STUDIES ON VARIOUS ASPECTS OF THE VANADIUM CHEMISTRY OF THE STRETFORD PROCESS

By

R. J. Falkiner

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STUDIES ON VARIOUS ASPECTS OF THE VANADIUM CHEMISTRY OF THE STRETFORD PROCESS

To

my parents

They gave me the opportunity to learn

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AUTHOR: Robert James Falkiner, HBSc. (University of Saskatchewan)

SUPERVISOR: Dr. O.E. Hileman

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ABSTRACT

This work touches on a wide variety of subjects associated with the vanadium process chemistry in the Stretford Process. A comprehensive literature survey of desulfurization systems is presented in chapter 1 and appendix II. Experimental work is focused on vanadium oxidation, reduction, and precipitation in Stretford-like solutions.

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CHAPTER 1

INTRODUCTION

1.1 Coke Oven Gas Desulfurization

Sulfur was a component of proteins and other biological material that fossilized to form natural petroleum and coal. Thus, it is a natural contaminant in all fossil fuels. In the processing of liquid petroleum, sulfurous compounds are removed from all the distillable fractions and thus, the lighter fuels that we normally encounter have a very low sulfur content when compared with the residuals. These "heavy ends" are similar to coal, both of which can have a combined organic (RSH, R_2S_n, etc.) and inorganic (MS) sulfur content of 0-10% wt. depending on their source.

The depletion of coal and oil reserves of low sulfur content, as well as the recent economic changes in importation of low sulfur ("sweet") feedstocks, have made the use of high sulfur coals ($\geq$ 4% wt.) more attractive as hydrocarbon sources. This trend is expected to continue into the 22nd century until the development of non-conventional energy sources (nuclear, solar, etc.) can meet the demands of society, or until hydrocarbon resources are depleted.

Curtailment of atmospheric SO_x emissions from stationary sources requires the removal of reduced sulfur compounds from the fuel prior to combustion or the removal of SO_x from the post-combustion flue gas. If elemental sulfur is the desired end product, the latter option has several drawbacks:

1) dilution by N_2 from combustion air;
2) necessity of handling a hot gas stream;
3) reduction of $S^{4+} \rightarrow S^0$ (vs. oxidation $S^{2-} \rightarrow S^\circ$);
4) reduction cost vs. oxidation cost ($4e^-$ reduction vs. $2e^-$ oxidation); and,
5) ease of removal of SO_x vs. H_2S.

These points can be illustrated with the example of 1 mole % H_2S in CH_4. The usual clean combustion condition of 10% excess air is assumed.

Feed Gas (~ 25°C)			Flue Gas (~ 400°C)	
Compound	Mole %		Compound	Mole %
CH_4	99.0	110%	CO_2	8.29
H_2S	1.0	theoretical air $\longrightarrow$	H_2O	16.75
			N_2	73.07
			SO_2	0.17
			O_2	1.72

In addition to having a lower concentration of sulfur compounds due to dilution by air, a treatment carried out at the higher post combustion temperatures would require facilities to handle > 10 x the original gas volume. Most treatment schemes require that the entire gas volume be cooled to near STP for treatment and then be re-heated, at extra cost, to a temperature sufficient for good stack dispersal.

Since SO_2 is a much stronger acid than H_2S (pKa_1 = 1.8 vs. 7.0) and is much more soluble in water (therefore, less easily desorbed) removal of H_2S is operationally less difficult. In addition, a flue gas may contain appreciable amounts of SO_3 which remain in solution as sulfuric acid.

Once SO_2 is removed from the gas stream, it must be reacted chemically to produce a saleable or easily stockpiled product. One can, of course, oxidize further to produce sulfuric acid, ammonium sulfate (fertilizer) or calcium sulfate (gypsum), etc. with the inexpensive and readily available atmospheric oxygen. Given the rapidly increasing rate of sulfur recovery, the possibility of oversupply of oxidized forms of sulfur is quite real; the ability to produce the more easily stockpiled elemental sulfur may become a necessity. In our example, this would require the reduction of the removed SO_2 to the elemental form at a cost of four electrons per molecule. This requires a minimum of 1/2 CH_4 per SO_2 (or equivalent) and represents a further expense in hydrocarbon fuel.

It becomes apparent, then, that the preferred method of desulfurization in our example is the removal of H_2S prior to combustion with subsequent air oxidation to elemental sulfur. This route offers the flexibility of being able to produce (in a separate process) oxidized forms of sulfur and gives a cleaned fuel (which is also non-poisonous) better suited for transportation to off-site sale.

This distinction becomes less clear when the fuel is a heavy liquid or solid hydrocarbon. Existing goal gasification and solvent refining technologies produce the more easily removed H_2S. Hydrothermal leaching produces soluble sulfides which can be oxidized in a similar manner. All these approaches upgrade fuels with desulfurization prior to combustion.

Besides being a primary energy source in the ordinary sense (heat, electricity, vehicles, etc.), hydrocarbons fulfill what is perhaps a less glorified, but equally important role as the primary chemical reductant. All reducing chemical species of industrial importance are ultimately tracable to a hydrocarbon feedstock. The three most important reducing agents H_2, CO, C are all directly obtainable from hydrocarbon sources.

(1.) $H_xC_y \xrightarrow{\text{HEAT}} CH_4$ + lower hydrocarbons

(2) $CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2$

(3) $CO + H_2O \rightarrow CO_2 + H_2$

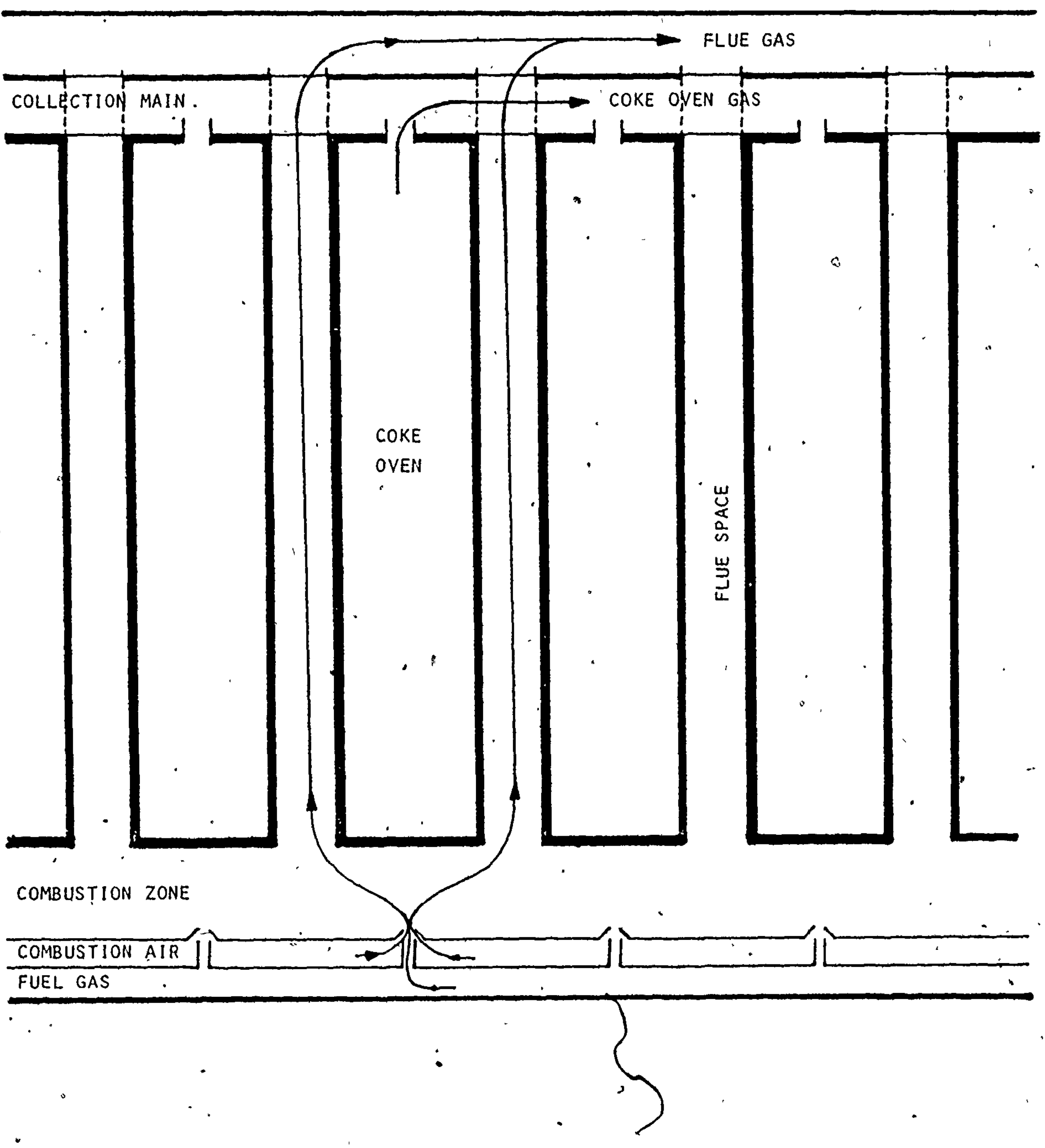
(4) $H_xC_y \xrightarrow{\text{HEAT}} C + H_2$ + lighter hydrocarbons

An example important to this thesis can be found in the steel industry where a coal hydrocarbon is destructively distilled (pyrolized) to give gases, volatile liquids and coke, the carbonaceous residue of the process. This residue is subsequently used in the blast furnace reduction of iron ore to iron (pig iron).

(5) $Fe_3O_4 + 3C \rightarrow 3Fe^\circ + 3CO_2$

Present-day coking operations utilize batteries of coking ovens that collect all the volatile constituents as well as produce coke. A diagram of a byproduct oven is given in Fig. 1. Each oven has the typical dimensions 1.5' x 10' x 30' and is charged with 15-20 tons of coal per coke. This charge is fired in the absence of air for 15-24 hrs

FIGURE 1. Byproduct Coke Oven


FLUE GAS
COLLECTION MAIN
COKE OVEN GAS
COKE OVEN
FLUE SPACE
COMBUSTION ZONE
COMBUSTION AIR
FUEL GAS

at temperatures of 800-1000°C. The coke production is ~ 70 wt % of the charge with the coke oven gas (COG) making up the remainder. The composition of this gas from any one oven changes with time and temperature, but since collection is made from > 100 ovens, each in different stages of coking, the gas from all ovens has a relatively constant composition. A medium sized coke plant may have a throughput of 500 tons/hr giving a gas output of ~ 3 Mscft/hr (~ 80 KNm^3).

The collected gas has an appreciable heat content and can be used for underfiring the coke ovens, general plant fuel or even town gas for general distribution. To facilitate these uses, the gas is treated to recover valuable byproducts and to remove chemical pollutants prior to use. A typical analysis of a COG is given in Table 1. A flow sheet of a byproducts plant is given in Fig. 2.

The focus of this thesis is on H_2S removal. As can be seen from Table 1, H_2S is a minor component of the gas with a typical concentration of ~ 8-20 grams/Nm^3, however, the scale of operation of this plant (50 KNm^3) (2 MMscft/hr) gives a sulfur output of 10-25 tonne/day. The largest existing plant handles ~ 350 KNm^3/hr of gas coming forward from 19 batteries and produces 70-100 tonne/day S^0.[1]

1.2 Desulfurization Methods

Ten years ago, no more than a handful of viable COG desulfurization schemes was available as options for choice. Today, this number has grown to 50 or so named processes vying for attention in the marketplace. After accounting for similar processes marketed by license under

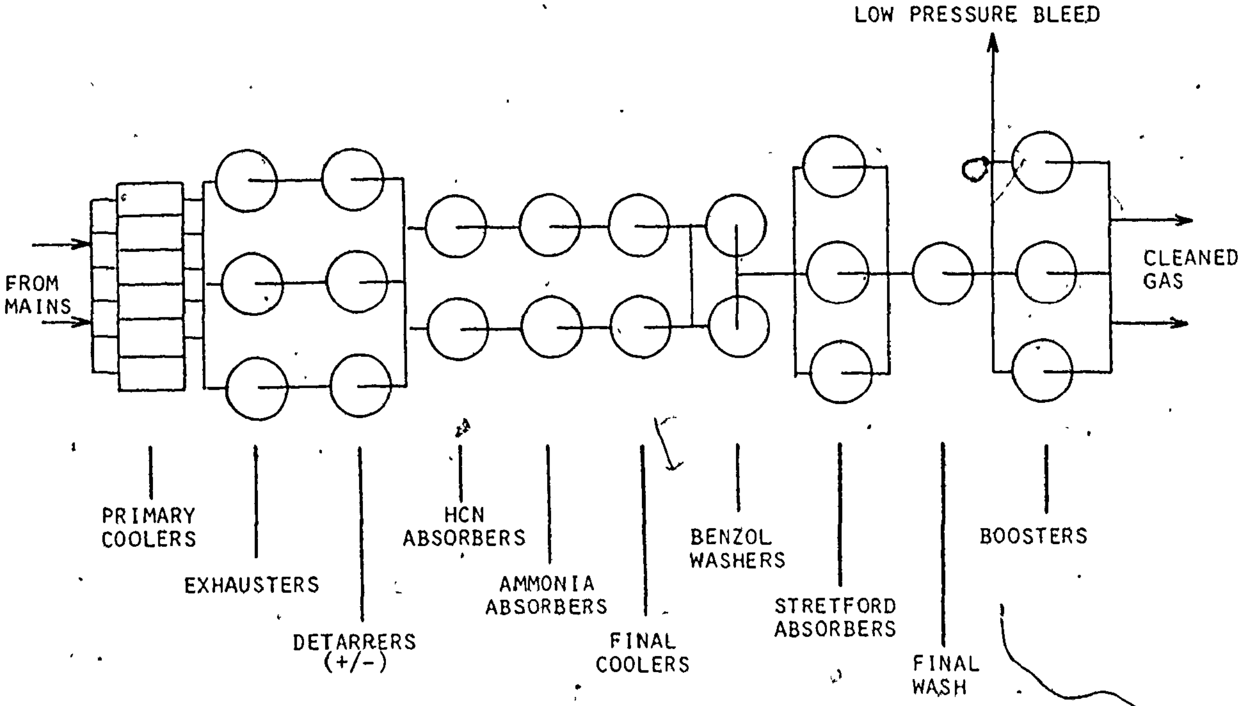
TABLE 1

COKE OVEN GAS COMPOSITION

1) HEAVY HYDROCARBONS	8 GAL/TON COAL	LIQUID/SOLID CONTAMINANTS
2) LIGHT HYDROCARBONS	3 GAL/TON COAL	
3) CH_4 +	40 %VOL	DESIRED GASEOUS PRODUCTS
4) H_2 & CO	30-45 %VOL	
5) NH_3	1-2%	GASEOUS CONTAMINANTS
6) HCN	1-2%	
7) H_2S	1-2%	
8) O_2 N_2 SO_x NO_x CO_2	$<$10 %VOL	
TOTAL GAS	6000 FT^3/TON COAL	

FIGURE 2. Coke Oven Byproducts Plant Flow Diagram from Plenderleith[40]

BYPRODUCTS PLANT FLOW DIAGRAM



different trade names and for "variations on a theme", the actual breadth of choice is roughly halved. No one technology seems to have come to the forefront, therefore, choice among processes has often been very dependent on local conditions rather than technological advantage. Site constraints, the salability of a process product, the ease of stockpiling for a cyclic demand, or the ease of disposal of a process byproduct may become the overriding influence in the decision. For example, ammonia is used as a fertilizer feedstock when produced in North America but is incinerated in the U.K.. Ease of stockpile becomes an important consideration in markets which face a possible long term surplus in sulfur and sulfuracids as high sulfur coals make up larger fractions of energy feedstocks.

One goal of this thesis is the categorization of currently available and some potential sour gas sweetening processes according to their fundamental chemistry. On this basis, the individual processes are grouped into five named categories:

1. Absorption/regeneration
2. Gas Phase Conversion to sulfur
3. Tail gas cleanup
4. Liquid Redox (Solution Redox)
5. Liquid Claus (Solution Claus)

Processes, or a given process within any category may not constitute a complete desulfurization scheme. For example, an alkanolamine plant (category 1) yields cleaned gas and an enriched H_2S gas stream. It, therefore, may require a Claus unit (category 2) and a tail gas cleanup (category 3) before the scheme is considered complete. This interdependence will be diagrammatically represented in the following manner.

$$\text{COG} \Longrightarrow \overset{\text{CG}}{\textcircled{1}} \Longrightarrow \textcircled{2} \Longrightarrow \textcircled{3} \qquad \text{CG=cleaned gas}$$

These, along with a general overview of the characteristics mutually shared by the separate processes within a category, are presented in an introductory statement. A series of individual process descriptions are listed in Appendix II.

1.2.1 Absorption/Regeneration

Absorption/regeneration (A/R) processes are those that absorb acid gases from a sour gas into a circulating liquid with subsequent desorption (regeneration of the liquor) at a higher temperature and/or lower pressure. The overhead gas from the regeneration step is an enriched acid gas stream suitable for feed to a Claus or sulfuric acid plant or, in some instances, to a liquid redox plant.

Within this category, processes are characterized by either physical or chemical absorption process depending on the nature of the interaction of the absorbed gas molecules with the solvent. Physical absorption processes are those in which no formal chemical reactions occur and the solubility of the gas is a function of partial pressure and temperature. They have obvious advantages in high pressure applications (i.e., sour natural gas wells at several hundred psig). Intermediate pressure flashes can provide acid gas removal, some hydrocarbon separation and, occasionally, process power from onstream expansion turbines. They are, for equally obvious reasons, not of great use in low pressure COG applications. A graph of gas loading vs. partial pressure for some model systems is given in Appendix II, Fig. 5.

At low pressures, Chemical A/R systems have a much higher equilibrium loading almost independent of pressure until such time as the solvent or solvent buffer becomes neutralized. At this point, the system then approximates the physical absorption characteristics of the solvent alone. For the most part, CA/R solvent systems are aqueous nitrogenous bases (NH_3, alkanolamine) or aqueous carbonate solutions. Some systems utilize a specialty solvent ($\overline{CH_2CH_2CH_2CH_2S}O_2$ or CH_3OH) with an alkanolamine base to give a combination physical and chemical absorbent.

The predominant reactions occurring in solution are of the acid/base type, but this does not preclude the possible use of some other reversible process. An example of this might be the "extra equilibrium" step of CO_2 in alkanolamines to give carbamic acids in solution. Arguments of this type have been proposed to account for the "anomalous" H_2S solubility in some specialty solvents, for example in molten sulfur by reaction (6)

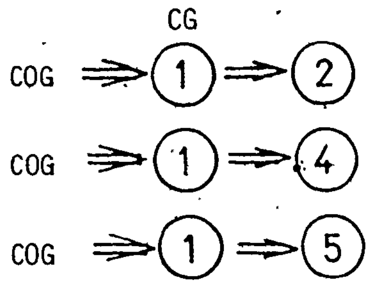
$$(6)\quad H_2S + nS_{8Liq} \rightleftharpoons HS_xH_{Liq}$$

This process is the cause of some concern when it occurs in a liquid sulfur product but is used to advantage for H_2S removal with liquid sulfur based oxidative processes.

The selectivity of an A/R process is, in part, a function of absorption/desorption parameters and the rate and extent of reactions which occur in solution (see also liquid redox). By manipulation of these variables either H_2S or CO_2 may be absorbed in higher relative ratios. Although useful for some applications, the same reactions illustrate the limiting factors in the use of some systems. For example, carbonate based systems require a substantial loading of CO_2 in order to get satisfactory desorption of H_2S. Without a CO_2 input, the pH will tend to higher values through a gradual net desorption of CO_2. Eventually, the solution would be sulfide based rather than carbonate based. The same reactions which limit its use to CO_2 containing gases give carbonate processes a high loading capacity of CO_2 relative to H_2S.

The ability to optimize over a wide range of gas compositions is not usually considered an important factor in COG desulfurization since gas composition is constant relative to the differences observed between sources in hydrocarbon or natural gas industries. A more important consideration is one of byproduct formation from reaction in solution with HCN, NH_3, COS, CS_2, O_2 and other trace contaminants in the gas. Heat degradation in regenerators and corrosion from hot off gases may become more severe in the presence of these contaminants. Systems commonly have some provisions for blowdown and/or regeneration of solution. The rate of oxidative byproduct formation (SCN^-, $S_2O_3^=$, $SO_4^=$) is dependent on the H_2S loading and O_2 content of the COG.

COG Desulfurization Package



1.2.2 Gas Phase Conversion

Gas phase conversion processes may be grouped using end products as the distinguishing feature, i.e., processes based on S and H_2O (Claus kiln, iron oxide, etc.), on H_2 and S (disproportionation) and on H_2SO_4. The latter will not be considered in this paper and can best be approached from the H_2SO_4 trade literature. Processes can be further distinguished on the basis of being designed for Claus tail gas cleanup (i.e., on the basis of total throughput). As the total amount of H_2S to be treated increases, gas phase (and therefore Claus) processes become more advantageous. The mechanical work required to run any of the other processes becomes so large as to preclude their use. (Claus plants exist with sulfur tail gas outputs greater than the average coke oven battery.)

Gas phase conversion processes may require an enriched H_2S feed and, thus, usually follow an absorption/regeneration process unit. Those that do not (i.e., iron oxide) invariably have been associated with low loading applications. As the H_2S feed decreases, the cost of a total package (i.e., ①②③) becomes competitive with other methods such as liquid redox. The output range of 5-1500 tons/day S° is given as the typical Claus kiln range; coking operations fall near the low end of this range.

The overall reaction (7) can be considered as the sum of two different schemes (A,B).

$$(7)\quad H_2S + 1/2\ O_2 \rightleftharpoons H_2O + S \qquad \Delta H^\circ_R = -63\ \text{kcal/mole}$$

$$\text{A)}\quad H_2S + 3/2\ O_2 \rightleftharpoons SO_2 + H_2O \qquad \Delta H^\circ_R = -77.5$$

$$\underline{2H_2S + SO_2 \rightleftharpoons 3S + 2H_2O \qquad \Delta H^\circ_R = -112}$$

$$3H_2S + 3/2\ O_2 \rightleftharpoons 3S + 3H_2O \qquad \Delta H^\circ_R = -189.5/3\ \text{moles sulfur}$$

or

(7) $H_2S + 1/2\ O_2 \rightleftharpoons S + H_2O$ $\Delta H^\circ_R = -63$ kcal/mole sulfur

B) $H_2S\ (\text{heat}) \rightleftharpoons H_2 + S^0$ $\Delta H^\circ_R = +5$ kcal

$H_2 + 1/2\ O_2 \rightleftharpoons H_2O$ $\Delta H^\circ_R = -68$ kcal

(7) $H_2S + 1/2\ O_2 \rightleftharpoons S^\circ + H_2O$ $\Delta H^\circ_R = -63$ kcal/mole S°

Scheme A is easily recognizable as the Claus sequence. Note that it is exothermic in both steps at STP. The excess heat appears as excess process heat. Scheme B illustrates the potential use of H_2S as a source of H_2. If the thermal decomposition of H_2S could be made to occur at a reasonable temperature, a fraction of H_2 produced could be oxidized to provide the necessary process heat giving a net hydrogen credit.

1.2.3 Tail Gas Cleanup

Optimization with respect to sulfur product recovery in the Claus kiln unit usually results in parallel increases in the levels of COS and CS_2 in the tail gases (5000 ppm or greater). Attempted reduction of these levels to values below 500 ppm usually increases the H_2S and SO_2 levels in the tail gases (ca. 5% of feed). Thus, successful treatment of the tail gas requires the removal of COS, CS_2, H_2S and SO_2 from a hot gas stream.

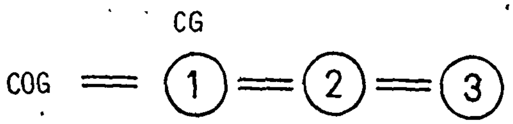
Over the years, several approaches have been taken:

- selective removal;
- total oxidation to SO_2 with subsequent recycle or S° production;
- total reduction to H_2S with subsequent recycle or S° production;

- completion of the Claus reaction at lower temperatures than those possible in the main unit.

Representative processes of each of these approaches are presented in Appendix II.

