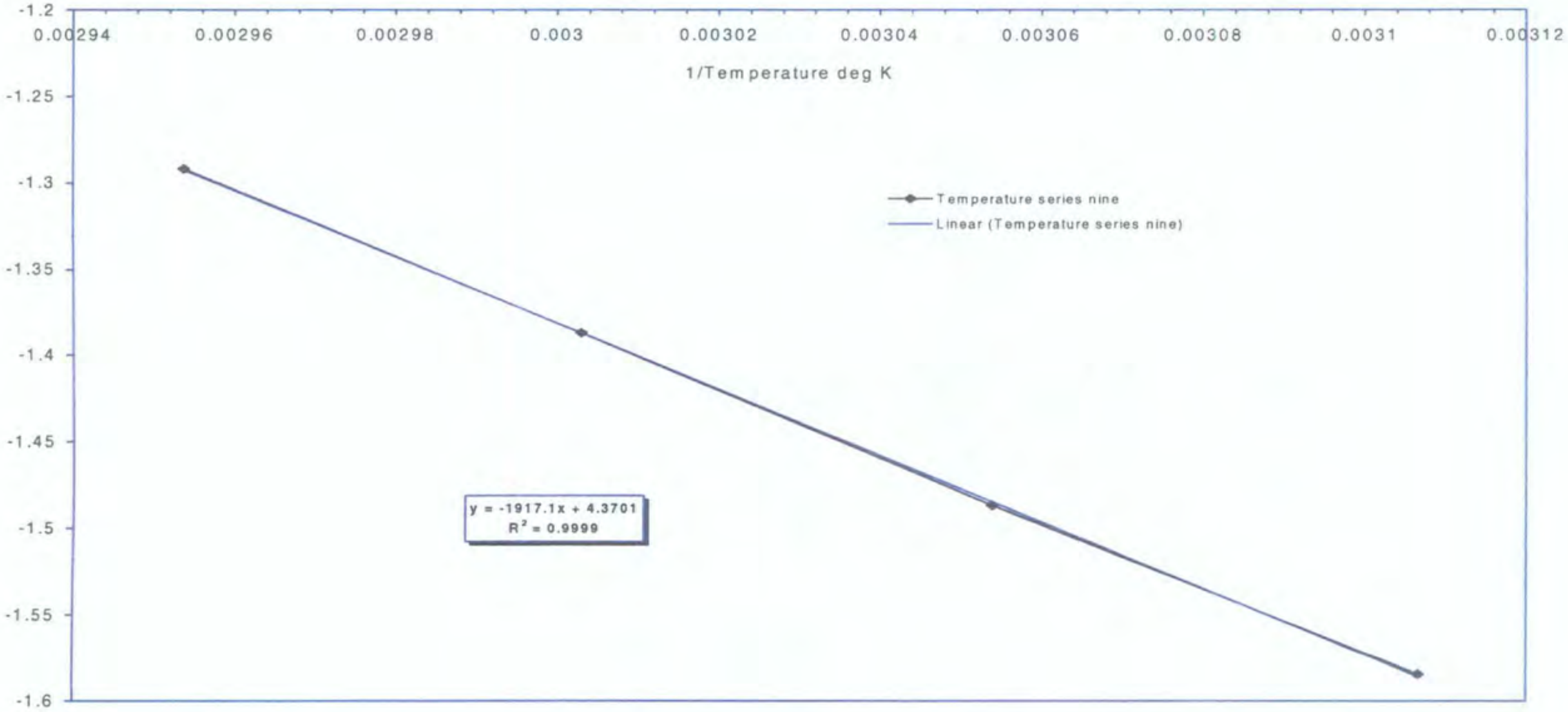
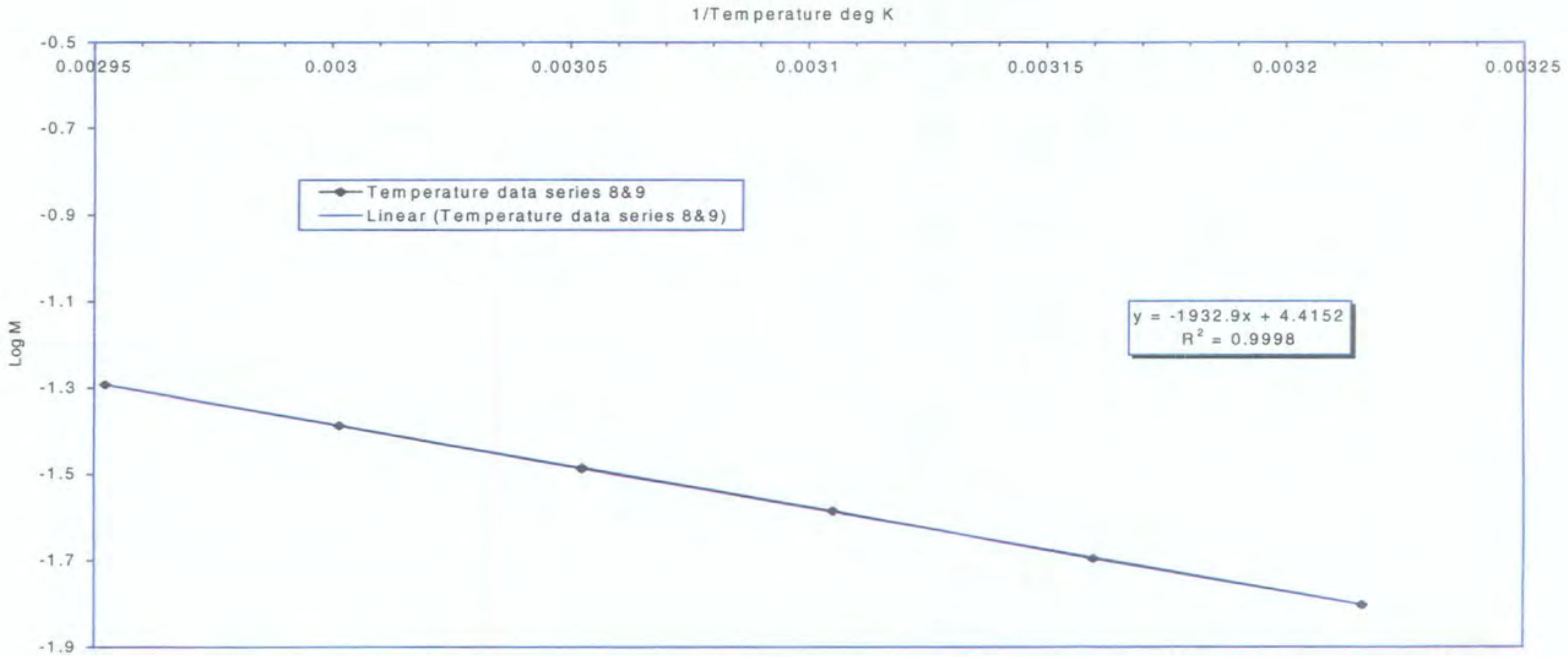
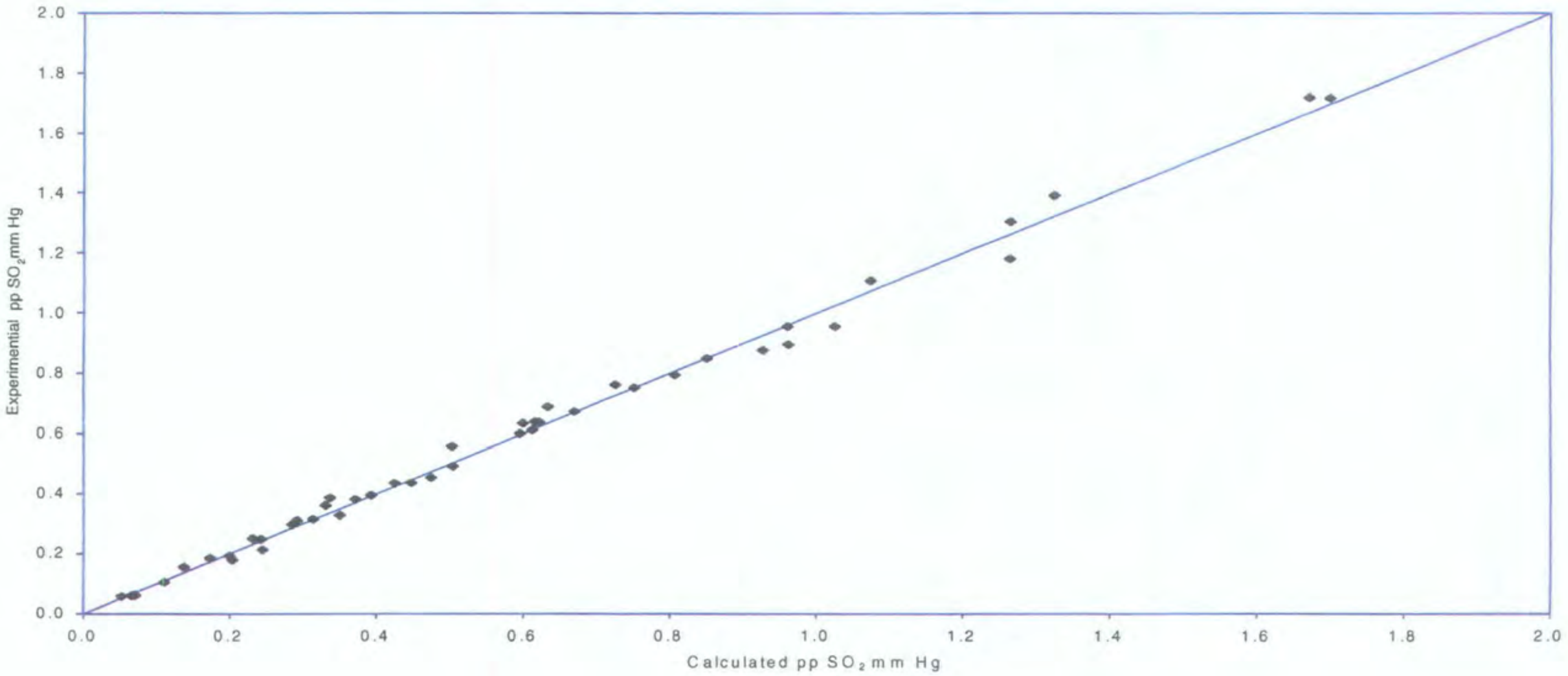