COG Desulfurization Package



1.2.4 Liquid Redox

Liquid redox processes are those that combine together in one solution, the absorption and subsequent air oxidation of H_2S to elemental sulfur. Chemically each is based on the overall reaction (7),

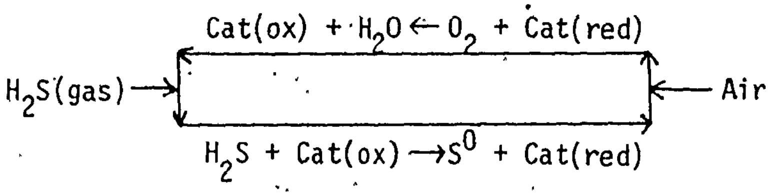
$$(7)\quad H_2S + 1/2\ O_2 \rightleftharpoons S^0 + H_2O \qquad \text{(slow)}$$

Each liquid redox solution contains a catalyst which increases the rate of reaction by providing a kinetically labile pathway for it.

$$(8)\quad H_2S(aq) + \text{Catalyst(ox)} \rightleftharpoons S^0 + \text{Catalyst}(H_2\ \text{red}) \qquad \text{(fast)}$$

$$(9)\quad 1/2\ O_2 + \text{Catalyst}(H_2\ \text{red}) \rightleftharpoons H_2O + \text{Catalyst(ox)} \qquad \text{(fast)}$$

These two reactions are usually separated in time and space; consequently the equipment list for a process plant generally includes an absorber, a reaction tank (reaction (8)), a regenerator (reaction (9)), and sulfur product handling facilities. The process can be illustrated as:



Some details of the chemistry of each step of a liquid redox process are described below.

ABSORPTION: The important solution factors which affect the extent of H_2S absorption from a gas stream are; the solubility of H_2S in the process liquor, the amount of base present in solution available for the neutralization reaction (buffer capacity), the solubility of the salt produced in the neutralization reaction and the process liquor pH over which operation is practical.

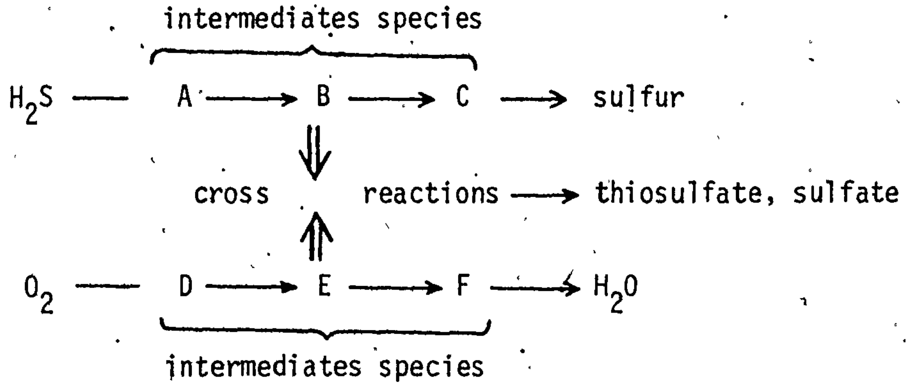
The solubilities of NaHS and NH_4HS are each greater than 1000 gm/liter - several orders of magnitude above usual process design loadings of 250-1000 ppm - and pose no real limitations in practice.

The effect of pH on the relative concentrations in solution of $H_2S/HS^-/S^=$ is given in App. II, Fig. 1. The aqueous solubility of H_2S is about 4 gm/l (0.1 M) at 100 % H_2S(STP) and the Henry's law constant is 5.45×10^4. Thus, pH 7-8 seems to be a practical lower limit since the concentration of H_2S(aq) is reduced to a small fractional amount of the solution loading so that its solubility is not exceeded. The upper value of the range is often controlled by corrosion rates, with pH 11 a practical limit. The base selected for solution makeup and its concentration range are determined by these practical pH limits.

The buffer capacity (β) curves for two common scrubbing solutions are shown in Appendix II. Each is much more than adequate for the task of maintaining the solution pH in that range at normal loadings. This minimizes H_2S slip from the absorber and, in addition, allows liquid redox process plants to be very forgiving with respect to wide fluctuations in H_2S loadings and to temporary overloadings.

REDOX REACTIONS: The design loading of some solution redox processes is limited by the amount of catalyst available in solution for S° production. This usually arises from a desire to separate the sulfide oxidation reactions from the oxygen reduction reactions.

Each of these reaction pathways is thought to be comprised of a series of rather complex reactions that involve reactive intermediates such as peroxide and peroxy, hydroperoxy, hydroxyl, hydrosulfide and polysulfide radicals. They can be visualized as diagramed below. Oxidative byproducts (thiosulfate, sulfate) arise primarily from cross reactions of the intermediates.



Separation of these reactions in time and space minimizes the extent of byproduct formation. Therefore, the design H_2S loading is such that the sulfur oxidation catalyst can convert it to polysulfide and sulfur before the air injection step. Excess of H_2S over design loadings could contribute to cross reactions by allowing unreacted HS^- to be carried to the oxidation portion of the plant. Fixation rates under overload conditions of greater than 5 times normal have been observed. The oxidation byproducts are nonvolatile salts that collect in solution. Their concentrations must be controlled by blowdown and/or dilution. Solution recovery technologies are currently becoming available for handling these effluent streams.

Some liquid redox processes employ two separate catalysts, one tailored specifically for the oxidation of H_2O to sulfur and the second for the reduction of oxygen, while others rely on one catalyst to carry out both functions. The catalysts may be metal ion redox couples (V^5/V^4, Fe^2/Fe^3, As^3/As^5) or organic redox couples (hydroquinone/quinone) or combinations of both. In the latter case, the metal ion redox couple is active primarily in the oxidation of H_2S while the organic couple facilitates the reactions of oxygen.

In all cases, sulfur product formation is via polysulfide chain buildup. This is illustrated by reactions 10, 11 and 12.

(10) $2H_2S + \text{Catalyst(ox)} \rightleftharpoons HSSH + \text{Catalyst(red)}$

(11) $2HSSH + \text{Catalyst(ox)} \rightleftharpoons HSSSSH + \text{Catalyst(red)}$

(12) $2H_2S_x + \text{Catalyst(ox)} \rightleftharpoons H_2S_{(2x)} + \text{Catalyst(red)}$

Note that the sulfide ion in H_2S must react twice with the catalyst to go from oxidation state -2 to -1 to 0. The terminal sulfur atoms in a polysulfide chain (HSS_xSH) are in a -1 formal oxidation state while the other polysulfide sulfur atoms are in a zero formal oxidation state. Sulfur product formation occurs by elimination of an S_8 ring from linear polysulfide chains with x values > 9 - no redox reaction is involved at this point in the reaction sequence (reaction 13). A more complete discussion of the nature of polysulfides is found in chapter 3,

(13) $H_2S_{2x} \rightleftharpoons S_8 + H_2S_{2x-8}$

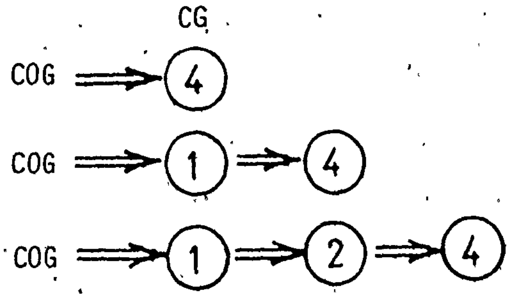
Any solution process that completes with, interrupts or prevents polysulfide chain production will block the formation of sulfur product by keeping the average chain length small. For example, reaction with CN^- or $SO_3^=$ will decrease the chain length by one sulfur atom.

(14) $HS_xH + CN^- \rightleftharpoons HS_{x-1} + SCN^-$

(15) $HS_xH + SO_3^= \rightleftharpoons HS_{x-1}H + S_2O_3^=$

When the average polysulfide chain length falls below 4-5, the concentration of those species in solution with x values > 9 is too low for sulfur product formation. Excess amounts of H_2S or HS^- in solution beyond the total oxidative capacity leads to large numbers of short chains. For example, a process plant liquor overloaded by 500 ppm (equilibrium conditions) could have dissolved elemental sulfur levels up to 2,500 ppm as polysulfides.

COG Desulfurization Package



1.2.5 Liquid Claus

Processes that combine together in one solution the absorption and subsequent conversion of H_2S and SO_2 to elemental sulfur and water are classified as liquid Claus processes. Chemically, each is based on the overall reaction (16)

$$(16) \qquad 2H_2S + SO_2 \rightleftharpoons 3S^\circ + 2H_2O$$

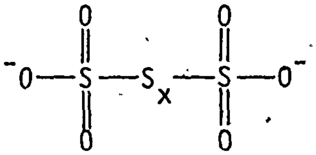
Usually the source of SO_2 is a flue gas, a smelter off gas or pre-incinerated Claus tail gas, H_2S can be indigenous to the plant as in the case of coke oven operations, or can be produced on site from hydrocarbons and sulfur product. The chemistry of the liquid claus process is rather complex but an attempt will be made to illustrate some of the important features of it in the discussion that follows.

ABSORPTION: SO_2 is only slightly soluble in water. Some of that which dissolves reacts with water establishing the equilibrium shown as equation (17).

$$(17) \qquad SO_{2(aq)} + H_2O \rightleftharpoons H_2SO_{3(aq)} \rightleftharpoons HSO_3^- + H^+$$

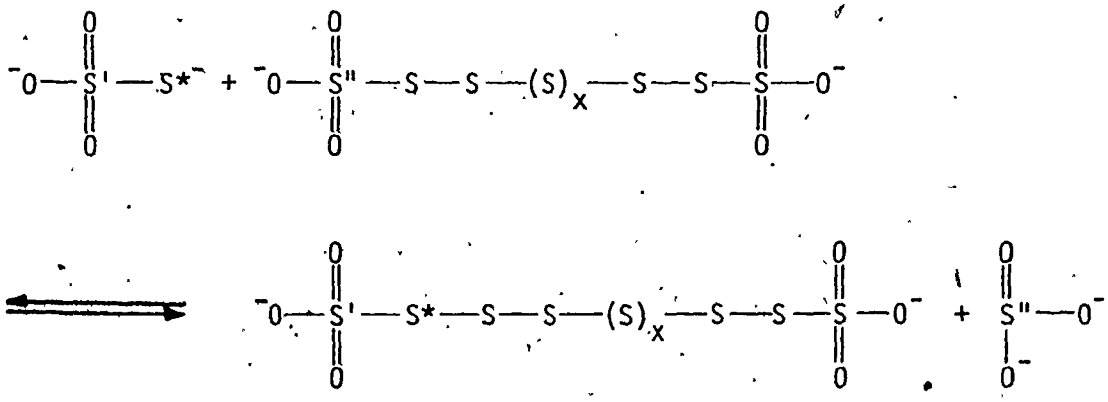
As the pH increases above the pKa, of H_2SO_3 (1.8) a smaller fraction of the total absorber SO_2 is in the $SO_{2(aq)}$ form. Therefore, the apparent solubility can be increased by effecting the removal of H^+ from solution by addition of pH buffers. Fig. 3,4, Appendix II show the ionization diagrams for two buffer systems currently in use (citrate, phosphate). Because the buffer capacity of the desorbing solution is greater than that required for design SO_2 loading liquid Claus processes are rather forgiving of fluctuations in SO_2 levels in the feed and of temporary overloadings.

REACTION: In the reaction vessel H_2S is brought into contact with the SO_2 rich buffer solution. The reaction sequence is extremely complex, is not well understood (i.e., Wackenroder's solution), and ultimately leads to the formation of product sulfur, H_2O and some sulfate byproduct. (Because of the low solubility of H_2S in acidic solutions, arrangement must be made for sufficient H_2S to be absorbed, i.e., closed H_2S recycle). In aqueous solution sulfur chain buildup is through polythionate intermediates. These have the structure shown below and are analogous to the polysulfide intermediates present in basic solution.



$$^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S_x-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{-} \quad \text{or} \quad S_xS_2O_6^{2-} \qquad x = 0,1,2,\ldots,N$$

As with polysulfides, product sulfur (S_8 rings) will only form from those intermediates with $x > 8$. Therefore, the average x value, taken over all polythionate species in solution, must be greater than 4-7 so that a reasonable fraction of them will be large enough for product formation. Perhaps the best way to conceptualize the chemistry is through the reaction of thiosulfate and polythionate to give a higher polythionate.



$$^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S'}}-S^{*-} + {}^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S''}}-S-S-(S)_x-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{-}$$

$$\rightleftharpoons\ {}^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S'}}-S^{*}-S-S-(S)_x-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{-} + \overset{\overset{O}{\|}}{\underset{\underset{O^{-}}{|}}{S''}}-O^{-}$$

(*,",', ≡ labels)

Sulfur product formation then occurs by elimination of an S_8 ring. The step is an equilibrium process and does not involve an oxidation or reduction of sulfur. The collected sulfur is expected to be rhombic or monoclinic crystals of S_8 rings.

$$(18) \quad SO_3^- \text{-} S \text{-} S_y \text{-} S \text{-} SO_3^- \rightleftharpoons SO_3^- \text{-} S \text{-} S_{(y-8)} \text{-} S \text{-} SO_3^- + S_8$$

Any solution component that competes with or blocks the chain building process would inhibit the production of sulfur. Cyanide reacts to form SCN^- in a manner analogous to that of Liquid Redox solutions.

$$(19) \quad S_2S_xO_6^{2-} + CN^- \rightleftharpoons S_2S_{x-1}O_6^{2-} + SCN^-$$

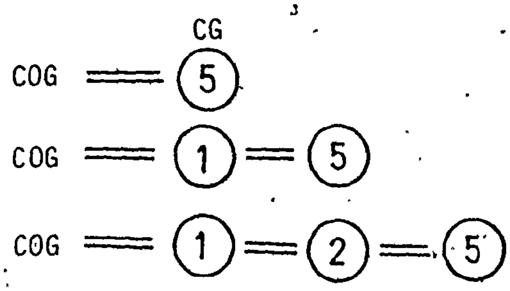
or

$$(20) \quad S_2O_3^{2-} + CN^- \rightleftharpoons SCN^- + SO_3^-$$

The least understood chemistry is the initial redox reaction which produces thiosulfate or some other intermediate capable of the chain building process with polythionates. Balanced redox reactions such as (21) give the overall stoichiometry but do little to explain the actual reactions in solution. Unfortunately there is little to replace them.

$$(21) \quad 2H_2S + 4SO_2 + H_2O \rightleftharpoons 3H_2S_2O_3$$

<u>COG Desulfurization Package</u>



1.3 The History of the Stretford Process

The iron oxide or "iron box" process was the first chemical desulfurization system. It originated in England in the mid-19th century and still has some specialty applications today. The process consists of loosely packed beds of supported ferric oxide through which the sour gas was passed (reacting any H_2S in the gas to form ferric sulfide). The bed was regenerated with an air flow by reaction (23).

$$(22)\quad 2Fe_2O_3 + 6H_2S \rightarrow 2Fe_2S_3 + 6H_2O$$

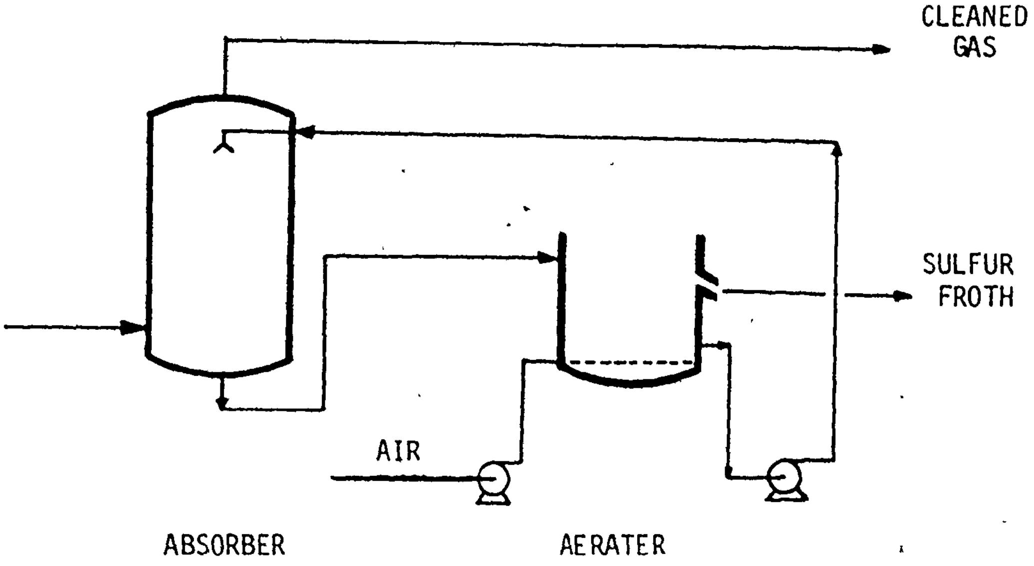
$$(23)\quad 2Fe_2S_3 + 3O_2 \rightarrow Fe_2O_3 + 6S^\circ$$

This method had some very serious limitations.

1) A large bed volume was required. With the low pressure of COG this required a very large surface area.
2) Contaminants in COG made the bed life short necessitating frequent changes.
3) The recovered sulfur was severely contaminated and had little or no commercial value.
4) There were severe handling problems associated with cleaning the boxes, not the least of which was opposition by labour to what was considered the dirtiest job in the industry.

The Ferrox and Manchester processes are natural extensions of the iron-box approach. They consist of an aqueous suspension of iron oxide which is used as a circulating scrubbing solution. The solution is pumped to the top of an absorbing tower (Fig. 3) where it is contacted with the sour gas allowing reaction 22 to proceed. Spent solu-

FIG. 3 Schematic Flow Diagram of the Ferrox Process



tion from the bottom of the tower is contacted with oxygen in the aerater/flotator producing iron oxide and sulfur and thusly regenerates the solution. This arrangement worked extremely well giving < 1 ppm H_2S in the cleaned gas, but it also had serious limitations:

1) operational problems associated with handling a slurry;
2) adverse effects of CN^- on iron/sulfur chemistry;
3) contamination of S° with frothed iron suspension; and,
4) high thiosulfate byproduct formation rate.

The first three problems were eliminated with the advent (ca. 1950) of the original Stretford A.D.A. process. It utilized a 10% quinone solution for the absorption of H_2S and subsequent oxidation of sulfide to sulfur. The flow diagram of a Stretford A.D.A. plant is essentially the same as the Holmes-Stretford plant shown in Appendix II.

In Stretford, the quinone used is anthraquinone-2,7-disulfonic acid (ADA) however other quinones of suitable redox potential and chemical stability can be used (i.e., sulfonated naphthaquinone in the TAKAHAX process). The reaction between H_2S and ADA is slow and does not appear to go to completion. At the plant operating pH of 9, approximately 30% of all sulfide that entered the oxidizer after ~ 30 min in the delay tank appeared as sodium thiosulfate.[2] Over the years several attempts were made to improve the performance of quinone plants by modification of the basic chemistry. The most significant of these was the addition of trace amounts of metal ion catalysts of which vanadium (Stretford), iron (Locat, Cataban) and arsenic (Grammarco-Vetrocoke) were the most successful and form the basis of commercially important processes of this type today.

With the Holmes-Stretford process, a gradual evolution of relative concentrations of metal ion and quinone took place as it was discovered that the metal ion/sulfide reactions went to completion in a short period of time compared to the quinone alone. It became standard practice to use an equinormal metal ion/design sulfide solution. The quinone is then considered to be an oxygen activator or oxygen carrier which facilitates the air oxidation of the metal ion. With this view, it is usual to adjust the concentration of the activator such that the process is mass transfer controlled in the oxidizer (i.e., the reaction proceeds as fast as oxygen diffuses into solution and the steady state concentration of O_2 in the oxidizer is near to zero). In a batch process then, the time for oxidation of a reduced solution is proportional to the original loading of H_2S. In continuous flow conditions, the system approximates steady state with fluctuations in chemical and operational parameters (i.e., concentrations and flow rates) as perturbations.

The standard chemical composition of a Holmes-Stretford solution is given in Table 2. Physical plant data of an existing installation (Fig. 4) is given in Appendix I. The chemistry of this solution is most often visualized as a series of elegantly coupled one electron redox reactions (Appendix II, page 30) reminiscent of a biological pathway. It is known, however, that the actual reactions occurring in solution are more complex than this and could be radical chain processes.

1.4 Justificatication for this Work

The Stretford Process as it exists today is the latest in a continuing series of chemical desulfurization processes that have evolved from the iron box technology. The improvements made in the past have come more from empirical optimization than from knowledge of the detailed chemistry. This work is centred about the fundamental process chemistry of vanadium, present in the liquor as a redox catalyst, in the hope that the knowledge gained can be applied in the evolutionary process.

27 Aug

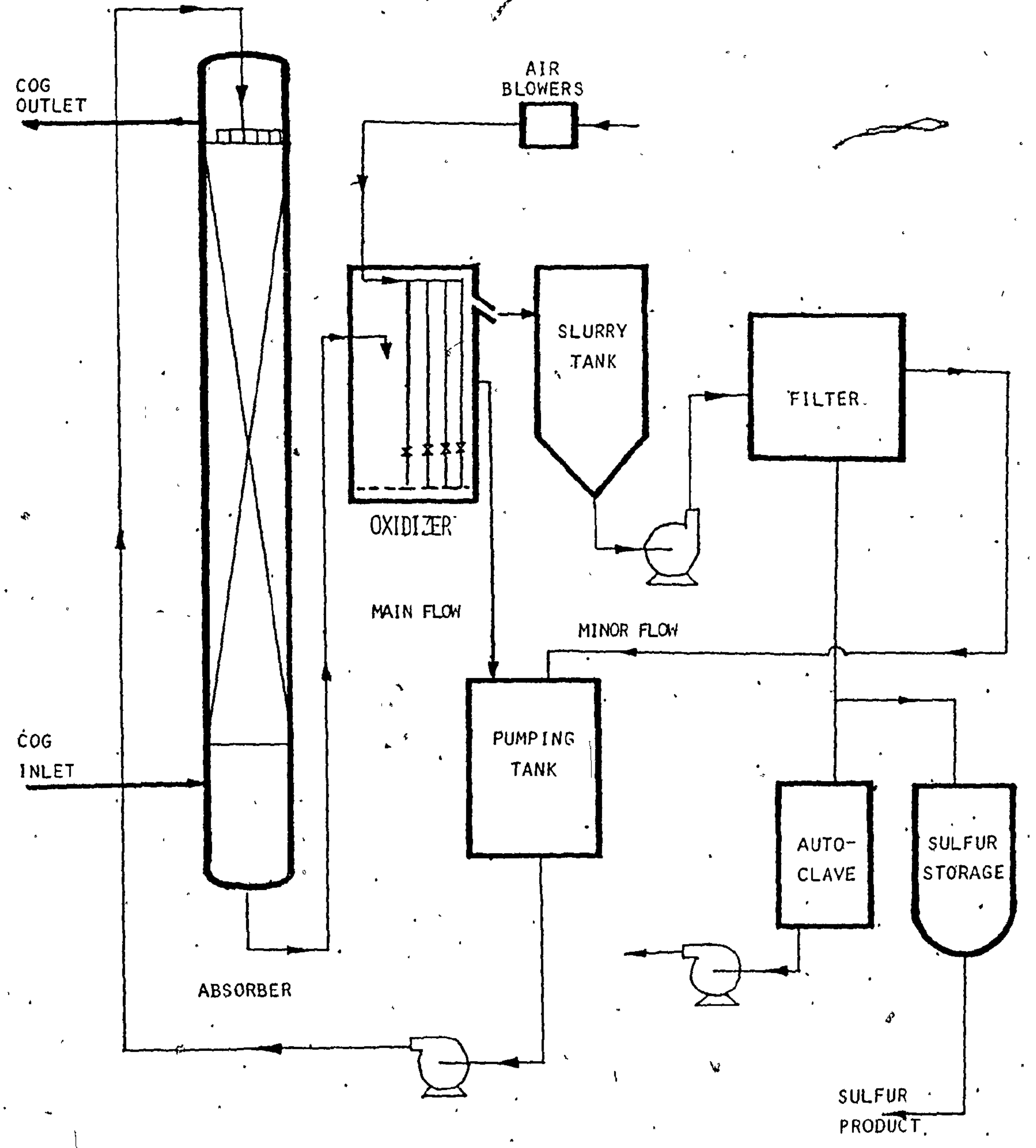
TABLE 2

STRETFORD LIQUOR COMPOSITION

1)	ANTHRAQUINONE DISULFONIC ACID	3 GM/L 7.3×10^{-3} M	AS SODIUM SALT
2)	SODIUM VANADATE	1.7 GM/L 3.25×10^{-2} M	AS VANADIUM
3)	TRI-SODIUM CITRATE	10 GM/L 3.6×10^{-2} M	10% MOLAR EXCESS OVER V
4)	SODIUM CARBONATE	25 GM/L $\sim 2.5 \times 10^{-1}$ M	pH = 9 ± ?
5)	$Na_2S_2O_3$		
6)	NaSCN	<500 GM/L	
7)	Na_2SO_4		

7

FIGURE 4. Holmes-Stretford Process Flow Diagram from Plenderleith[40]


COG OUTLET
AIR BLOWERS
SLURRY TANK
FILTER
OXIDIZER
MAIN FLOW
MINOR FLOW
COG INLET
PUMPING TANK
AUTO-CLAVE
SULFUR STORAGE
ABSORBER
SULFUR PRODUCT

CHAPTER 2

STUDIES ON THE VANADIUM CHEMISTRY OF THE HOLMES-STRETFORD PROCESS

2.1 Introduction

Aqueous solutions of vanadium have been extensively studied both to characterize the species present and to determine the equilibrium relationships among them. The study is by no means complete having been hampered by:

1) the instability of the species formed;
2) the complexity and pH dependence of the equilibria;
3) the ease of air oxidation of vanadium +4; and,
4) the slow approach to equilibrium between vanadium species.

Additionally, the results of these studies cannot be taken as a description of vanadium chemistry in Stretford solutions for several reasons.

1) Stretford liquor contains from 30-500 gm/l of dissolved ionic compounds as well as slightly soluble organics which are present in the COG. By comparison, the systems reported in the literature were prepared from analytical reagents with strict control of solution composition.
2) At any one time in a Stretford solution there may exist a high concentration of species capable of direct complexation with vanadium. These include CN^-, SCN^-, $CO_3^=/HCO_3^-$, citrate and $H_2S/HS^-/S^=$ as well as oxygen, nitrogen or sulfur containing

organics that may be carried forward from upstream treatment.

3) Vanadium 4+ and 5+ species present together in aqueous solution in the pH range 4-10 are known to interact. The impact of this on Stretford solutions is, at present, unknown.
4) The pH of a Stretford plant fluctuates with gas flow and composition, and with solution buffer strength.
5) The temperature of Stretford liquors varies seasonally. Heating or cooling may be required in extreme cold or hot environs.

2.1.1 The Chemistry of Oxovanadium 4+

Most of the aqueous solution chemistry of vanadium +4 is dominated by the presence of the strong V=O bond in VO^{2+}. This vanadyl unit remains intact even in primary sphere ligand exchange reactions and in V^{4+}/V^{5+} redox reactions.[3] Additionally, the ion has available 4 or 5 other coordination sites to give distorted square pyrimidal or octahedral structures. The H_2O molecule trans to the VO bond in $VO(H_2O)_5$ has a somewhat longer bond length[4] indicating a possible trans effect,[5] and a weaker ligand interaction at this site. The ion is usually quoted therefore as having pseudo C_{4v} symmetry.[6]

Ducret,[7] on the basis of pH titrations, assumed two hydrolysed derivatives of VO^{2+} formed in solution, $-VO(OH)^+$ and the insoluble $VO(OH)_2$. He estimated the pK for reaction (24) to be 4.8, and the solubility product, S, of the hydroxide to be $\sim 10^{-22}$.

$$(24)\quad VO(OH)^+ + H^+ \rightleftharpoons VO^{++} + H_2O \qquad pK = 4.8$$

$$(25)\quad VO^{++} + 2OH^- \rightleftharpoons VO(OH)_2\downarrow \qquad S = [VO^{++}][OH^-] \approx 10^{-22}$$

Later Rossetti and Rossetti[28] suggested the existence of an additional aqueous ion - $(VO)_2(OH)_2^{++}$ - an isopolyanion whose equilibria is described by equations 26 and 27.

$$(26)\quad VO(OH)^+ + H^+ \rightleftharpoons VO^{++} + H_2O \qquad pK = 6.0$$

$$(27)\quad (VO)_2(OH)_2^{++} + 2H^+ \rightleftharpoons 2VO^{++} + 2H_2O \qquad pK = 6.9$$

The precipitation of the hydroxide was observed to occur, as in the experiments reported by Ducret,[7] upon the addition of approximately 1:1 equivalents of base to VO^{++}.

The marked decrease in ESR signal intensity observed by Francavella and Chasteen[8] over the pH range 4.5-5.0 was interpreted to confirm the existence of two hydroxides $[VO(OH)]_2^{+2}$ and the insoluble $[VO(OH)_2]$. Each of these is ESR silent because of weak V-V interactions in the polynuclear structures. The values of pK_1 and S for reactions 24 and 25 were confirmed.

The amphoteric hydroxide $VO(OH)_2$ $[V_2O_4 \cdot 2H_2O]$ dissolves very slowly in excess base giving a light orange/brown supernatant liquid.[7,9] Also, addition of VO^{2+} to excess base gives a clear orange/brown solution which Iannuzzi ascribes to mononuclear $VO(OH)_3^-$. The 8-line spectra of this solution at pH > 12 is very similar in both line splitting and intensity to that of acidic VO^{2+} of the same concentration. This indicates that at pH > 12 polynuclear vanadium 4+ species can comprise only a small fraction of the total vanadium present in solution.

The acid titration curve of $VO(OH)_3^-$ in excess base exhibits an endpoint 1/2 equivalent prior to the precipitation of $VO(OH)_2$. This is explained by the formation of $V_4O_9^=$ and/or $V_2O_5^=$ ions by either reaction

28 or 29.

$$(28)\quad 4VO(OH)_3^- + 2H^+ \rightleftharpoons V_4O_9^= + 7H_2O$$

$$(29)\quad 4VO(OH)_2 + 2OH^- \rightleftharpoons V_4O_9^= + 5H_2O$$

In a similar titration, Ostrowetsky[10] observed a "light precipitate" at a point corresponding to $VO(OH)_2$ and then a clear solution by one equivalent later, at a point corresponding to $VO(OH)^+$.

Polarographic evidence[11] suggests that only two isopolyanions - $V_2O_5^=$, $V_4O_9^=$ - are of importance in the presence of such noncomplexing ligands as $SO_4^=$, Cl^-, F^-. The individual waves which Lingane associated with each of these species in ∿ 0.03 N KOH solutions collapsed into one in a carbonate buffer of pH < 0.03 N KOH. This single wave was attributed to the $V_2O_5^=$ ion. Ostrowetsky[10] points out that the system exhibits a double wave at pH 11 in ammoniacal buffer which collapses into one by pH 9.7. He also found that Lingane's use of sulfite as an oxygen scavenger was unacceptable as "being able to upset the results". Lingane[12] himself pointed out that "the stabilizing effect of sulfite ion [on vanadium solutions] is peculiar and warrants further investigation". In a later paper, Lingane[13] demonstrated complexation of V^{4+} by thiocyanate, citrate, tartrate, borate and phosphate, and non-complexation by sulfate, fluoride, chloride, and pyrophosphate. Pecsok and Juvet[14] demonstrated strong complexation by EDTA up to pH 12.

Although not conclusive, these studies do have application to the understanding of Stretford chemistry. The most noteworthy results are:

1) weak but rapid interaction of carbonate with the main vanadium species present in intermediate pH ranges;
2) sluggish attainment of equilibria between V^{4+} anions;
3) complexation of V^{4+} by EDTA, tartrate, citrate, oxalate and carbonate in basic solution, with diffusion currents and pH titrations indicating the relative strengths to be EDTA ∿ tartrate >> citrate > oxalate > carbonate; and,
4) equilibria between V^{4+} polyanions as a function of pH with large changes in relative ratios of species over narrow pH ranges.

2.1.2 The Chemistry of Oxovanadium 5+

Vanadium 5+ is capable of condensation to form polynuclear anions (isopolyvanadates) and exhibits this behaviour to a greater extent than does V 4+. Three general reaction types are involved:

1) fast protonation or hydrolysis reactions, i.e., $H^+ + VO_3^- \rightleftharpoons HVO_3$;
2) slow polymerization reactions, i.e., $3VO_3^- \rightleftharpoons V_3O_9^=$; and,
3) slow condensation reactions, i.e., $2HVO_4^= \rightleftharpoons V_2O_7^= + H_2O$.

Cotton and Wilkinson[15] warn that the degree of hydration of species cannot be implicitly stated, and therefore species such as $HVO_4^=$ are equivalent to $VO_3(OH)^=$, $VO_2(OH)_3^=$ and $VO_2(OH)_3^= \cdot H_2O$, for example. They also note the now standard warning against equating crystallographic structures with structures of species in solution.

In a series of fast acid titrations of cold alkaline pyrovanadate

($VO_4^{\equiv}$) solutions, Ducret[7] obtained reproducible endpoints at 1, 2 and 2.5 equivalents. The solution remains colourless until after the addition of the second equivalent. The result is consistent with the following scheme:

$$2VO_4^{\equiv} \xrightleftharpoons{2H^+} 2HVO_4^{=} \xrightleftharpoons{2H^+} 2H_2VO_4^- \xrightleftharpoons{1H^+} H_3V_2O_7^- + H_2O$$

Based on arguments of the usually slow condensation rates and the termolecularity of $V_3O_9^{\equiv}$, Ducret[7] makes the assignment of $H_2VO_4^-$ to the species formed in the pH range 10-8, but concedes it may not be the most stable product thermodynamically, and may be in equilibrium with the forms VO_3^- and $V_3O_9^{\equiv}$ (metavanadate). A marked dependence upon the rate of addition of acid was noted between 2 and 2.5 equivalents added. A transient red colour was observed if the addition was made quickly. The fading of this colour was observed to be temperature-dependent and was associated with an increase in pH. This he ascribed to fast acid/base titration of $H_2VO_4^-$ to give an unknown initial product, with subsequent reaction to $H_3V_2O_7^-$. At elevated temperatures, the rates of condensation and polymerization reactions are enhanced and one obtains non-reproducible titration curves due to the variable formation of condensed structures. At elevated temperatures, the solution becomes coloured after the first ∿ 0.5 equivalent of acid has been added. This behaviour is consistent with the formation of homopolyanions in the pH range 7 - 12. Pope and Dale[16] summarize some of the equilibria in vanadate solutions (Fig. 5). It should be noted that neither V^{4+} nor ligands capable of complexation were present in these solutions.

FIGURE 5. Equilibria in Aqueous Vanadium 5+ Solutions from Pope and Dale[16]

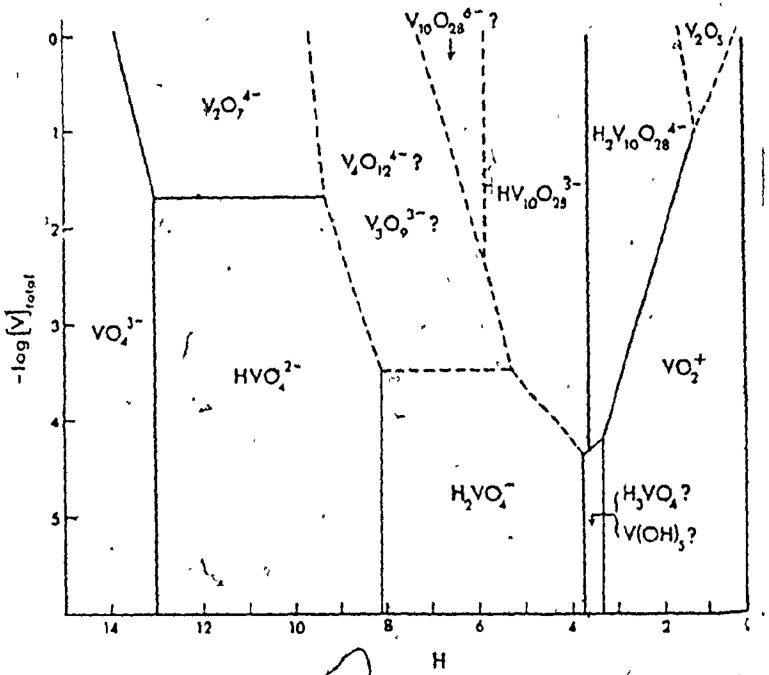


Figure 1 *The approximate conditions of pH and total vanadium concentration under which given species would be the major solute component of a vanadate solution at 25°. Demarcatio about which there is considerable doubt are represented by broken lines. The data used in the construction of this diagram were taken from: L. Newman, W. J. LaFleur, F. J. Brousaid and A. M. Ross,* J. Amer. Chem. Soc., 1958, 80, 4491; *N. Ingri and F. Brito,* Acta Che Scand., 1959, 13, 1971; *D. Dyrssen and T. Sekine,* Acta Chem. Scand., 1961, 15, 1399; *F. J. Rossotti and H. Rossotti,* Acta Chem. Scand., 1956, 10, 957. *The data regarding the solubili of* V_2O_5 *are approximate*

Lingane[12] found polarographic results reproducible only if solutions prepared from acidified stock solutions were allowed to age for ∿ 1-4 hours before use. During this aging period, the solutions changed from yellow to colourless. The time required for the colour change to occur could be reduced by heating or by the addition of sulfite. Souchay[17] recorded the cathodic waves exhibited by V^{5+} solutions from pH ∿ 3 to > 12. At pH ∿ 8, a complicated polarogram was obtained having at least 4 ill-defined cathodic waves. At pH > 9, these had collapsed from four to two and corresponded to 1 and 2 Faradays. These were ascribed to V^{5+}-V^{4+} and $V^{4+}\rightarrow V^{2+}$. At higher pH's these two waves merged. He suggested that the ill-defined pre-waves at medium pH's were due to the adsorption of highly charged ions such as decavanadates ($V_{10}O_{28}^{-6}$) or metavanadates ($V_3O_9^{\equiv}$, $V_4O_{12}^{\equiv}$, etc.) that are unstable at both higher and lower pH values. On this basis he ruled out the mononuclear vanadate VO_3^- in preference of more highly charge species. The presence of EDTA[14] or oxalate[11] does not completely remove the pre-waves from these polarograms, indicating that the complexes of these ligands are not sufficiently strong to prevent the formation of polyvanadates.

2.1.3 Mixed V^{4+}/V^{5+} Systems

A problem common to all Stretford plants is the precipitation of vanadium from process liquors. The deposit is usually found in non-turbulent or stagnant flow areas of the system and in close association with deposited elemental sulfur. Since vanadium 5+ was known to be soluble in basic solutions, the "black deposit" was assumed to be an insoluble hypovanadate. This was supported by the observation that fully oxidized

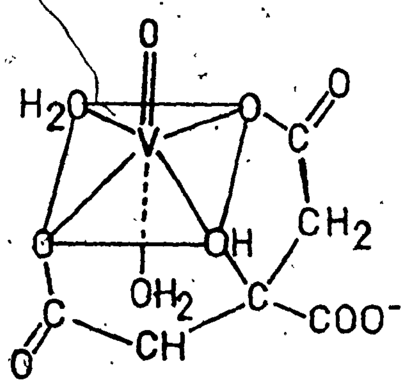
Stretford liquors did not precipitate vanadium-containing compounds while reduced liquors did. It was not until 1967 that it was shown by ion exchange that this deposit probably contained both V^5 and V^4.[18] The vanadium content of plant samples was observed to have a variable total vanadium content within the range 30-41%. This percentage seemed to increase with washing time in the sample preparation. The sodium content fluctuated between 10-25%. Elemental analysis of a sample of the precipitate gave 0.64% C, 2.08% H, 0.03% N and 1.22% S. The precipitate was tentatively labelled vanadyl vanadate after reports of similar compounds were found in the literature.[19]

Ducret[7] suggested that the vanadyl vanadates have a variable V^4/V^5 ratio of 3-4. Ostrowetsky[10] isolated at pH 4-6.5 compounds with the V^4/V^5 ratios of 8/2, 7/3, 6/4, 5/5, 4/6 and 3/7 confirming the accepted decacondensation of the ions. Above pH 7 a compound of V^4/V^5 and Na/V ratios of 2.0 and 0.5 coprecipitated with $(NH_4)_2V_4O_9$, to which he ascribed the hexacondensed structure $Na_3V^4_4V^5_2O_{15}H \cdot 6H_2O$. Lukacs[20] later isolated anions with V^4/V^5 ratios of 1/2 at pH 5.5-6.5 and 1/4 (≡2/8?) at pH 2.7-4.9. Ostrowetsky[10] reported that at pH 8.5, and with the initial V^4/V^5 ratio changing from 0.3 to 0.42 the V^4/V^5 ratio in each solution after precipitation was constant at 2/1. This indicates that the deposit could not have been homogeneous. This behaviour was not explained even though it is at odds with his conclusion of a fixed chemical composition.

In an attempt to prevent vanadium precipitation from Holmes-Stretford solutions, an organic complexing agent is usually added to the process liquors. Several molecules including EDTA, tartrate, citrate, hexahydroxyheptanoic acid and oxalate have been utilized for this purpose, but it has been found that citrate is the least susceptible to chemical decomposition and does not interfere significantly with overall process chemistry. This is consistent with the two electron mechanism of α-hydroxy carboxylic acid oxidation as put forth by Kemp and Waters.[21]

In acid solution, α-hydroxy acids have been shown to form strong complexes with vanadium 5+ cations. Tartrate anions do not form complexes with metavanadate solutions while the protonated acid does.[22] Thus, the possibility that vanadium 5+ is complexed in Stretford liquors by carboxylate ligands is remote.

It has been demonstrated by conductance, titration and spectroscopy that citrate forms a strong 1:1 complex with vanadium +4. In excess V^{4+} and at pH < 4 [pH < 6], a 2:1 complex has been shown to exist.[7] However, Nikolova[23] found that above 4.5 only the 1:1 complex is stable. The NMR results of Canneri[24] and the IR results of Nikolova[6] indicate that one hydrogen exists on the citrate ligand in the complex. This is consistent with the structure proposed by Selbin[4] and others[7,23,6] given below:



Nikolova[6] suggests that coordination to the fifth site trans to the V=O bond would not have serious consequences and may lead to slight changes in strength of the VO bond with changes in relative energies of two MO's. This would be expected to give slight changes in the IR absorption spectra that he discusses but it is not clear what changes would occur in the UV spectra. One concludes, then, that two positions are therefore immediately available in VO(cit) for primary sphere reactions.

Ducret[7] showed that oxalate ions form a 2/1 ligand/metal complex that was stable to a pH of ∿ 6.5. He suggested, on the basis of solution colour, that the complex breaks up to give vanadium 4+ anions and free oxalate above this pH level.

The regions of pH stability of complexes has a direct bearing on the vanadium chemistry of Stretford liquors. Although oxalate forms a strong complex, it probably could not be used to prevent the formation of black deposit since the complex decomposes at a lower pH than the 8.5-9.0 design pH of a Stretford plant. The data of Ducret[7] suggests that the citrate complex is stable to a pH of < 8, a region which makes it difficult to rationalize the stabilizing effect of citrate on black deposit formation, given a usual operating pH of 8.5 or higher.

2.2 Experimental Details and Results

2.2.1 Apparatus and Chemicals

2.2.1.1 Reaction Cell

A one litre thermostatted reaction cell was assembled from perspex (polymethylmethacrylate) pipe and sheet as diagrammed in Fig. 6 a,b. The

FIGURE 6a. Reaction Cell - body

A - 5" outer wall
B - 1/4" water jacket
C - 4" inner wall
D - diffuser plate

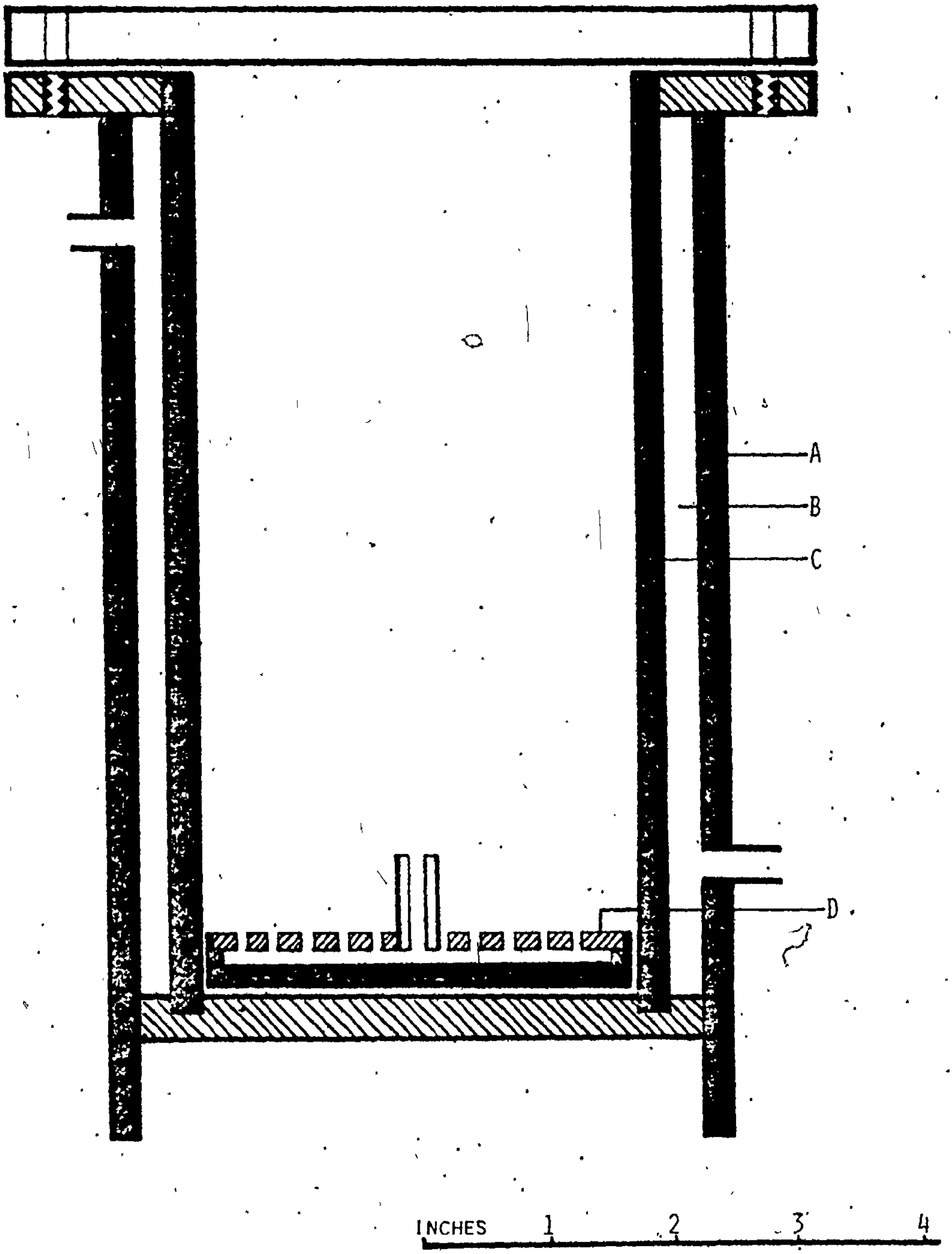
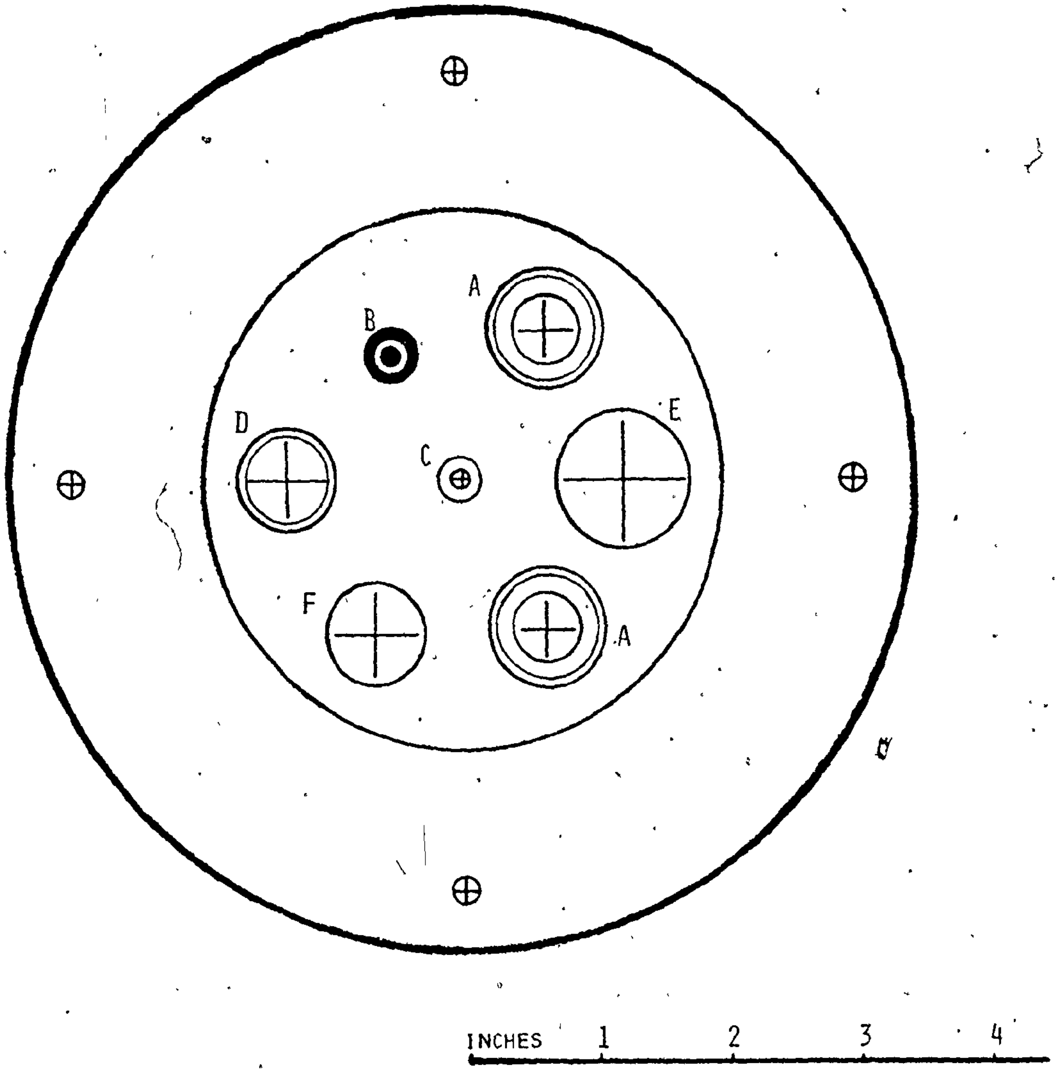
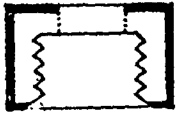
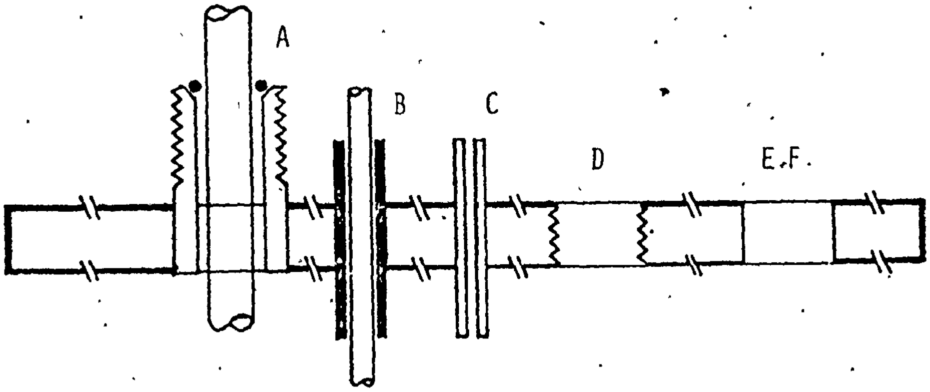