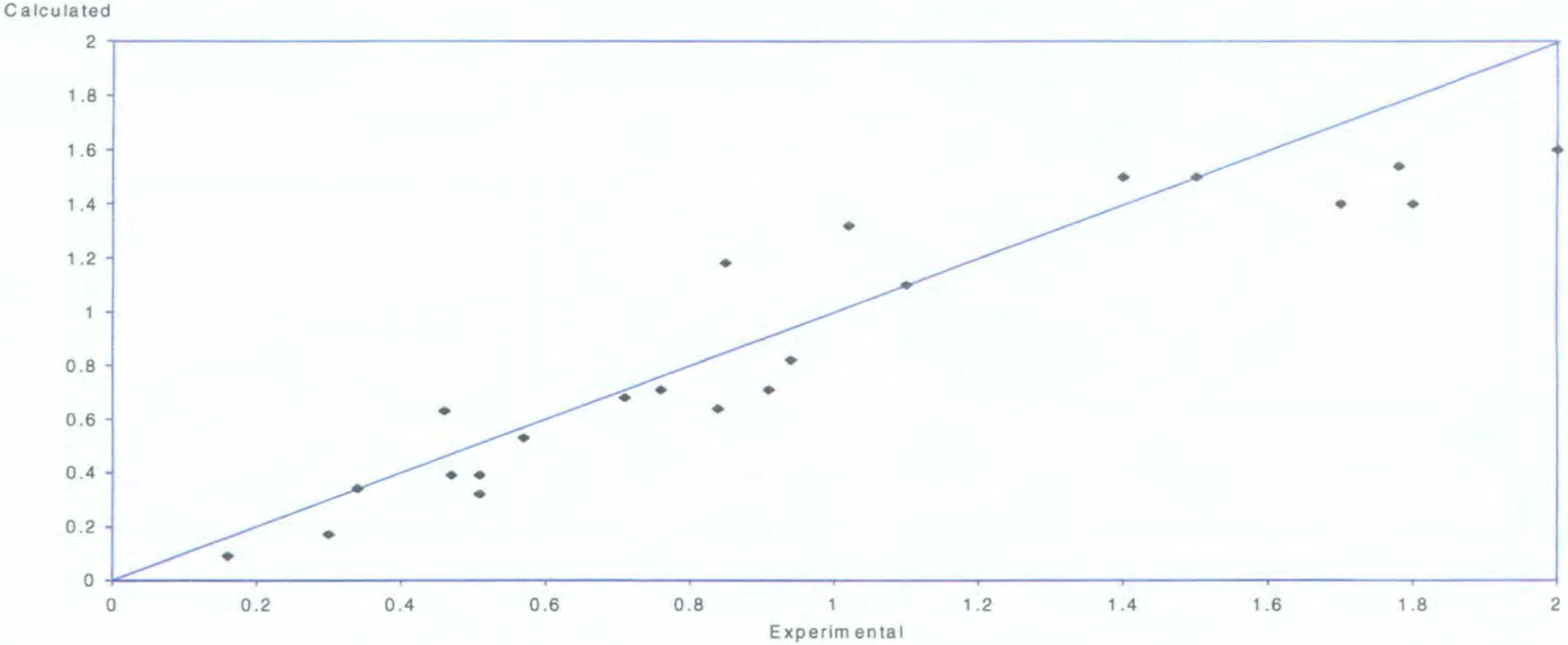
Appendix 12 1/Temperature K vs. log M series 8&9



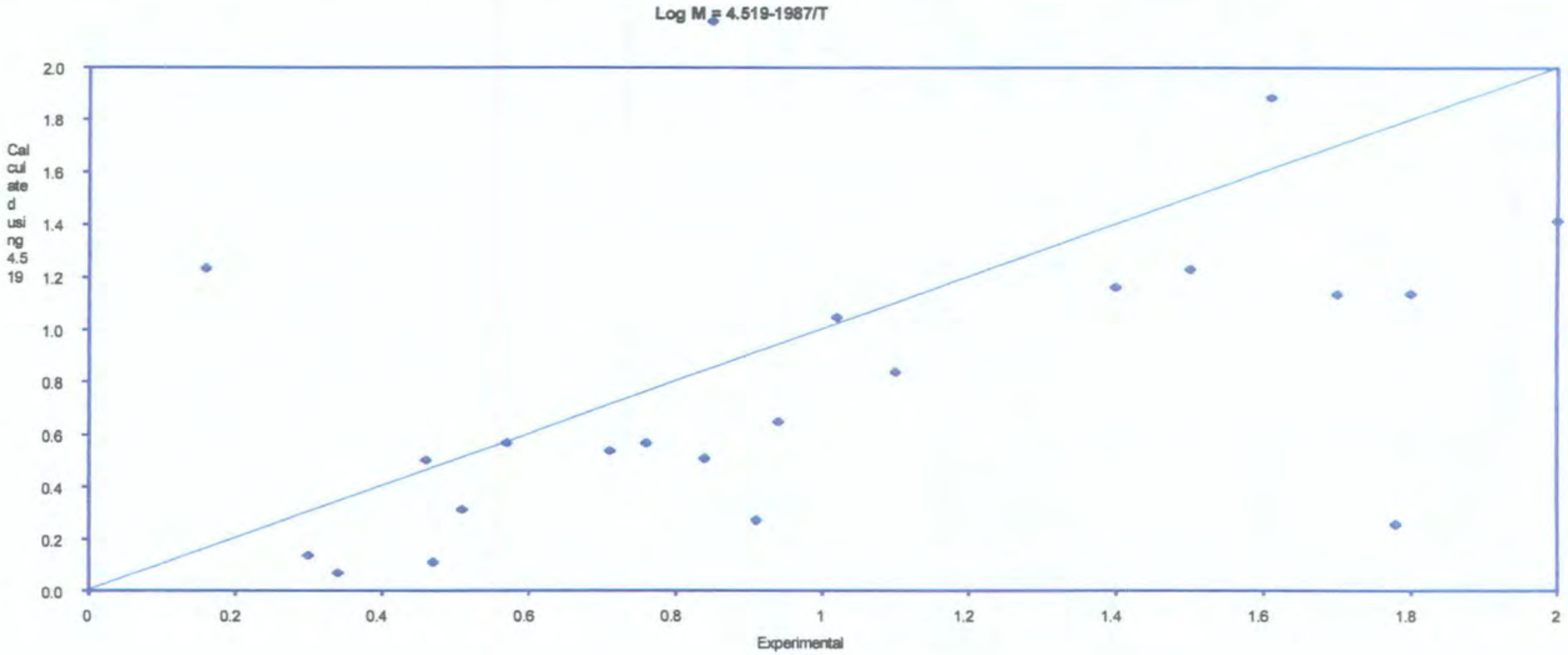
Appendix 13 Experimental vs. calculated ppSO$_2$ all series of tests



Appendix 14 Johnstone's experimental vs. calculated data as presented



Appendix 15 Johnstone's experimental vs. calculated using Log M=4.519-1987/T



Appendix 16 Regression of Johnstone's data with C approximately 8