A
B
C
D
INCHES
1
2
3
4

FIGURE 6b. Reaction Cell - top

A - gas-tight electrode seal
B - stirring rod bushing
C - gas inlet
D - threaded hole
E - O_2 electrode
F - pumping lines


A
B
E
D
C
F
A
INCHES
1
2
3
4




A
B
C
D
E.F.

flanged top contained 7 orfices, one each for reagent addition, glass pH electrode, platinum electrode, calomel electrode, O_2 electrode, gas inlet and agitator shaft. The common agitator speed used in all studies gave thorough mixing of an added aliquot of $KMnO_4$ within 5 seconds at no gas flow and < 2 second with maximum gas flow through the diffuser plate.

A variable speed Harvard Instruments peristaltic pump gave a continuous closed loop flow of solution at a rate of 0-200 ml/min (Fig. 7) through an on-line filter and a uv-vis flow cell placed in the sample compartment of a spectronic 600 uv-vis spectrophotometer. The lines in contact with the solution were glass tube with flexible tygon joints and had a total volume of ∿ 100 mls. The tygon tubing in the peristaltic chamber was sheathed with a latex tube of a slightly larger diameter to prevent electrical interference with the electrodes and probes in the solution. If required, the solution was grounded to the pH meter chassis via a platinum wire.

Water from a thermostatted bath was circulated through the cell jacket at a rate of approximately 1/2 l/min. The heat transfer through the perspex was found to be poor and as a result the bath temperature required to maintain the cell at 25 ± 2°C varied between 0 and 28°C.

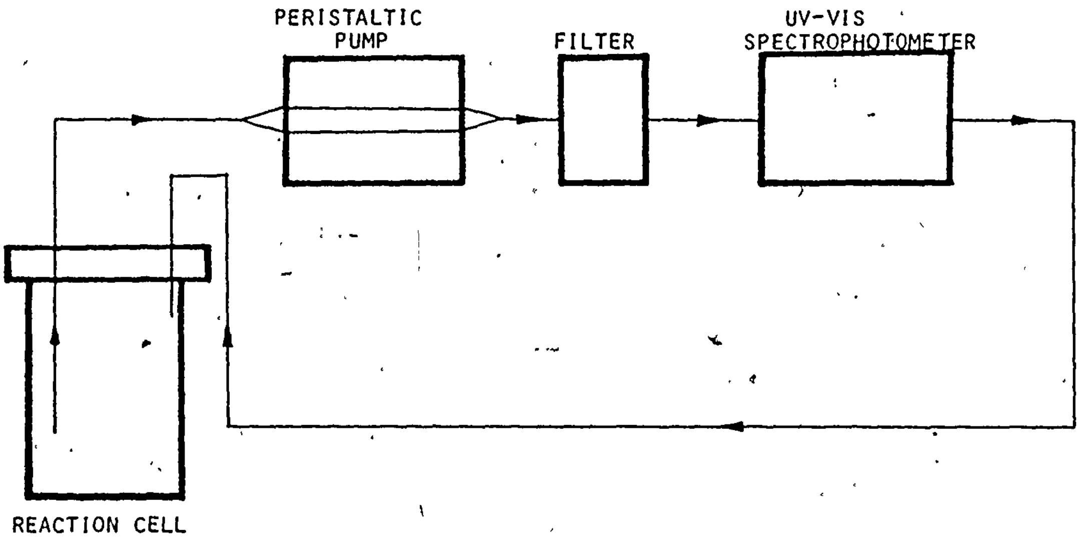
The quartz flow cell (Fig. 8) was found by comparison with a cell of known dimensions to have a light path of 2.0 ± 0.05 cm. This allowed study of solutions with $\varepsilon C < 1$.

2.2.1.2 Gas Manifold and pH Controller

A diagram of the gas manifold is given in Figure 9. The 50 mv/pH output of a Fisher accumet 310 expanded scale pH meter was fed through

FIGURE 7. Reaction Cell Pumping Diagram

FIGURE 8. UV-VIS Spectrophotometric Flow Cell


PERISTALTIC PUMP
FILTER
UV-VIS SPECTROPHOTOMETER
REACTION CELL

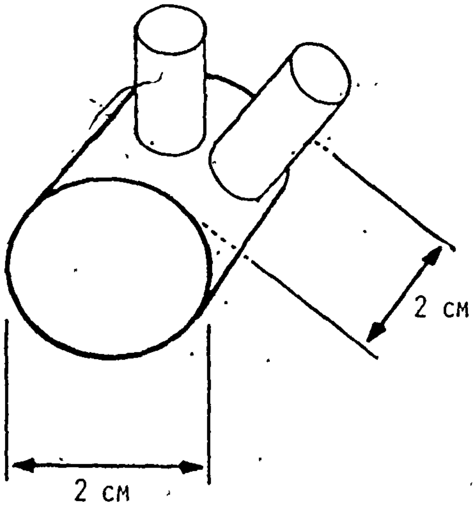

2 CM
2 CM

FIGURE 9. Gas Manifold

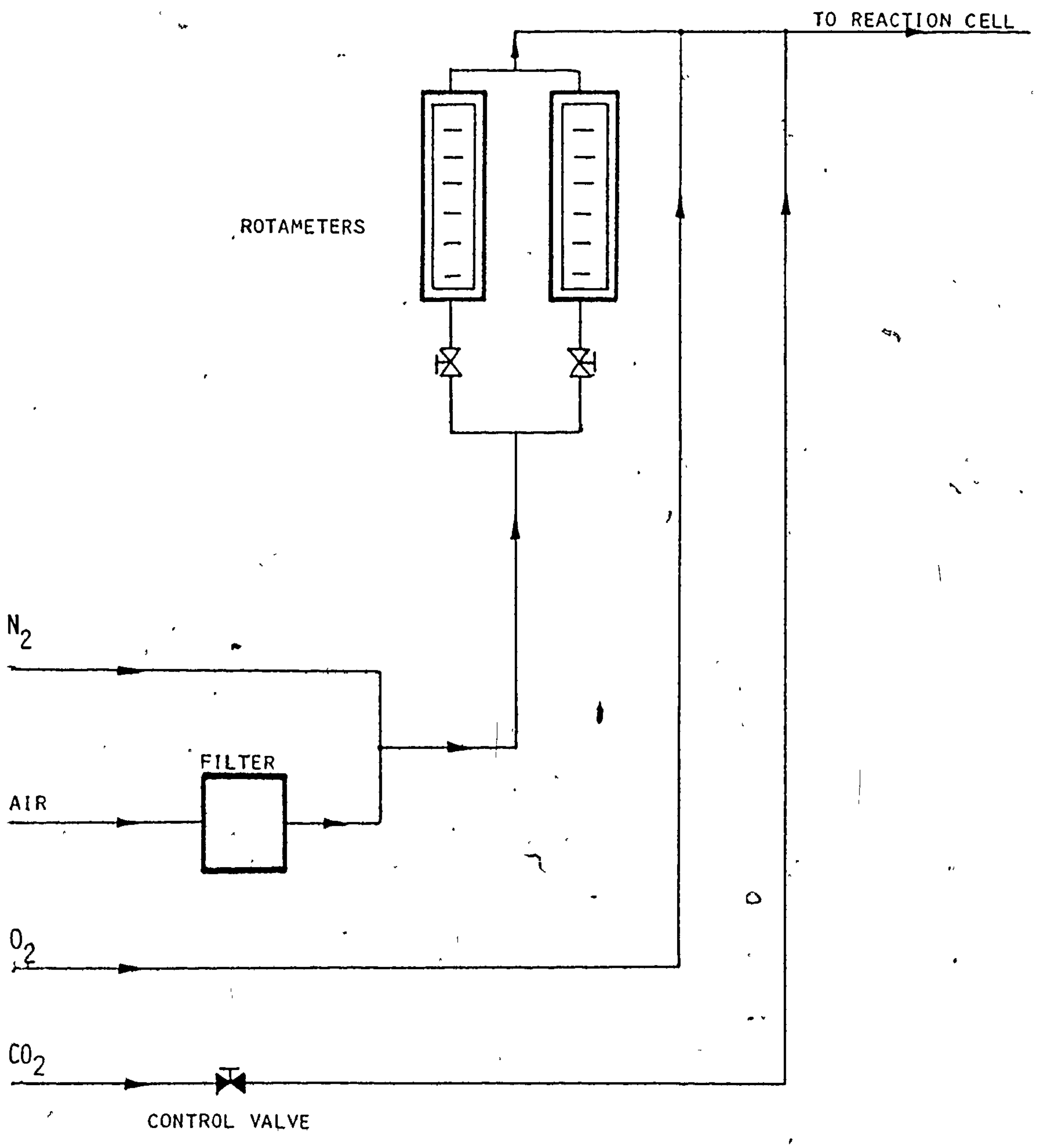
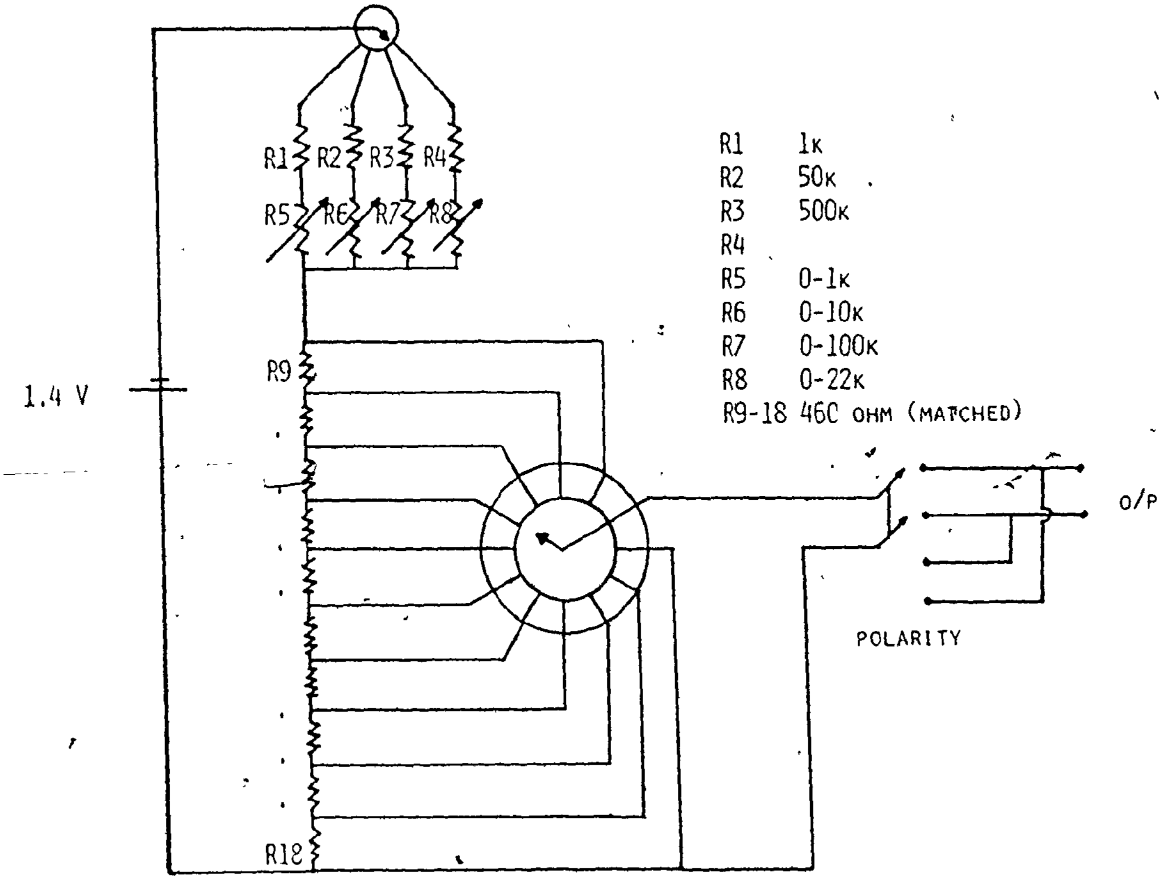

TO REACTION CELL
ROTAMETERS
N_2
FILTER
AIR
O_2
CO_2
CONTROL VALVE

FIGURE 10. Millivolt Calibration Source

FIGURE 11. Variable Bucking Potential Apparatus



R1	1K
R2	50K
R3	500K
R4	
R5	0-1K
R6	0-10K
R7	0-100K
R8	0-22K
R9-18	460 OHM (MATCHED)

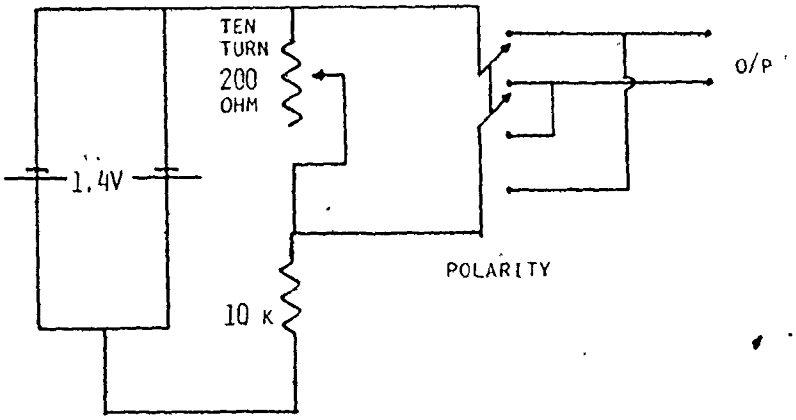
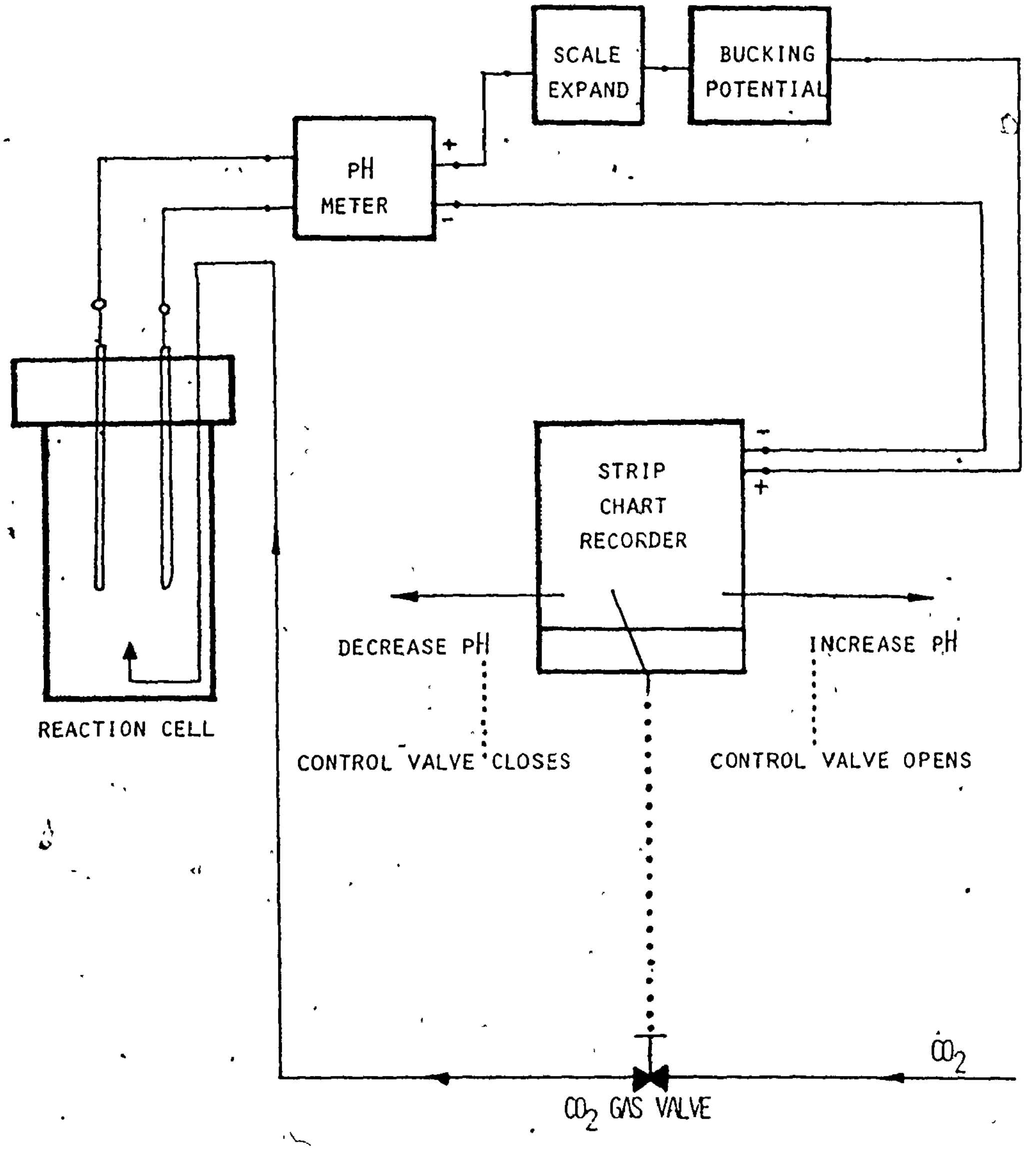


FIGURE 12. pH Controller Apparatus


SCALE EXPAND
BUCKING POTENTIAL
pH METER
+
-
STRIP CHART RECORDER
-
+
DECREASE pH
INCREASE pH
CONTROL VALVE CLOSES
CONTROL VALVE OPENS
REACTION CELL
CO_2
CO_2 GAS VALVE

a variable bucking potential apparatus (Fig. 11) to a variable range Sargent-Welch strip chart recorder. The pen carriage of this recorder was mechanically linked to a gas valve such that an increase in pH opened the valve.(fig 12)When the pH of the test solution increased, more CO_2 was thusly bled into the gas inlet line maintaining the solution pH at a point fixed by the bucking potential. Adjustment of the CO_2 back-pressure compensated for the change in buffer capacity of the solution at different pH's. At high oxidation rates, the solution pH changed faster than the response time of the apparatus and the pH was maintained by the dropwise addition of NaOH.

The oxygen content of the test solution was monitored with a Chemtrex type 30 oxygen meter. Leakage of the test solution onto the Chemtrix probes caused zero set drift and high readings. A YSI 5739 oxygen probe, although not a pin for pin replacement, was found to be compatable with the meter after minor wiring changes. The meter was calibrated immediately before use with O_2 free N_2 and air saturated distilled water at 25.0°C as zero and 100 oxygen meter response (OMR). Corrections were not made for barometric pressure. A strip chart record could be made of the output from this meter.

To facilitate calibration of meters and recorders a decade type millivolt source (Fig. 10) was designed and constructed with output ranges of 0-1000 , 100, 10, and 592 mv (pH units). It is suitable for use with devices with medium to high input impedences.

2.2.1.3 Chemicals

Vanadium 4+ stock solutions were prepared from vanadyl sulfate$\cdot xH_2O$

(BDH) or vanadyl sulfate·$2H_2O$ (Fisher purified) in deionized distilled water. After addition of 10 drops/l concentrated H_2SO_4, each was stored in glass. Vanadium 5+ stock solutions were prepared from $NaVO_3$ (BDH) in deionized distilled water. These were stored in glass after filtration. Tri-sodium citrate dihydrate (BDH analar) Na_2CO_3 and $NaHCO_3$ (Fisher purified) were used as supplied. Sodium sulfhydrate (Fisher purified) was found to be unsuitable as a sulfide source due to a high and variable elemental sulfur (polysulfane?) content. $Na_2S\cdot 9H_2O$ (BDH analar) recrystallized once in water gave clear colourless solutions.

Vanadium solutions were titrated with ∿ 0.05 N Fe^{2+} standardized against dichromate by the method described in Appendix III. The endpoint was determined potentiometrically.* In cases where very small amounts of vanadium were present (i.e., analysis of precipitates), the titrations were performed under N_2 in a beaker fitted with a 3-holed electrode holder.

Buffered solutions of V^{4+}/citrate were prepared by mixing together selected volumes of the vanadyl and citrate stock solutions and then

---

* The same titration with a diphenyl sulfonate indicator was rejected as being too uncertain. The determination of vanadium by atomic absorption was discontinued after several months use when it was found to be unreliable at higher concentrations of vanadium when in Stretford-like backgrounds. A comparison of titration and A.A. results is available in Fig. 19. This interference was not present in solutions (such as stock solutions) which contained neither citrate or any of the other salts that might be present in a Stretford liquor.

adding the resulting solution to a deaerated carbonate buffer of the desired strength at a pH < 8.5. It is important that the pH not exceed 9.4. The pH of the carbonate solution was controlled by CO_2 addition.

Unbuffered solutions of V^{4+}/citrate were prepared by premixing selected volumes of V^{4+} and citrate stock solutions, and adding the mixture to deaerated deionized water in the reaction cell. The solution at this point had a pH of ∿ 2.9.

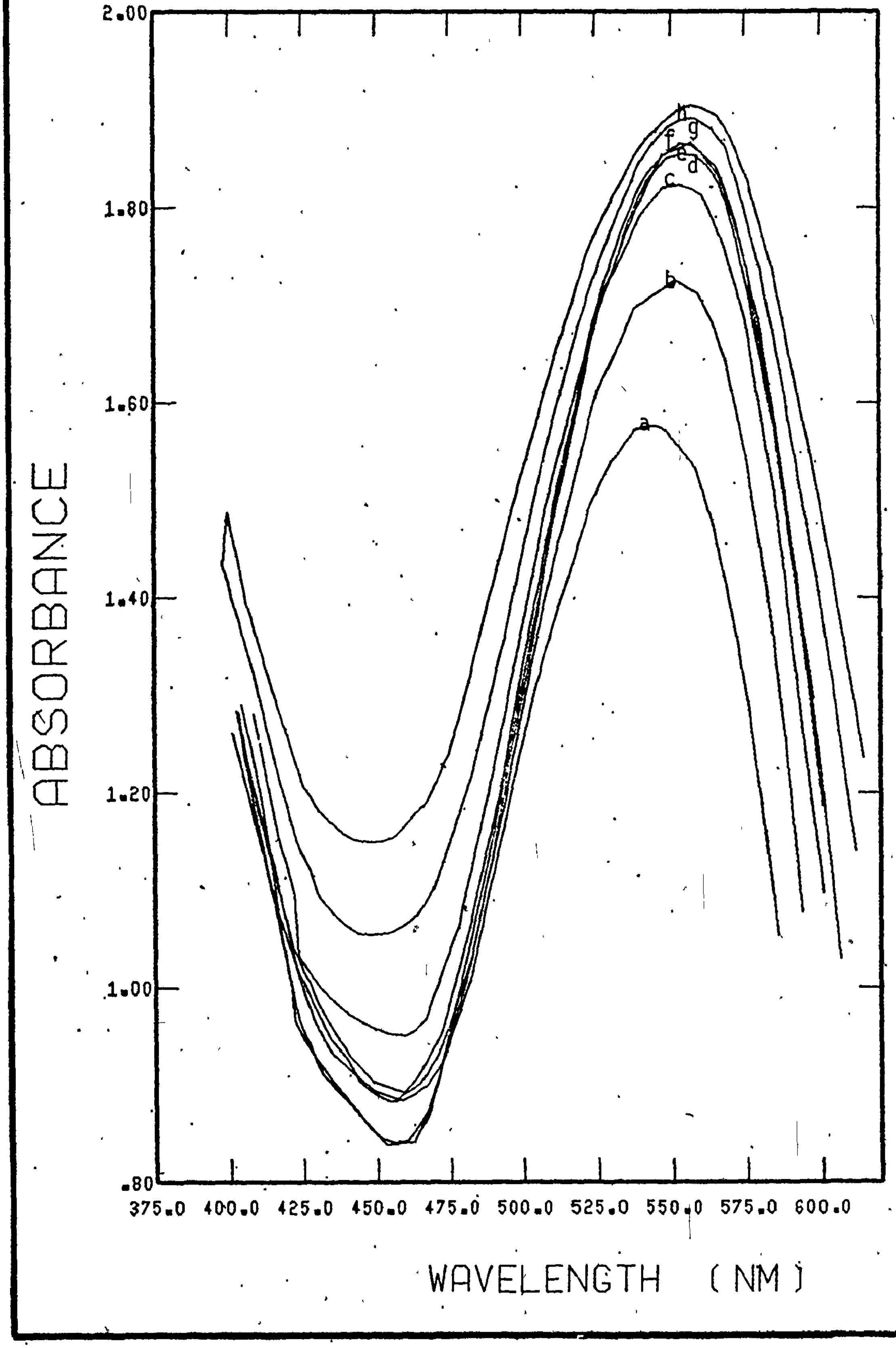
2.2.2 Detailed Procedures and Results

2.2.2.1 The Effect of pH on Unbuffered Vanadium 4+/Citrate Solutions

The spectra of unbuffered V^{4+}/citrate (1:1, 0.020 M) solutions were obtained at several pH values over the range 3-10. Small additions of H_2SO_4 50% v/v or saturated NaOH were made to the solutions to bring the pH to the desired value, a spectrum was obtained and a check of the absorbance maximum at 560 nm was made after 20 minutes to ascertain if any changes had occurred. In the pH range 3-7.4, the spectra (Fig. 13) were found to be a reproducible function of pH. Above pH 7.5 changes in spectra,unlike those observed at the lower pH's occurred over a much longer period of time compared to the rapid equilibration at the lower pH's. The absorbance was seen to increase at all wavelengths from 400-650 nm coincident with the development of a brown colouration. The rate of increase was greater at higher pH values. A solution that had developed a brown colouration at pH 9.0 did not return completely to the original spectra of V^{4+}/citrate at pH 7.4 when left at pH 7.4 for ∿ 12 hours. By contrast, a brown solution at pH 10 taken to pH 2.8 for only a few minutes exhibited the same spectra over the pH range 3-7.5 as it had

FIGURE 13. Spectra of vanadium 4+/citrate

a. pH 9.25
b. pH 8.50
c. pH 7.40
d. pH 6.11
e. pH 4.55
f. pH 3.90
g. pH 3.50
h. pH 2.92


ABSORBANCE
2.00
1.80
1.60
1.40
1.20
1.00
.80
375.0
400.0
425.0
450.0
475.0
500.0
525.0
550.0
575.0
600.0
WAVELENGTH (NM)
a
b
c
d
e
f
g
h

prior to being taken to pH $>$ 7.5.

When allowed to stand under N_2 for several hours, a solution at pH 7.4 exhibited a small increase in absorption. At pH 8.3 the absorption increases substantially but is seen to approach a limiting value. This is shown by a graph of absorbance at 450 nm vs time at pH 7.4 and 8.3 (Fig. 14).

2.2.2.2 The Effect of pH on Carbonate Buffered Vanadium 4+/Citrate Solutions

The spectra of Vanadium 4+/citrate (0.0218 M, 1:1) in 25 gm/l Na_2CO_3 were obtained in the pH range 7.5-10. The pH was adjusted with CO_2 over the range 7-9.1 and by additions of NaOH (saturated) above this value. After obtaining a spectrum at a new pH value, the pH was re-adjusted to an arbitrary reference pH at which a spectrum had been previously obtained, thus allowing a check for irreversibility.

Below a final pH of 9.5, the spectra were found to be reproducible and exhibited an isosbestic point at 470 nm (Fig. 15). A graph of the absorbance maximum vs $1/H^+$ is given in Fig. 16.

Above pH 9.5, the absorbance was seen to increase with time at all wavelengths between 400-650 nm. A graph of absorbance at 560 nm vs time at pH 9.85 (Fig. 17) shows a possible convergence. The changes in spectra on returning to pH 7.5 are exceedingly slow, with no significant changes in ∿ 12 hours.

Addition of oxygen to a series of solutions that had been aged at pH $>$ 9.8 for several hours showed significant, but non-reproducible changes in spectra. These solutions showed virtually no oxygen demand

FIGURE 14. Plot of Absorbance vs. Time of Vanadium 4+ / Citrate Solution at Two pH's

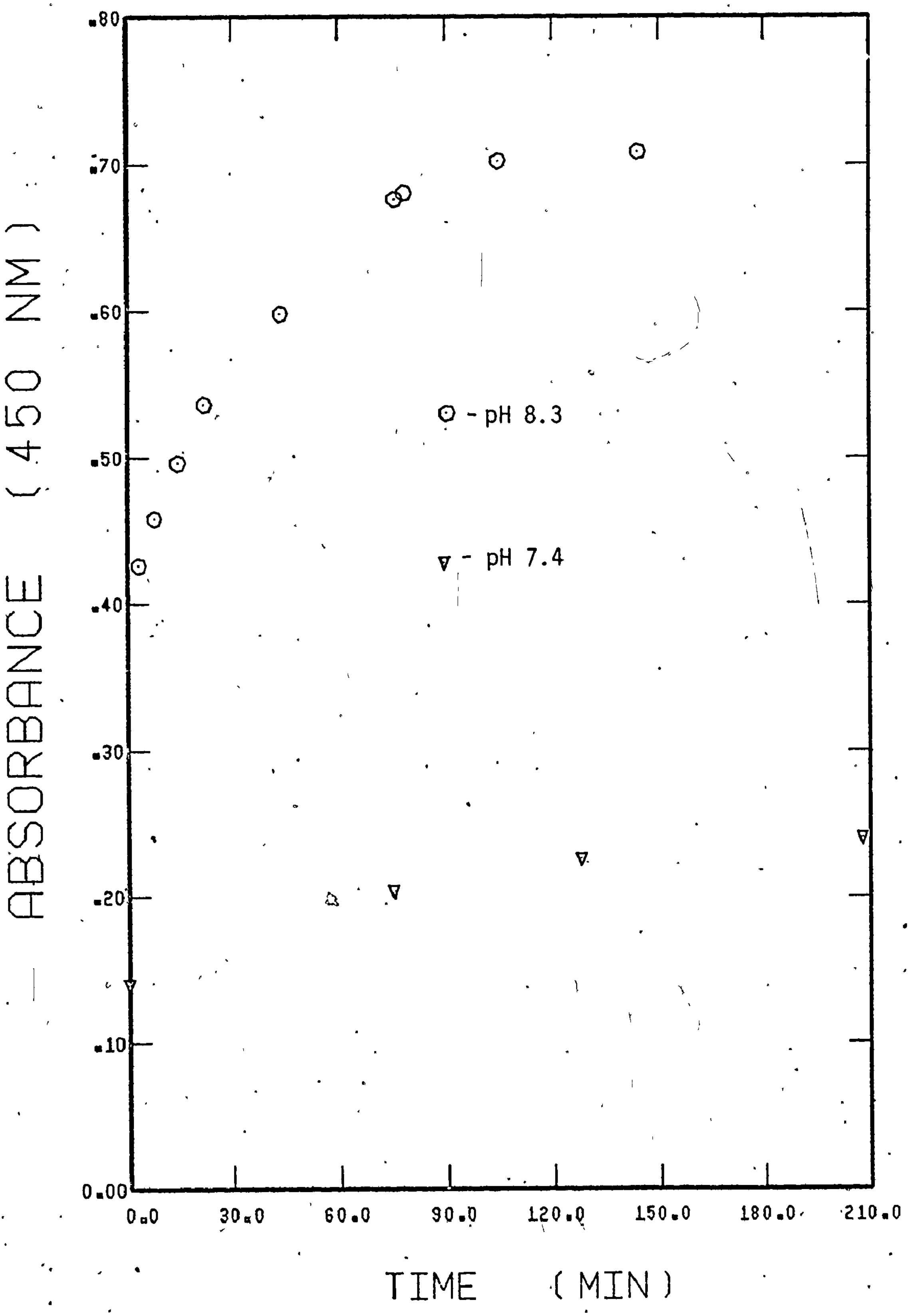
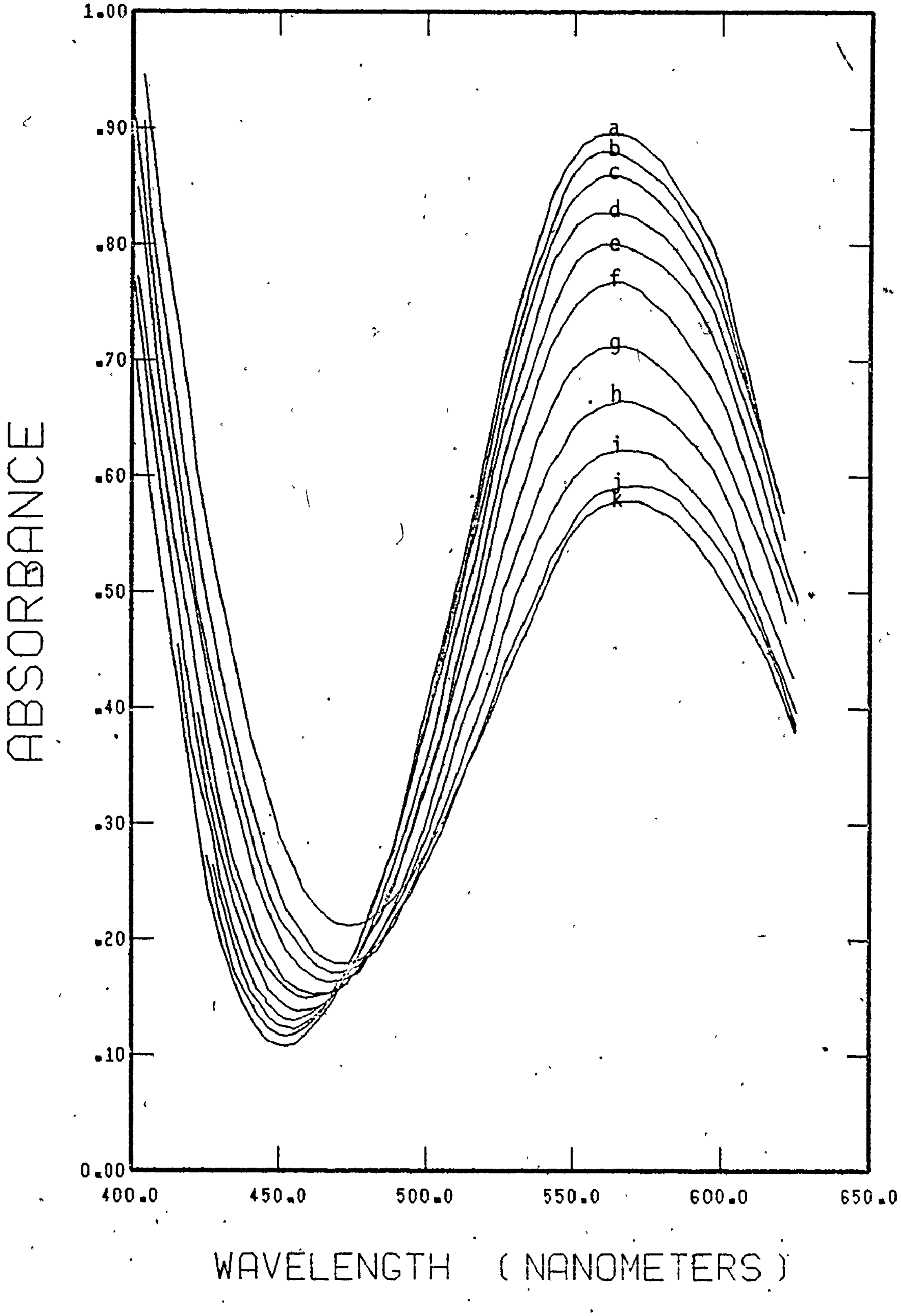

ABSORBANCE (450 NM)
.80
.70
.60
.50
.40
.30
.20
.10
0.00
0.0
30.0
60.0
90.0
120.0
150.0
180.0
210.0
TIME (MIN)
⊙ - pH 8.3
▽ - pH 7.4

FIGURE 15. Plot of Absorbance vs. Wavelength of Carbonate Buffered Vanadium 4+ / Citrate Solution at Several pH's

a - 8.21
b - 8.37
c - 8.54
d - 8.79
e - 8.87
f - 9.03
g - 9.19
h - 9.36
i - 9.52
j - 9.69
k - 9.85



1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
0.00
400.0
450.0
500.0
550.0
600.0
650.0
ABSORBANCE
WAVELENGTH (NANOMETERS)
a
b
c
d
e
f
g
h
i
j
k

FIGURE 16. Plot of Absorbance Maxima of Buffered Vanadium $4+$/ Citrate Solution vs. $1/H^+$

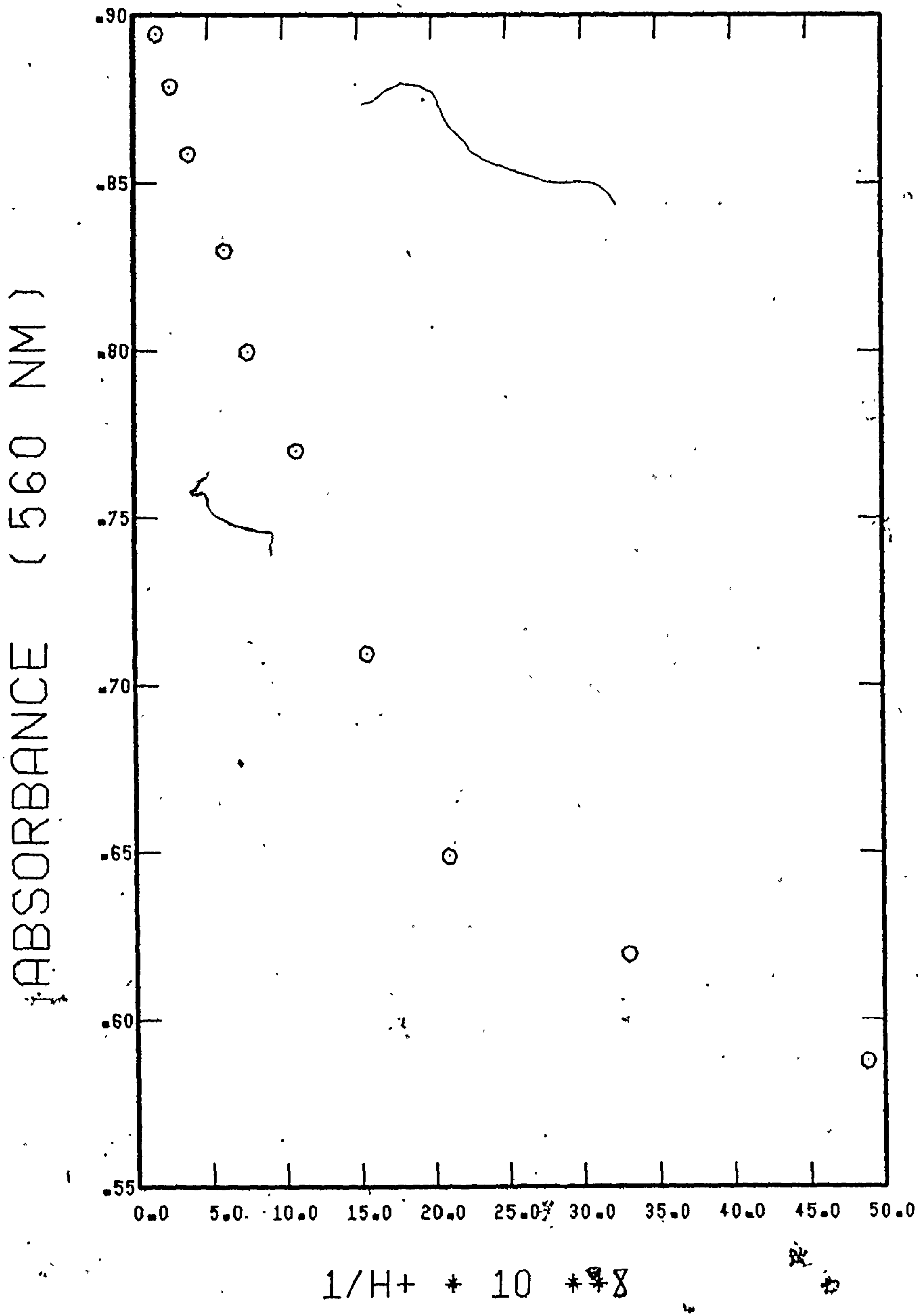
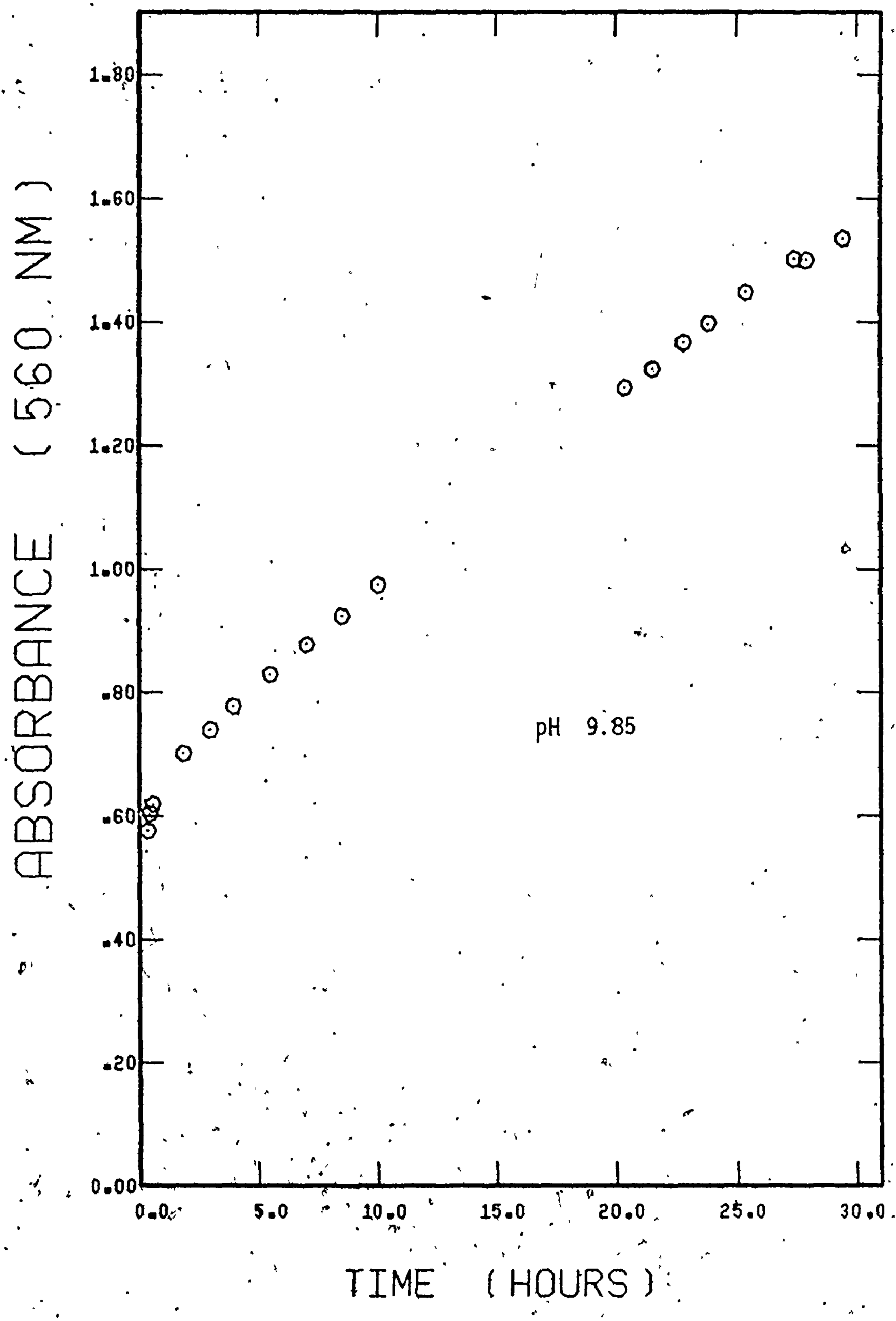

ABSORBANCE (560 NM)
.90
.85
.80
.75
.70
.65
.60
.55
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
1/H+ * 10 **8

FIGURE 17. Plot of Absorbance Maxima of Buffered Vanadium 4+/Citrate Solution vs. Time


ABSORBANCE (560 NM)
1.80
1.60
1.40
1.20
1.00
.80
.60
.40
.20
0.00
0.0
5.0
10.0
15.0
20.0
25.0
30.0
TIME (HOURS)
pH 9.85

and were stable in air saturated solution for several hours at least.

Addition of oxygen to a solution below pH 9.5 caused a gradual decrease in absorbance with time without change in spectral shape. Addition of 100 mls of 1.0 M V^{5+} or V^{5+}/citrate (1:1) to V^{4+}/citrate solutions at pH 8.8 and 9.3 gave no change in absorbance at 560 nm after correction for dilution.

2.2.2.3 The Uncatalysed Air Oxidation of Carbonate Buffered Vanadium 4+ / Citrate Solutions

Based on the results reported in 2.2.2.2, an attempt was made to determine the rate constant for the uncatalysed air oxidation of V^{4+}/citrate/carbonate solutions at pH < 9.5 using the absorbance at 560 nm as a measure of the V^{4+} concentration. The procedure used was as follows.

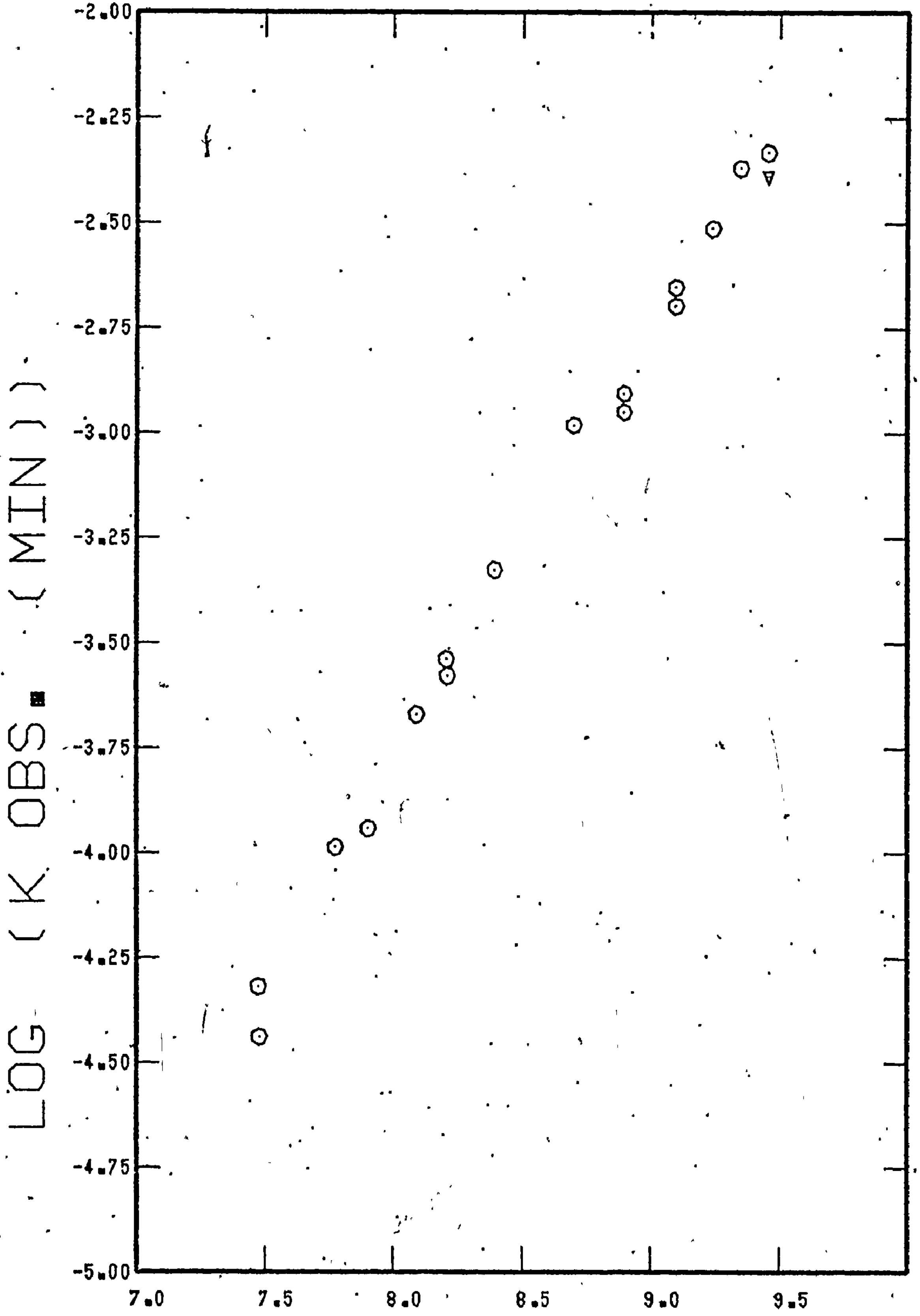
To 80 mls of deionized distilled water in the reaction cell were added 100 mls of 250 gm/l Na_2CO_3. This solution was treated with N_2/CO_2 until the OMR < 3% and pH < 8.5. A baseline spectrum was obtained at this point, with adjustments being made in baseline settings and spectrophotometric cell positioning as necessary. The appropriate volumes of V^{4+} and citrate were premixed, added to the reaction vessel and the total volume was adjusted, if necessary, to one litre. The pH controller was set so that the desired pH would be maintained, and the system was allowed to equilibrate. An initial spectrum was obtained while the system was under N_2. The N_2 gas flow was then exchanged for an ∿ 1/2 l/min air flow, and the absorbance at 560 nm was recorded as a function of time. Oxidations at pH > 9.1 required an O_2 supplement and a dropwise addition of NaOH to maintain the OMR and pH at the set points. Rate constants were calculated from a least squares fit of the linear regression line of $y = a \exp(-bx)$ utilizing all data derived from absorbances greater than 0.1. Below this absorbance value, even small deviations (for example, in baseline) make up a considerable fraction of the absorbance and can give rise to large uncertainties in the data points. Data is summarised in Fig 18a.

The addition of large amounts of finely divided perspex did not affect the reaction rate. The reaction rate in triply distilled deionized water was found to be the same as in deionized distilled water.

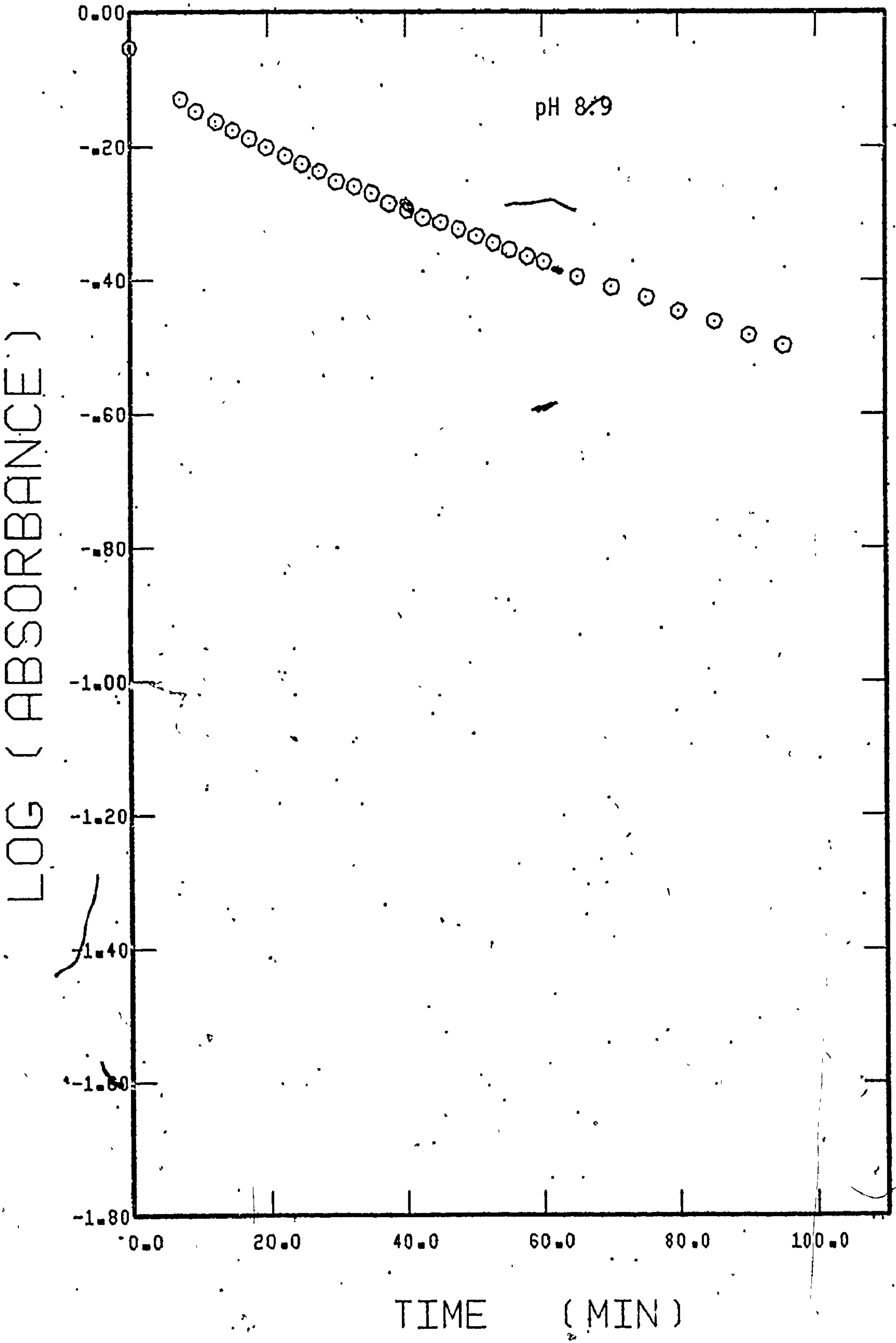
Stretford solutions can contain high concentrations of SCN^- and $S_2O_3^=$. Twenty grams each of NaSCN (recrystallized from water) and $Na_2S_2O_3$ were added to a test solution during oxidation. The rate did not change. A similar addition of Na_2SO_3 caused an excessive oxygen demand, while addition of NaCN altered the V^{4+} or V^{5+} spectra and prevented the comparison of rate data.

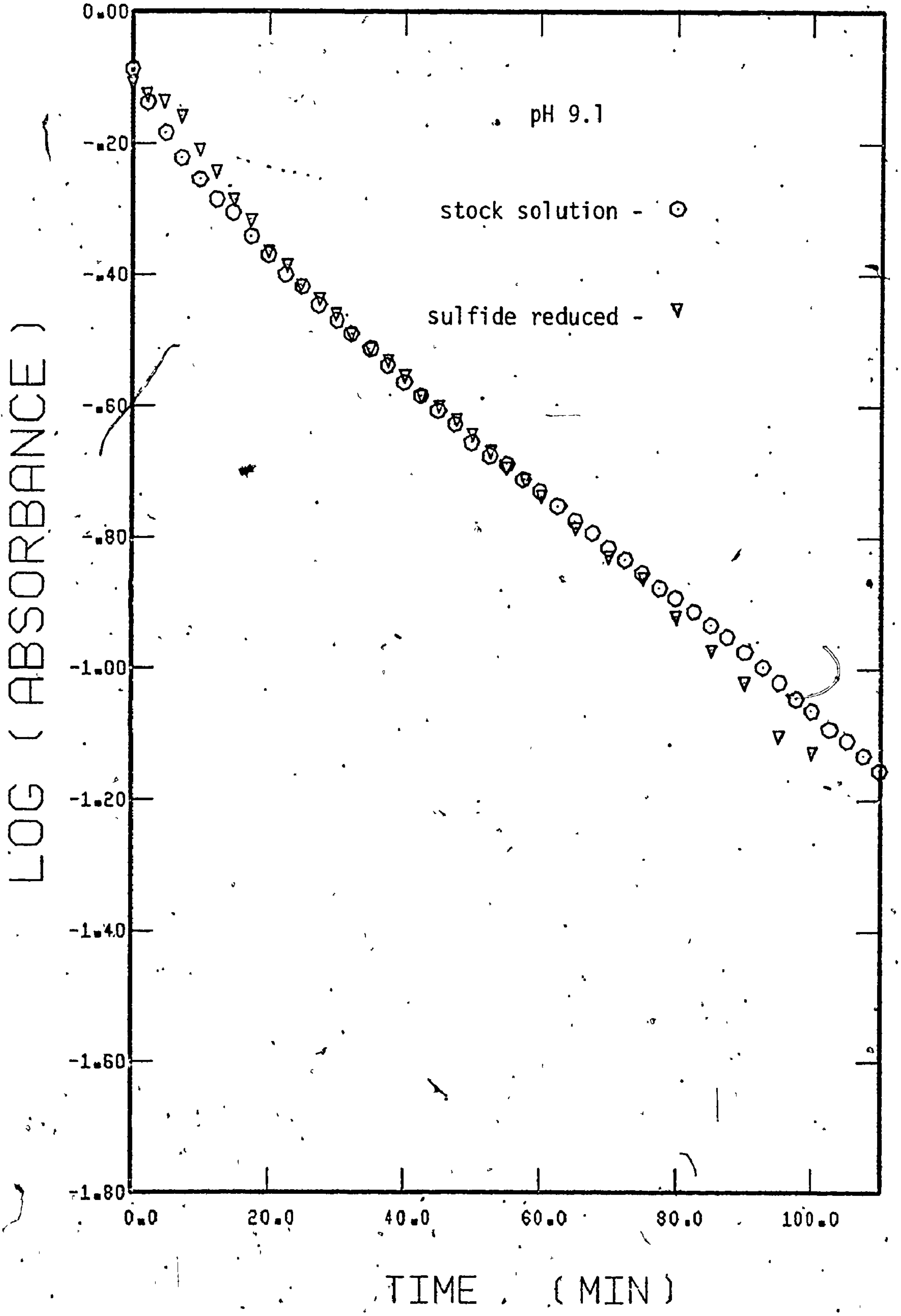
At pH values of 9.1 and 9.25, the test solution was reduced under N_2 with an equinormal aliquot of Na_2S. The solution was pumped through the on-line filter for several hours until the last visible traces of elemental sulfur had been removed. The spectrum of this solution was similar to the original solution; the small differences observed are thought to be due to sulfur deposition on the spectrophotometric cell windows. The solution was re-oxidized with air. A comparison of the rates of oxidation at two pH values are given in Figs. 18b and 18c.

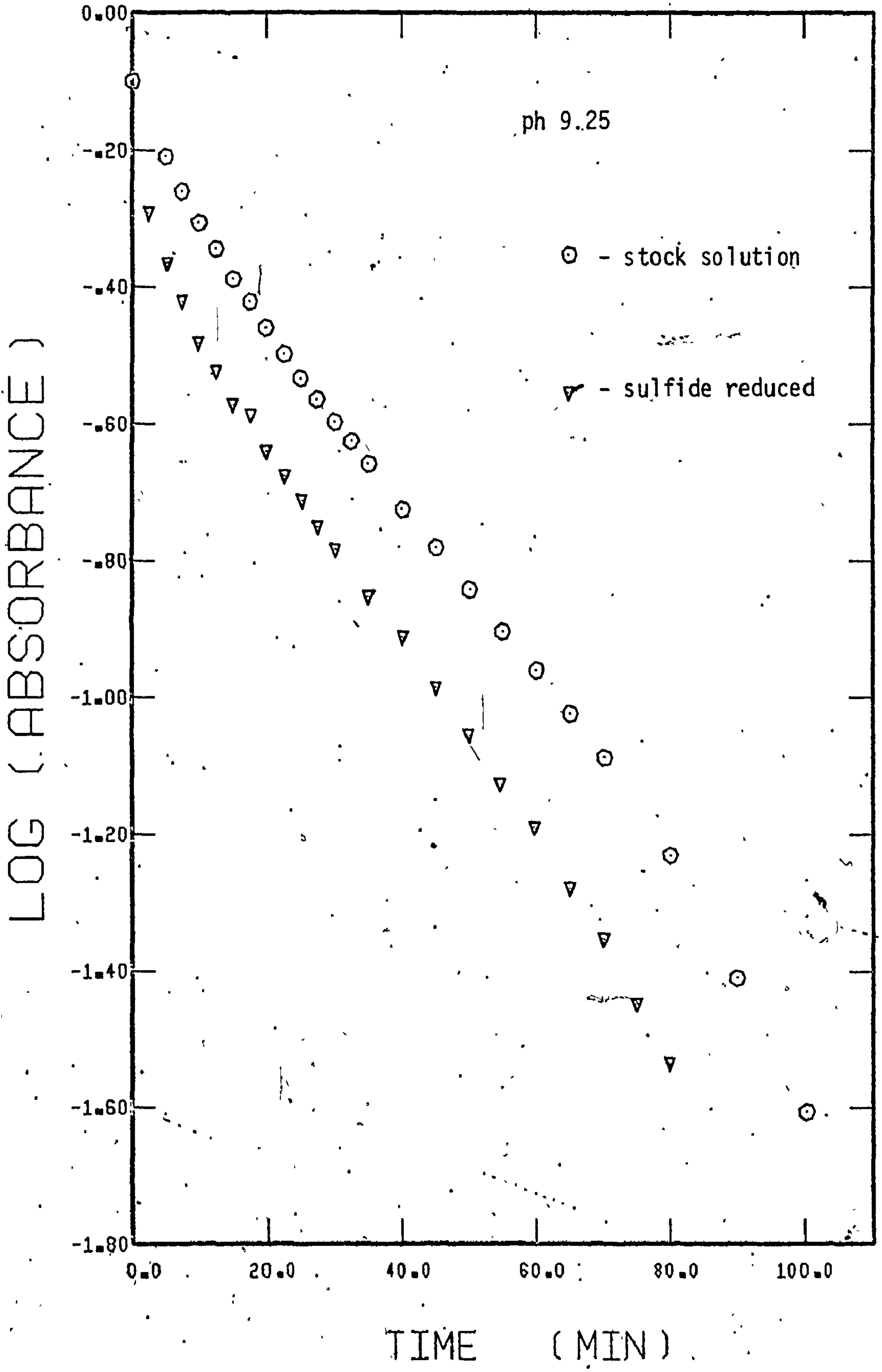
FIGURE 18a. Plot of Log (Kobs.) vs. pH for the Uncatalysed Air Oxidation of Vanadium 4+/ Citrate

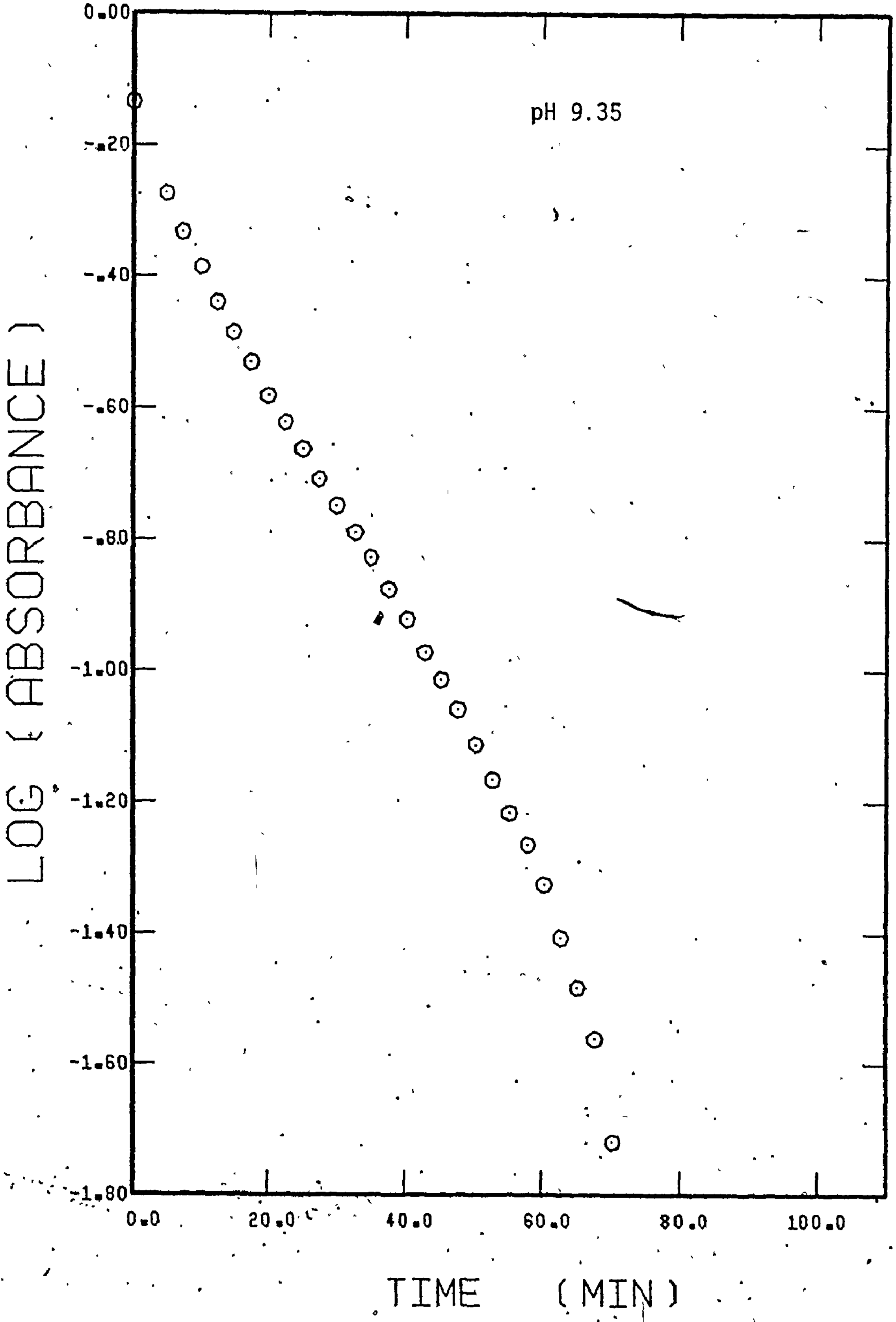

LOG (K OBS. (MIN))
-2.00
-2.25
-2.50
-2.75
-3.00
-3.25
-3.50
-3.75
-4.00
-4.25
-4.50
-4.75
-5.00
7.0
7.5
8.0
8.5
9.0
9.5

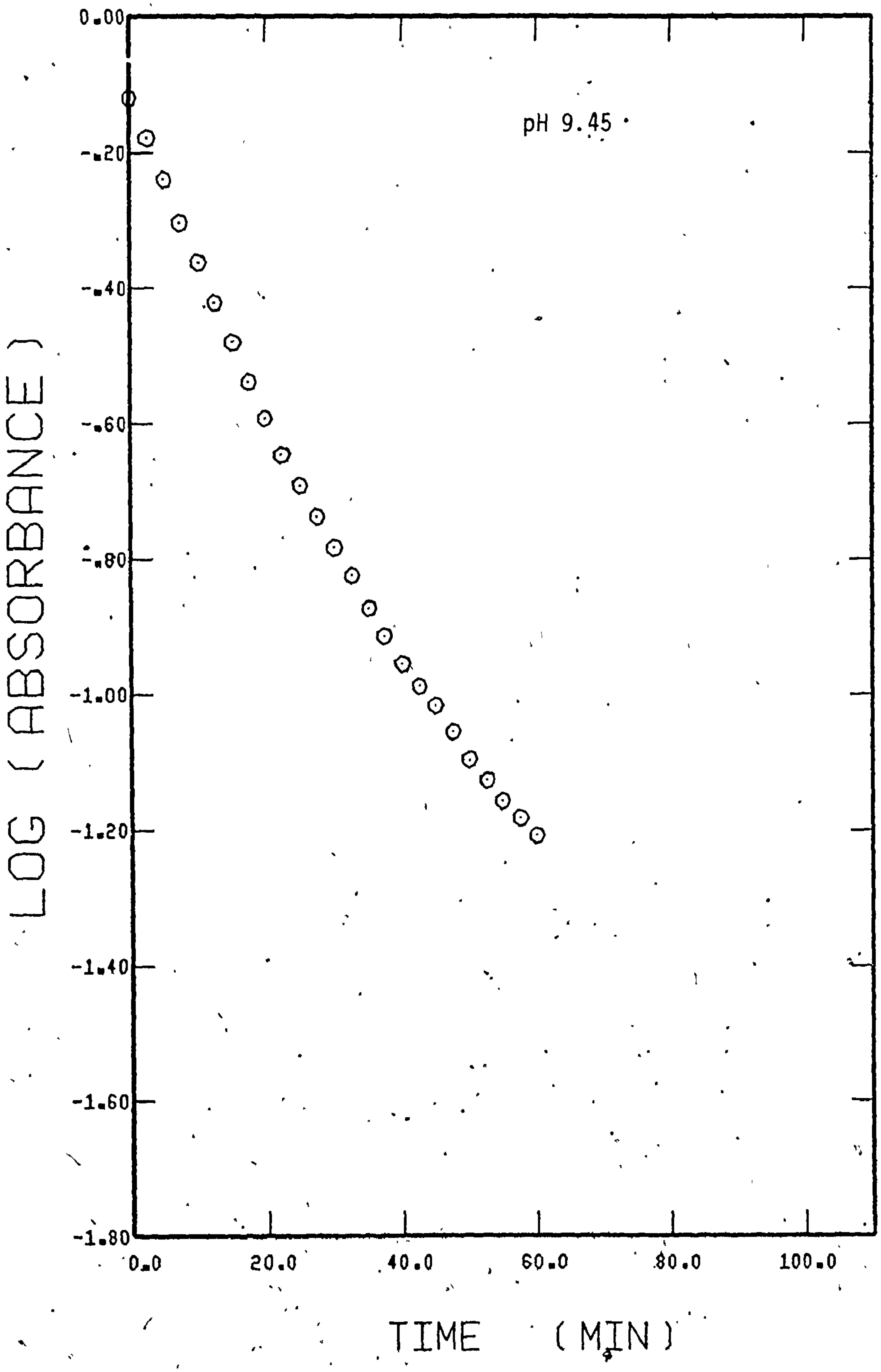
FIGURES 18b-f. Plots of Log Absorbance vs. Time for the Uncatalysed Air Oxidation of Vanadium 4+ / Citrate


0.00
-.20
-.40
-.60
-.80
-1.00
-1.20
-1.40
-1.60
-1.80
LOG (ABSORBANCE)
0.0
20.0
40.0
60.0
80.0
100.0
TIME (MIN)
pH 8.9


pH 9.1
stock solution - ⊙
sulfide reduced - ▽
0.00
-.20
-.40
-.60
-.80
-1.00
-1.20
-1.40
-1.60
-1.80
0.0
20.0
40.0
60.0
80.0
100.0
LOG (ABSORBANCE)
TIME , (MIN)


0.00
-.20
-.40
-.60
-.80
-1.00
-1.20
-1.40
-1.60
-1.80
LOG (ABSORBANCE)
0.0
20.0
40.0
60.0
80.0
100.0
TIME (MIN)
ph 9.25
⊙ - stock solution
▽ - sulfide reduced


pH 9.35
LOG (ABSORBANCE)
0.00
-.20
-.40
-.60
-.80
-1.00
-1.20
-1.40
-1.60
-1.80
0.0
20.0
40.0
60.0
80.0
100.0
TIME (MIN)


pH 9.45
0.00
-.20
-.40
-.60
-.80
-1.00
-1.20
-1.40
-1.60
-1.80
0.0
20.0
40.0
60.0
80.0
100.0
LOG (ABSORBANCE)
TIME (MIN)

2.2.2.4 The Catalysed Air Oxidation of Carbonate Buffered Vanadium 4+ / Citrate Solutions

In the Stretford process, Vanadium 4+ oxidation is catalysed by a quinone/hydroquinone redox couple. Hydroquinones are known to form peroxy compounds,[25,26] on reaction with O_2, a behavior which has been cited as the mode of oxidation in Stretford process liquors.[27] In an attempt to test these hypotheses, the effect of added peroxide on the oxidation of V^{4+}/ citrate/carbonate solution has been studied.

The absorbance of a 0.218M V^{4+}/citrate/carbonate solution was determined at 560 nm using procedures previously described. To 1 ℓ of this solution, twenty 0.2-ml aliquots of 3.21 M H_2O_2 (standardized with $KI/S_2O_3^{=}$) were added sequentially. The absorbance of the resulting solution was measured after each addition. To effect complete oxidation - as measured by the absorbance at 560 nm - a 10% excess of peroxide was required. This difference is ascribed to the decomposition of the H_2O_2 after standardization.

The change in absorbance with each new addition at pH 9.0 appeared to be the same in both aerated and deaerated solutions. At pH 8.0, the absorbance change in air saturated solutions is 20-30% greater than that observed in deaerated solution. With no gas flow to the cell, four sequential additions of peroxide reduced the OMR from 100%-75%-52%-20%, respectively. In a second trial the OMR changed from 100%-84%-50%-22%, respectively. Larger additions of peroxide led to larger O_2 consumptions. By comparison, additions of peroxide to a carbonate solution did not affect the OMR.

2.2.2.5 Vanadium precipitation - The formation of the "black deposit"

2.2.2.5.1 The Effect of V^{4+}/V^{5+} Ratio on Vanadium Precipitation

Nine 250-ml of

concentrations were prepared from stock 0.42 M V^{4+} and 0.43 M V^{5+} in 25 gm/ℓ Na_2CO_3. The V^{4+}/V^{5+} volumetric ratio varied from 9:1 to 1:9 in a manner similar to the method of infinite variations. These solutions were allowed to stand at pH 9.0 ± 0.1 in 250-ml volumetric flasks fitted with greased ground glass stoppers at ambient temperature. After 21 days, a sample was taken of each supernatant liquid for the analysis of V^{4+} and V^{5+}. The analytical method used for the determination of V^{5+} consisted of reaction with excess Na_2S in a pH 8.5 carbonate buffer, addition to excess acidified I_2, and thiosulfate back titration to a starch endpoint. Each analysis was done in duplicate. Analytical details are available in Appendix 3. The determination of the total Vanadium content in solution by atomic absorption was found to be unreliable because deviations from Beer's law were dependent on concentration and/or matrix composition (see Fig. 19).

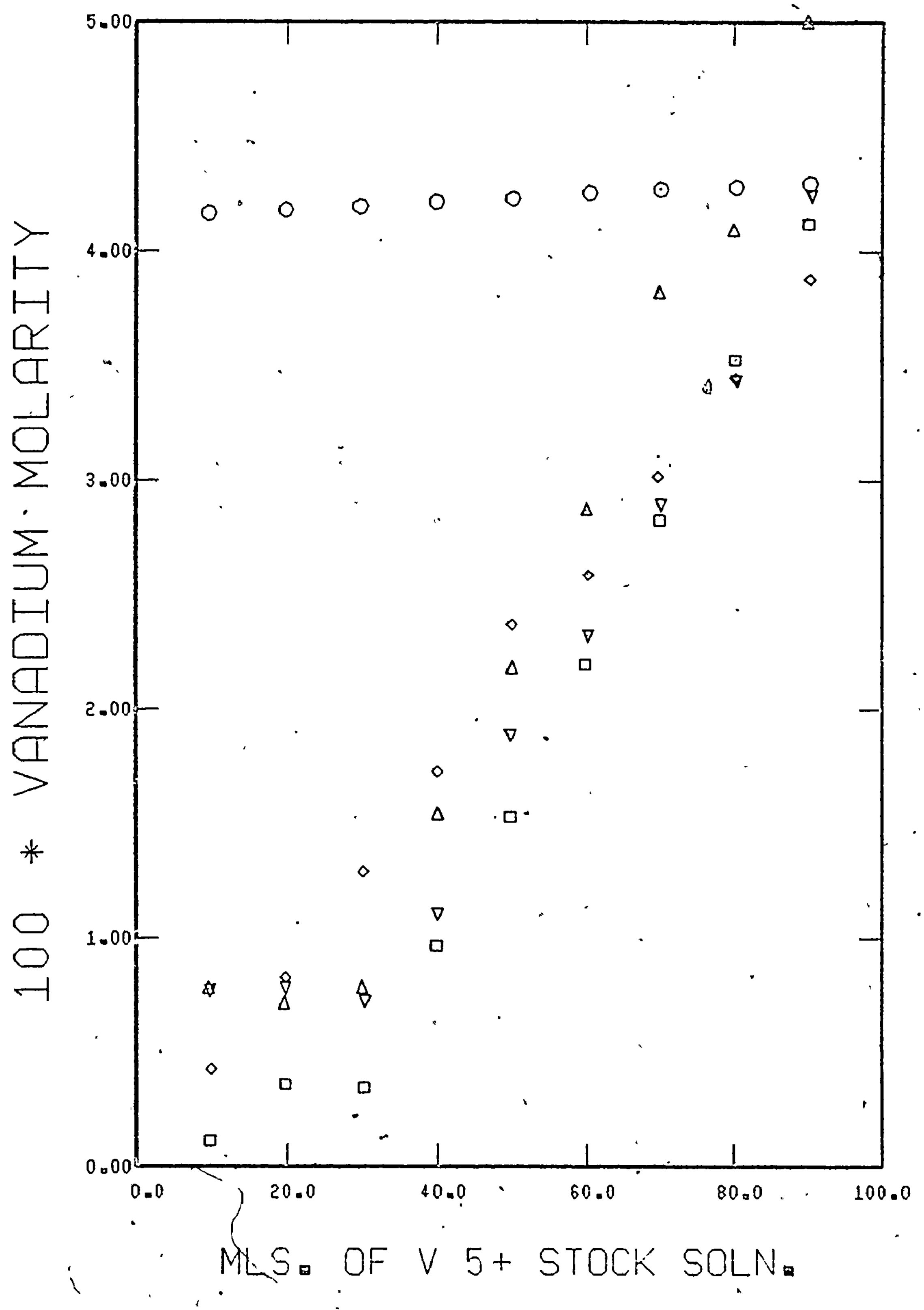
An apparatus for potentiometric titration with Fe^{2+} under N_2 was constructed. It was found that one can determine V^{5+} in the presence of V^{4+} by this method if no substance - such as citrate - oxidizable by V^{5+} in acid solution were present. Also, it was found that HNO_3 adversely affected the change on solution potential associated with the endpoint and therefore HNO_3/H_2SO_4 could not be used as a pre-oxidant. This procedure was replaced by the dropwise addition of $KMnO_4$ to a hot acidic solution.

The precipitates were collected on medium glass frit filters, dried at 140°C for 2 hours, weighed, and stored in a vacuum dessicator. A weighed sample (∿ 200 mg) of each of the eight precipitates was dissolved in the dearated titration matrix and titrated with Fe^{2+} to give the V^{5+} content. Oxidation of this solution with $KMnO_4$ converted all V^{4+} and Fe^{2+} to V^{5+} and

FIGURE 19 . Plot of Vanadium Concentration in Solution after Precipitation vs. Solution Composition

○ - Total Vanadium (calc. from stock soln)
△ - Total Vanadium (atomic absorption)
▽ - Total Vanadium (potentiometric titration)

◇ - Vanadium 5+ (calc. from stock soln)
□ - Vanadium 5+ (iodometric titration)


100 * VANADIUM MOLARITY
5.00
4.00
3.00
2.00
1.00
0.00
0.0
20.0
40.0
60.0
80.0
100.0
MLS. OF V 5+ STOCK SOLN.

Fe^{3+} allowing re-titration for total vanadium, giving V^{4+} by difference. The data is summarized in Table 3.

Sodium contents of the precipitates were determined with a Perkin Elmer flame photometer using 0-100 ppm NaCl solutions in 0.5 M HCl as standards.

The thermogravimetric analysis of 50 mg samples of the precipitates were done on a Stanton Redcroft TG-750 TGA over the range 20-400°C at 20°C/min. Water loss occurred at approximately 150-250°C. No other weight losses were observed to a temperature of 1000°C. The sample fused between 600-700°C. These data are summarized in Table 3.

In initial tests, the precipitates seemed to be slightly soluble in both concentrated and dilute NaOH, but tyndall effect tests and centrifugation later proved this to be a colloid or fine suspension. The material is soluble in water yielding a blue-green solution, and it is observed to decompose rapidly in acid solution with evolution of small amounts of gas. This was identified as CO_2 from the mass spectrum of the gas obtained by thawing 10 mls of 8% H_2SO_4 in the presence of 200 mg of the precipitate in an evacuated bulb. The CO_2 peak was 4 times the intensity of the water peak. The background spectra contained no traces of either H_2O or CO_2.

2.2.2.5.2 The Effect of pH on Vanadium Precipitation

Eight solutions with V^{4+}/V^{5+} ratio 2/1 and with a total vanadium concentration of ∿ 0.05 M were prepared under N_2 in 25 gm/ℓ. Na_2CO_3. The pH of the solutions were adjusted nominally to 8.0, 8.25, 8.5,...,10.0. Over the next several days, successive aliquots of these solutions were titrated for total vanadium content. An accurate determination of the pH was made

TABLE 3
VANADIUM PRECIPITATE ANALYSIS

SAMPLE NUMBER	WT. PPT.	% H_2O	% Na	% V_T	% V^{5+}
1	1.056gm	16.3	12.63	37.7	11.52
2	1.166	15.6	13.2	37.8	10.26
3	1.223	16.5	11.4	40.88	14.1
4	0.951	16.3	11.37	40.8	14.2
5	0.7915	24.3	11.25	36.23	12.77
6	0.652	15.6	11.96	39.67	13.58
7	0.4585	16.3	12.33	38.54	13.43
8	0.321	15.3	11.87	39.18	13.79
9	0.0	-	-	-	-
Avg.			12.00	38.85	12.956
st. dev.			0.685	1.608	1.39

$$V^{4+}/V^{5+} = \frac{38.85 - 12.956}{12.956} = 2.0 \pm .51$$

$$Na / V^{5+} = \frac{12.0}{12.956} = 0.92 \pm 0.15$$

on the third and last day of the experiment. The pH did not change appreciably over this period of time. The results are summarized in Fig. 20.

2.2.2.5.3 The Effect of Citrate on Vanadium Precipitation

Ten solutions were prepared with a pH of 9.5 as reported in 2.2.2.5.2, but containing additionally 1/10, 2/10, 3/10, ..., 10/10 molar ratios of citrate to total vanadium. Over the next several days, successive aliquots of these solutions were titrated for total vanadium. An accurate measure of pH was made after 4 days. The results are summarized in Figure 21.

2.2.2.5.4 The Effect of Buffer Strength on Vanadium Precipitation

Six solutions at pH 9.5 were prepared in carbonate buffer as reported in 2.2.2.5.2, but with buffer strength increasing from 0.05 M to 0.3 M in 0.05 M increments. The solutions were prepared with a $NaHCO_3$ stock solution using NaOH to increase the pH to 9.5 giving a controlled concentration of total carbonate by eliminating CO_2 evolutions due to additions of acid. Over the next several days successive aliquots of these solutions were titrated for total vanadium content. An accurate determination of the pH was made on the 6 th day. The results are summarized in Figure 22.

2.2.3 Discussion

2.2.3.1 The Effect of pH on Unbuffered Vanadium 4+/Citrate Solutions

The spectra of these solutions as a function of pH indicate that the V^{4+}/citrate complex begins to decompose at a pH as low as 7.4. Above this value, the time required for the convergence of the spectrum to a limiting value indicates that equilibrium is attained slowly. This data conforms to the observations of Ducret, who observed an endpoint at a pH of 2.8 in a titration of VO/citrate with hydroxide. The non-reproducibility of his

FIGURE 20. Plot of Fraction of Vanadium in Solution after Precipitation vs. Solution pH

○ - day 1

▽ - day 2

□ - day 3

◇ - day 6

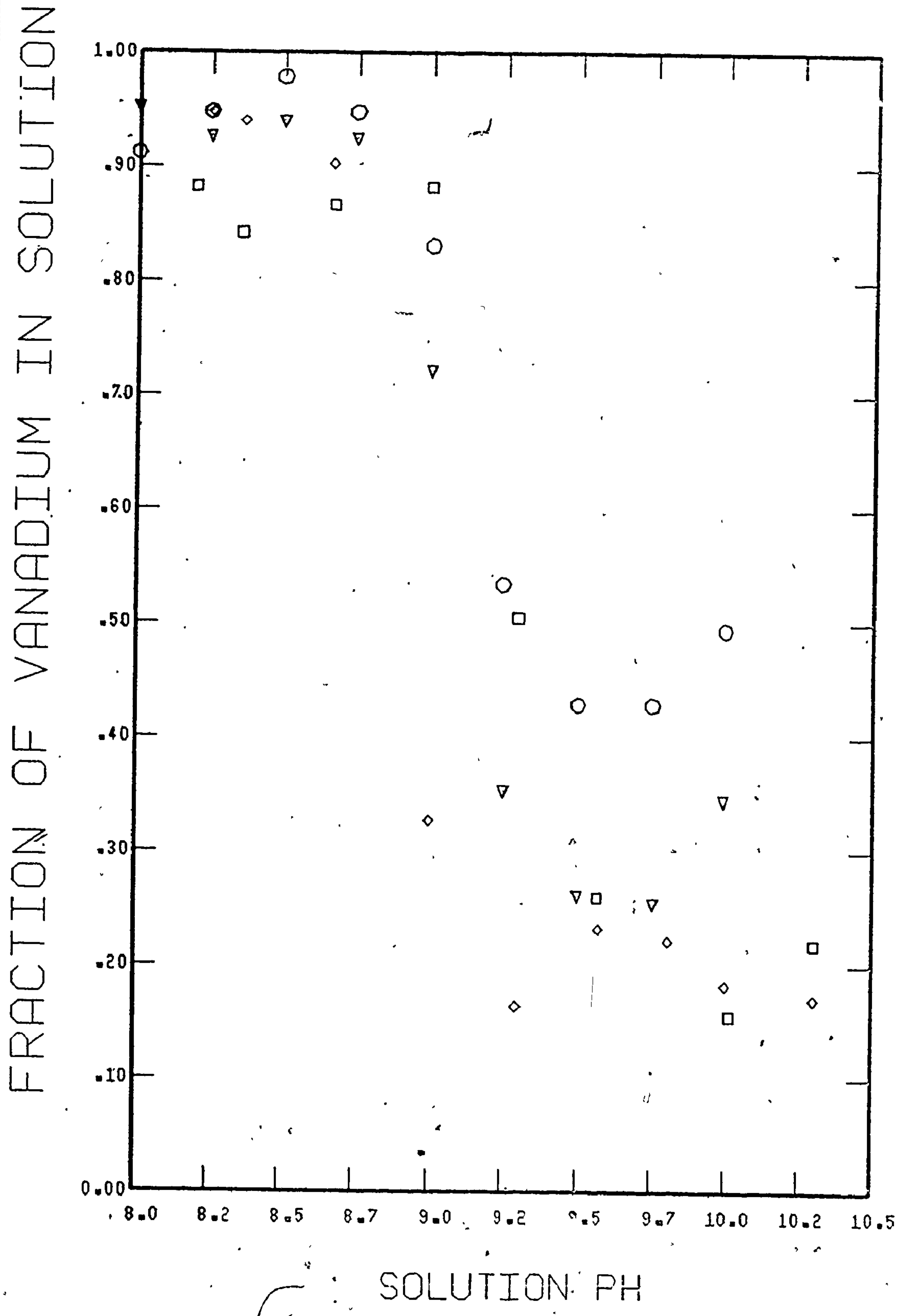

FRACTION OF VANADIUM IN SOLUTION
1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
0.00
8.0
8.2
8.5
8.7
9.0
9.2
9.5
9.7
10.0
10.2
10.5
SOLUTION PH

FIGURE 21. Plot of Fraction of Vanadium in Solution after Precipitation vs. Citrate / Vanadium Ratio

○ - day 1
▽ - day 4
□ - day 6
◇ - day 10

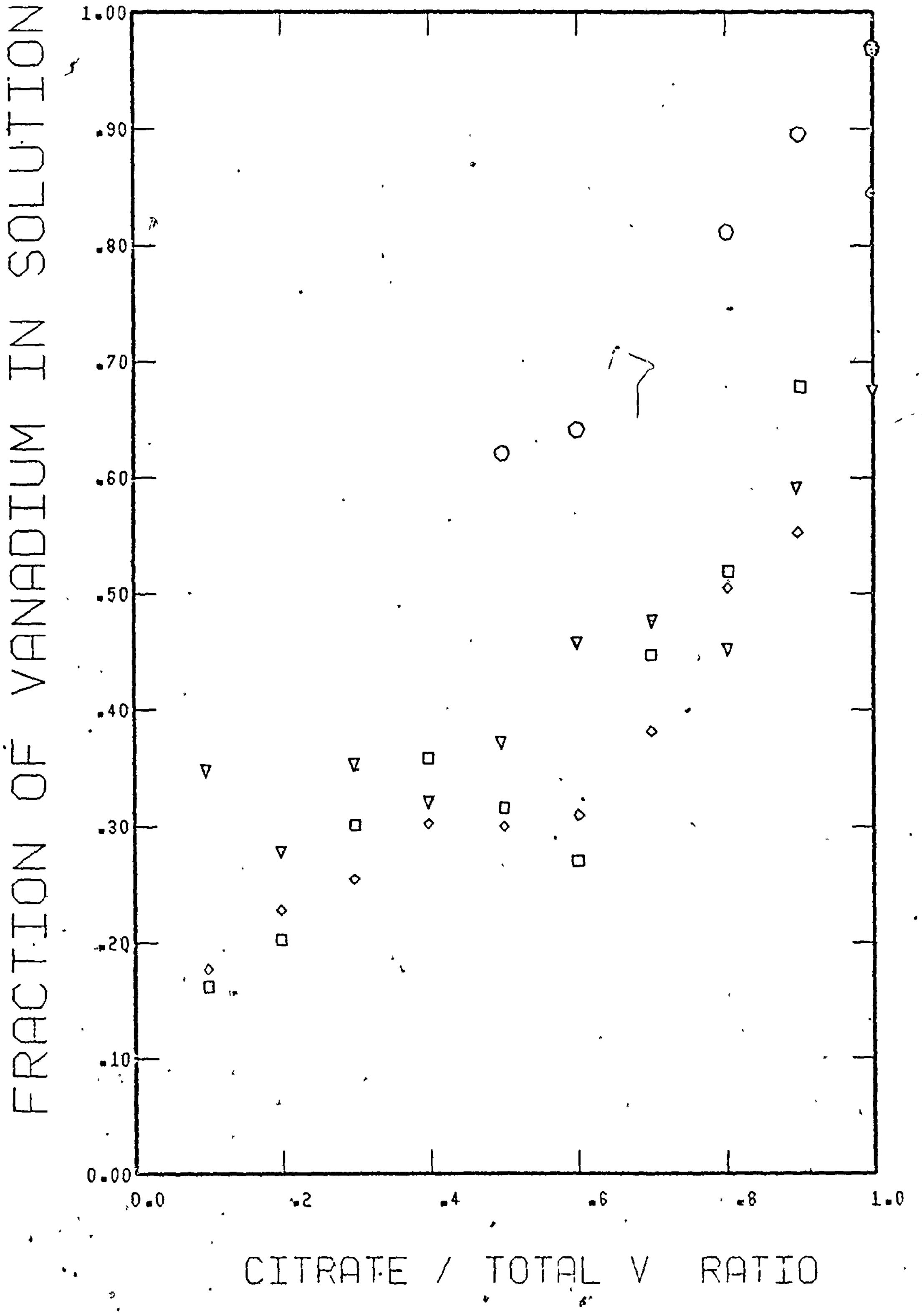
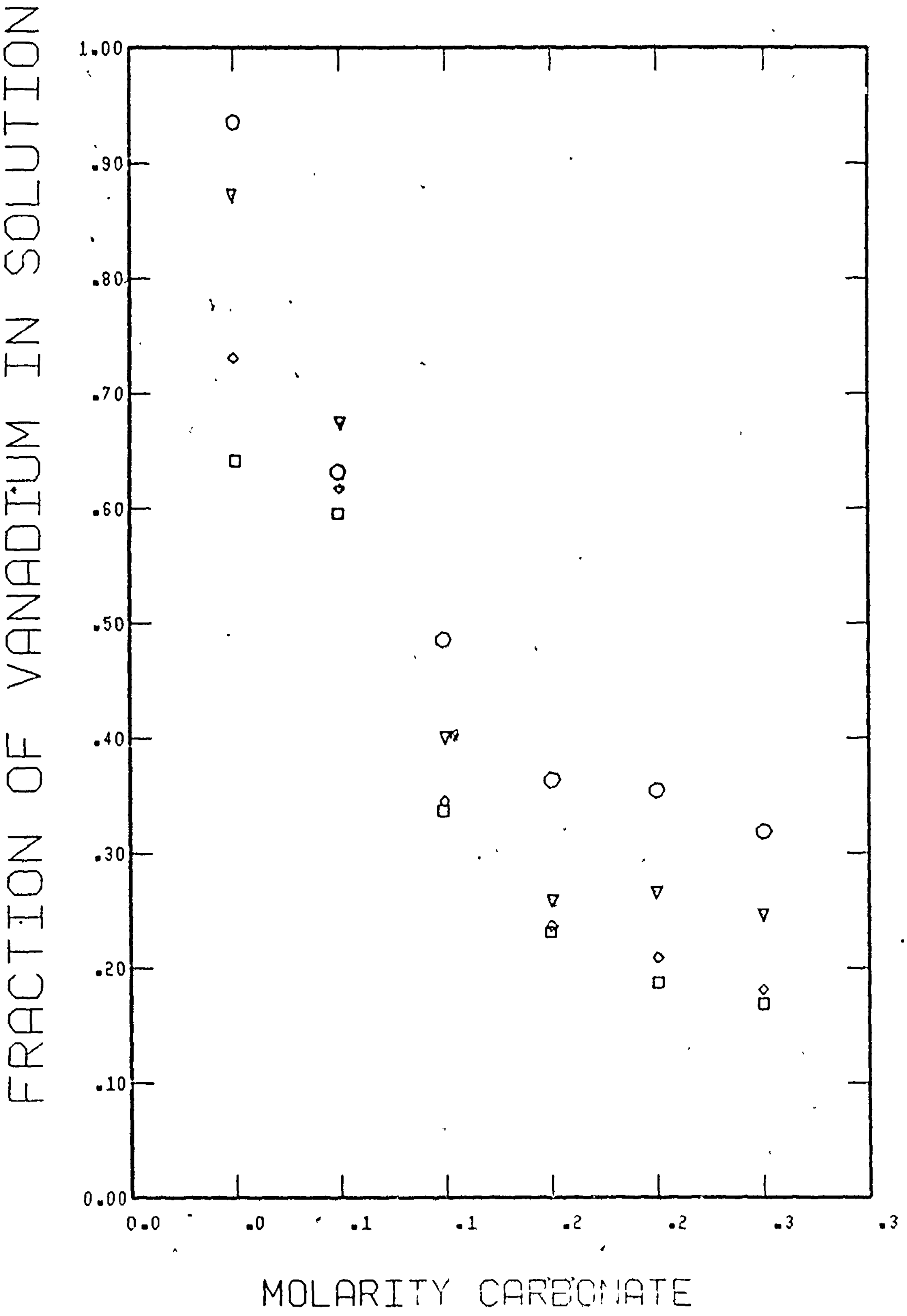

FRACTION OF VANADIUM IN SOLUTION
1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
0.00
0.0
.2
.4
.6
.8
1.0
CITRATE / TOTAL V RATIO

FIGURE 22. Plot of Fraction of Vanadium in Solution after Precipitation vs. Carbonate Buffer Strength

○ - day 1
▽ - day 2
□ - day 6
◇ - day 8


FRACTION OF VANADIUM IN SOLUTION
1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
0.00
0.0
.0
.1
.1
.2
.2
.3
.3
MOLARITY CARBONATE

titrations beyond this point can be explained by the existence of a sluggish equilibrium which would make the pH titration curve both a function of addition rate and temperature.

The slow reversal of the equilibria at neutral pH values may be explained by a slow reaction of citrate ion with V^{4+} anions. The fast reversal at low pH's is probably due to the breakup of V^{4+} anions into forms that can react readily with citrate, thusly re-establishing the complex.

2.2.3.2 The Effect of pH on Buffered Vanadium 4+ Citrate Solutions

The presence of carbonate as a buffer is seen to extend the stable range of stability of V^{4+}/citrate complex by about 2 pH units above pH 7.4. This behavior can be explained by the simultaneous complexation by both citrate and carbonate. The V^{4+}/citrate/carbonate species in solution are shown to be involved in a pH dependent equilibrium over the interval pH 8-9.5. A straight line plot, consistent with an acid/base equilibrium was found when the absorbance at 560 nm was plotted against $1/H^+$. If the K_a of the acid moiety is $< H^+$, then the following model is consistent with the observations.

$$\text{Abs.} = HA\varepsilon_1 \ell + A^- \varepsilon_2 \ell$$

$$= (C-A)\varepsilon_1 \ell + A^- \varepsilon_2 \ell$$

$$\text{Abs.} = C\varepsilon_1 \ell + \frac{K_a C(\varepsilon_2 - \varepsilon_1)\ell}{(H^+ + K_a)}$$

K_a = acid dissoc. constant; HA, A^- = acid, base form; $C = [HA] + [A^-]$;
$\varepsilon_1 \varepsilon_2$ = extinction coefficient of acid and base form; ℓ = path length.

This does not allow the identification of the species involved, but it seems the most likely process occurring is the deprotonation of a bicarbonate ligand ion or a trans aquo ligand bound to [VO Cit]$^-$. The individual extinction coefficients (and therefore the K_a) cannot be calculated because of the instability of the species at high pH values where only the base form should exist, and the nature of carbonate buffers in the low pH region where only the acid form should exist.

The increase in the absorbance of the V^{4+}/citrate/carbonate solution that is observed above pH 9.4 is similar to that observed with the V^{4+}/carbonate above pH 7.4 in that the absorbance increases at all wavelengths from 400-650 nm. In the case of the citrate complex the changes occurredmuch more slowly, and the solution did not develop the characteristic brown colouration of the V^{4+} anions during the > 30 hours of observation, but remains a black-blue solution. This is not conclusive proof that some other form exists since, for example, a slow air leak into the apparatus would allow the production of some V^{4+}/V^{5+} material giving a blue solution colour. Alternatively, if only small conversions had been observed, the combination of the V^{4+}/citrate /carbonate and V^{4+} anions could give the same solution colouration. This work was discontinued because the present apparatus was not reliable over a long enough period of time to produce valid experimental results. The differences in spectra and lability toward air oxidation between V^{4+}/cit/carbonate and V^{4+}/carbonate at pH's above their stable range leaves open the possibility that a different process (i.e., dimerization to $(\text{VO cit})_2^-$) may be taking place when the vanadyl ion is complexed by citrate.

The difference in metal/ligand complex stability at pH's close to the design value of Stretford plants can have serious ramifications in plant performance. If no metal complex exists, the Vanadium 4+ is free to precipitate from the solution as the "black deposit". Also, the form of Vanadium 4+ generated in the solution as a result of the reduction of V^{5+} with H_2S is expected to depend on pH. It has been demonstrated that essentially all V^{4+} present in solution can exist as the citrate complex if the solution preparation and storage is carried out below pH 9.4. If the solution is prepared above pH 9.4 in a high pH process liquor, some distribution (not necessarily an equilibrium distribution due to the slow rates of reactions) among V^{4+} forms may exist. This may be the case in the *in situo* generation of V^{4+} in high pH process liquors, and may allow some fraction of the V^{4+} to be in a form which can precipitate easily. It is possible, therefore, that above pH 9.4 citrate cannot prevent the production of some precipitate, while below pH 9.4 V^{4+} can be complexed in a form which cannot precipitate.

2.2.3.3 The Uncatalysed Air Oxidation of Buffered V^{4+} / Citrate Solutions

From Fig. 18a it is seen that the rate of V^{4+}/citrate/carbonate air oxidation varies directly with hydroxide. Taking the saturated O_2 concentration to be 2.5×10^{-4} M, a value of the rate constant, k, of equation 30 is calculated to be $6.7 \times 10^{2}\ \text{min}^{-1}$, assuming first order dependence on

$$\frac{dV^{4+}}{dt} = k[V^{4+}][OH^-][O_2] \tag{30}$$

oxygen.

The duplication of spectrum and rate data after reduction with sulfide indicates that the V^{4+}/citrate/carbonate complex is not modified by the redox cycle involving V^{4+}, V^{5+}, $S^{=}$ and O_2. This also indicates that the V^{4+} complex prepared from analytical reagents is probably the same as that which exists in Stretford plants at the design pH.

The presence of thiosulfate and thiocyanate at concentration levels approximately 6 and 12 times the initial vanadium 4+ molarity did not appreciably affect the rate of oxidation - indicating no complexation formation. The effect of $SO_3^{=}$ is unknown because of an enhanced solution O_2 demand although this in itself may indicate an increase in the concentration of reactive oxidizing species, a condition that would probably lead to enhanced Vanadium 4+ oxidation rates. A special case of this phenomena with peroxide has been studied (vide infra).

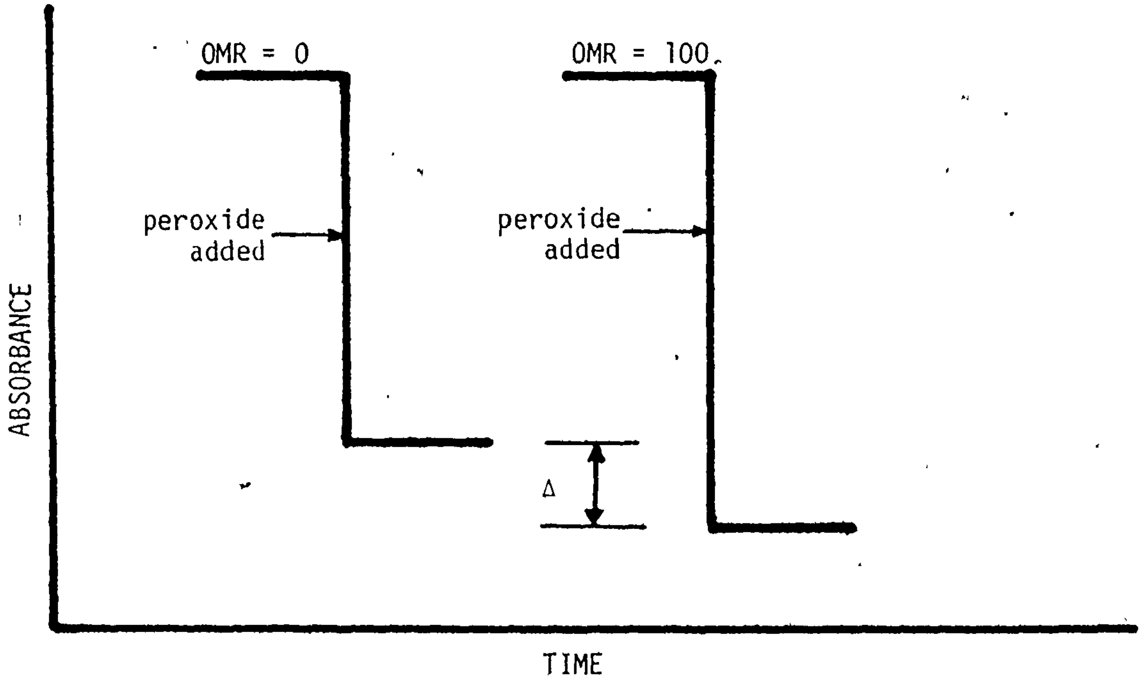
The lability of the citrate complex to air oxidation may indicate that this is the most desirable form of Vanadium 4+ in a Stretford solution since it combines this property with stability toward precipitation. Verification of this statement would require knowledge of the range of pH's at which this complex is the predominate product of the V^{5+}/H_2S reaction, and the effectiveness of the quinone catalyst with this form.

2.2.3.4 The Catalysed Air Oxidation of Buffered V^{4+} / Citrate Solutions

To effect the one electron oxidation of V^{4+} to V^{5+} with oxygen ($4e^-$ per molecule), one must admit the necessity of at least four elementary reaction steps. These reactions are most likely a series of radical reactions that would involve such reactive intermediates as H_2O_2, $\cdot HO_2^-$, O_2^- and $\cdot OH$. A potential catalyst would be any substance that enhances the production of one or more of these species from dissolved molecular oxygen.

We observed enhanced oxygen consumption upon the addition of hydrogen peroxide to aerated V^{4+} solutions. This indicates that some vanadium intermediate is reacting with oxygen or that O_2 is activated by reaction with some peroxy or peroxy-derived intermediate. The extent of this interaction can be seen from the following.

A 25% reduction of the solution oxygen content, as described in section 2224 , corresponds to approximately 2.5×10^{-4} electrical equivalents, or 2.5×10^{-4} moles of V^{4+} which can be oxidized by the molecular oxygen that is consumed. Each aliquot of peroxide added was observed to oxidize about 1/20 of all the total initial analytical amount of V in solution (0.0218 moles) or approximately 0.00109 moles. From this we can calculate that the V^{4+} oxidized by oxygen is about 23% of the amount oxidized by peroxide alone. This expected value corresponds well with the 20-30% increase in V^{4+} absorbance change observed when the solution was aerated. This is diagrammed below.



This "extra" O_2 consumption, Δ, at pH 9.0 appears to be much less than that at pH 8.0. The reason for this is at present not clear, however, it may be that the V^{4+}/citrate/carbonate species predominant at this pH is more labile and is competing more efficiently with oxygen for the reactive substrate.

2.2.3.5 Vanadium Precipitation - The Formation of the "Black Deposit"

The interpretation of the data in Fig. 19 and Table 3 is straightforward. The precipitate yield was maximized at solution V^4/V^5 ratios near 2/1, and all resulting precipitates had V^4/V^5 ratios of 2/1. The results of the analysis for Na, V^5, V^4 and H_2O (Table 3) fit the elemental formula for a viable compound -$NaHV_2O_5VO_3 \cdot 3.5H_2O$- within experimental error. This formula allows for an ∿ 0.5% Na_2CO_3 content to account for the gas liberated upon dissolution on acid. The results of the gas trapping experiment allows a rough estimation of CO_2 by comparison of the mass spectrum peak heights of CO_2 and H_2O (4:1) assuming that the concentration of H_2O in the trapped gas is that of the vapour pressure of H_2O above 8% wt. H_2SO_4 at 0°C. This assumes that the ionization efficiencies of CO_2 and H_2O at 80 ev in the source are equal and that the gases behave ideally at the low pressures involved.

Using

$$n_{H_2O} = \frac{P^*_{H_2O} V}{RT}$$

and

$$Wt_{NaCO_3} = n_{H_2O} \times 4 \frac{CO_2}{H_2O} \times \frac{106 \text{ gm } NaCO_3}{\text{mole } CO_2}$$

one obtains

$$\frac{4\ (0.185)}{760\ (0.082)(300)} \times 4 \times 106 = 1.7 \times 10^{-2}\ \text{gm} = \text{wt}\ Na_2CO_3$$

This corresponds to approximately 10% of the 200 mg sample, much higher than that allowed by the composition given in table 3.

It is possible that the black deposit may have the formula of the hexacondensed ion described by Ostrowetsky,[10] (page 37) co-precipitated with sodium carbonate. On the basis of vanadium and sodium balances, one can calculate, for example, that an 89%/11% mixture of vanadyl vanadate[10]/ sodium carbonate trihydrate would explain both the elemental analysis and the gas evolution. The possibility of co-precipitation is interesting since it could explain the variable nature of elemental analysis of different black deposits.

Figure 19 gives data for the estimation of the solubility product of the black deposit in 0.25 M Na_2CO_3 at pH 9.0. The value of Ksp = $[V^{4+}]^2[V^{5+}]$ is found to be $8.1 \pm 6.5 \times 10^{-8}$, based on the analysis of 7 of the supernatant liquids after 21 days of digestion at room temperature.

From Fig. 20 it can be seen that vanadium precipitation from citrate free solutions varies as some function of pH. The chemical changes that are occurring in solution are not known at this time, although the dramatic increase in the amount of precipitation over the range pH 8.6 - 9.0 suggests a greater than first order dependence on hydroxide concentration.

From the data in Fig.20 one would predict the very efficient production of V^{4+}/V^{5+} precipitates in process liquors above pH 8.6 that are deficient in citrate. This would be true especially if the liquor did not become fully oxidized and fully reduced during each plant cycle (approximately 1-2 hours), since V^{4+} and V^{5+} would be present in solution simultaneously for extended periods of time. At pH 10, the solution vanadium content was reduced by 50% in only one day - a short period of time compared with occasional off-optimal run times in process plant operation.

As can be seen from Fig. 22 , the extent of precipitation is dependent on the buffer strength of the solution at a constant pH value. Because of the experimental uncertainty and narrow range of concentrations used, the functional relationship between the two values cannot be determined with any certainty. The increase in precipitation with increase in carbonate concentration does lend support to the idea of co-precipitation of sodium carbonate with the black deposit. An alternative interpretation is that of a pH limiting batch reaction, in which OH^- is consumed by the precipitation. An increase in buffer strength would allow more precipitation to occur for the same decrease in hydroxide concentration. It may be possible to distinguish between these and other possibilities by the analysis of precipitate compositions prepared under a wide range of carbonate concentrations and alternative buffers.

A pH of 9.5 was chosen to study the extent of precipitation on systems which were not deficient in citrate, because this value is slightly beyond the stable range of the V^{4+}/citrate/carbonate complex. As can be seen from Fig. 21 , the presence of citrate under these conditions does not prevent the formation of the black deposit, even at citrate / V^{4+} ratios of 1.35. One anomalous point appears in this data.

Solution #10 with a citrate / V^{4+} ratio of 1.5 had a measured pH of 9.19. This solution exhibited the typical clear blue colour of the V^{4+}/citrate/carbonate solutions, and showed no evidence of precipitation by either deposition, millipore filtration or Tyndall beam dispersion. Precipitate was clearly visible in all the other solutions. This further illustrates that below pH 9.4, citrate is an effective complexing agent for Stretford liquors, while above pH 9.4, some vanadium is present in a form which can precipitate.

CHAPTER 3

STUDIES ON SULFUR PRODUCTION IN STRETFORD SOLUTIONS

3.1 INTRODUCTION

Sulfur precipitated by chemical reaction in homogeneous solutions is blue-grey to dull yellow in colour depending upon the particle size distribution of the precipitate and can have a purity in excess of 99.9%. This is comparable to "bright yellow sulfur", the allotropic mixture produced by the rapid cooling of a melt. Circulating industrial liquors are rarely homogeneous, since any system in closed recycle will accumulate a contaminant unless provision is made for its removal at the same rate as its input. In the case of a liquid redox plant, for example, a shot of heavy oil (i.e., non-volatile mist) reaching the absorber may become dispersed in the solution. Since the product sulfur is produced in and frothed from this solution, it can easily become contaminated with the dispersed component. In order to obtain a salable product from the collected sulfur slurry, it is usually filtered, washed and autoclaved giving a "bright yellow sulfur" product. It should also be noted here that during the formation of sulfur product , the physical characteristics of the sulfur become as important as the chemical characteristics of the species in solution. Any input which affects the physical properties of the colloid can have as devastating effect on sulfur production as the loss of one of the chemical species involved in the solution reactions. An example of this might be the injection of a surface active agent which stabilizes the sulfur colloid, effectively terminating sulfur precipitation, floatation and filtration. In a case such as this, sulfur may be produced chemically but none could be collected from the solution until the colloid were de-stabilized.

Sulfur is formed in the Holmes-Stretford process liquor by the reaction of V^{5+} with H_2S and/or related sulfur species such as HS^-, HS_xS^-, etc. A preliminary study of the V^{5+}/H_2S reactions in the pH range of a normal operating plant was initiated. These experiments were designed to detect gross changes in sulfur production as a function of pH and solution composition. The time required for an equi-normal $S^=/V^{5+}$ solution to precipitate sulfur was chosen as an indication of reaction rate. This was based on numerous reports in the literature, verified in the laboratory with S°-saturated Na_2S, that the average chain length in sulfur saturated polysulfide solutions is ∿ 3.6 $S^\circ/S^=$. This corresponds to ∿ 78% of all original $S^=$ oxidized to S° at equilibrium, giving an analogue to the half-life for comparison of rate data. It was also considered probable that the V^{5+}/H_2S reaction might follow a simple kinetic model, since it would seem unlikely that the anionic V^{5+}-containing moiety would react with a sulfur anion (HS^-, $S^=$, HS_xS^-, etc.) at a rate comparable to molecular H_2S. If, for example, the rate were first order in H_2S, one would expect a first order dependence on hydroxide due to the acid/base dissociation of H_2S. This would allow estimation of the pseudo first order rate constant of the reaction.

3.2 Experimental Details and Results

3.2.1 Allotropic Form of Recovered Sulfur

A standard Stretford liquor was prepared and taken through one full redox cycle at room temperature producing ∿ 0.5 gm precipitated sulfur. This was collected by filtration, water washed and dried unver vacuum. A powder X-ray photograph of the sample was obtained and compared to the known powder patterns of the allotropes of solid sulfur. The results are presented in Table 4.

3.2.2 Reaction of V^{5+} with H_2S in Stretford-like Solutions

Separate stock solutions of V^{5+}, citrate and Na_2S were prepared and standardized. Dilution of the calculated titre of each of the desired stock solutions shown below yielded a reaction mixture which was 0.010 N in each reagent.

	Stock Concentration	Titre (ml)	Concentration in 200 ml.
V^{5+}	0.191 M	19.47	0.010 N
Citrate	1.0 M	10.0	0.010 N
Na_2S	2.17 M	0.426	0.010 N
Na_2CO_3	200.0 gm/l	25.0	25.0 gm/l

A 200 ml sample of V^{5+}/carbonate or V^{5+}/citrate/carbonate was introduced into a well-stirred container under N_2. The pH controlling apparatus was used to bring the pH to a preselected constant value. After equilibration, the required titre volume of Na_2S was injected into the reaction solution with an 0.5 ml syringe, initiating the sulfur-producing reactions. An

Table 4

Literature	Intensity (%)	Observed	(Intensity)
7.69	6	--	
5.76	14	5.7	w
5.68	6	--	
4.80	2	--	
4.19	2	--	
4.06	12	--	
3.91	12	--	
3.85	100	3.85	vs
3.57	8		
3.44	40	3.44	M
3.38			
3.32	25	3.35	M
3.21	60	3.21	s
3.11	25	3.11(d?)	w
3.08	13	--	
3.06	2	--	
2.842	18	2.85	M-w
2.688	2	--	
2.673	2	--	
2.621	14	2.64	M-w
2.614	4	--	
2.569	8	2.59	vw
2.501	8	2.51	M-w
2.424	14	2.44	M-M
2.404	2	--	
2.375	4	2.38	w
2.336	4	--	
2.215	2	--	
2.146	4	2.15	vw
2.112	10	2.12	M-w

Continued......

Table 4 (Continued)

Literature	Intensity (%)	Observed	(Intensity)
2.098	2	--	
2.057	2	--	
2.041	2	--	
2.003	2	--	
1.988	4	2.0	vw
1.957	2	--	
1.926	2	--	
1.900	8	1.82	w
1.856	2	--	
1.838	2	--	
1.823	4	1.82	w
1.781	2	1.79	vw
1.754	8	1.76	w
1.725	8	1.72	w
1.698	8	1.7	w
1.665	2	--	
1.658	2	--	
1.647	6	1.65	vw
1.662	6	1.62	vw
1.607	6	1.61	vw
> 1.601	< 4		

unbiased measure of the time to precipitation was obtained by the apparatus shown in Fig. 23. The beam from a helium/neon laser (6328 Å) was directed through the reaction cell through a red filter to a CdS photo-conductive cell (200 Ω to 1.5 x 10^6 Ω). The precipitation of sulfur caused beam dispersion with a corresponding increase in resistance of the light sensitive resistor. A strip chart recording of the voltage drop across the resistor could be obtained as a function of time. Results are summarized in Fig. 24.

3.3 Discussion

3.3.1 Allotropic Form of Recovered Sulfur

Table 4 gives a comparison of the powder X-ray pattern of sulfur produced in and recovered from a synthetic Stretford liquor. Because no extraneous lines appear in the powder pattern at positions expected for other sulfur allotropes, it can be said - with a high degree of certainty - that the sulfur sample is composed of crystalline orthorhombic S_8. This suggests that a model of the solution chemistry include S_8 production, most probably by elimination from polysulfide molecules with subsequent crystallization and precipitation.

3.3.2 Reaction of V^{5+} with H_2S in Stretford-like Solutions

3.3.2.1 The Effect of Citrate on the Reaction of H_2S with V^{5+}

Comparison of the time required for sulfur precipitation from V^{5+}/citrate/carbonate and V^{5+}/carbonate solutions allows an estimation of the effect of citrate on the V^{5+}/H_2S reactions. These times are given as a function of pH in Fig. 24.

FIGURE 23. Laser Apparatus for the Detection of Sulfur Precipitation

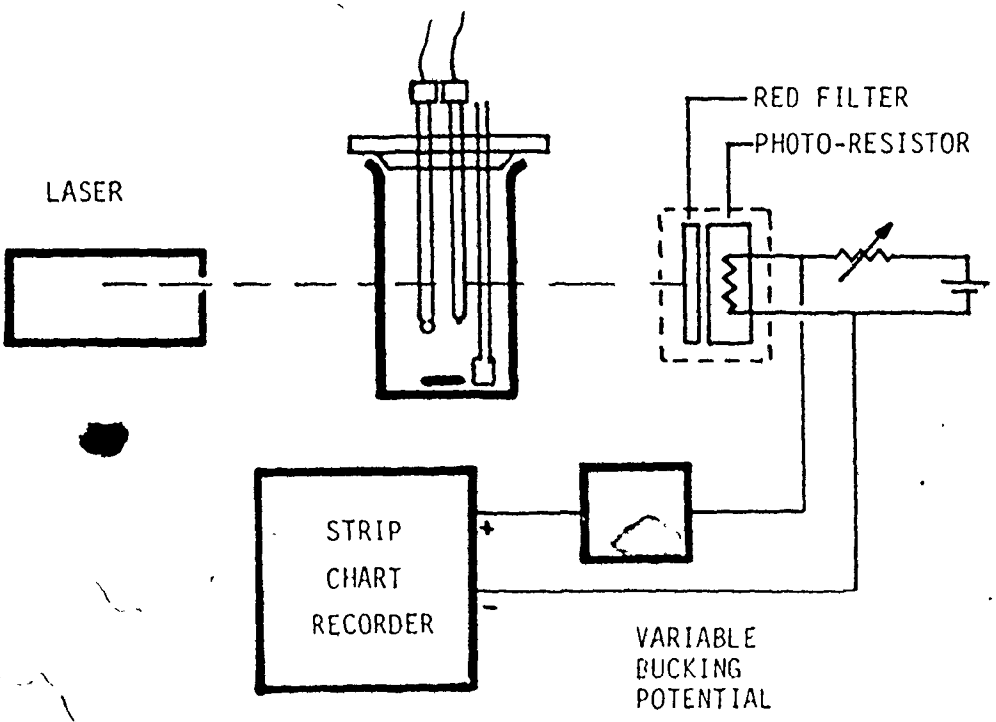
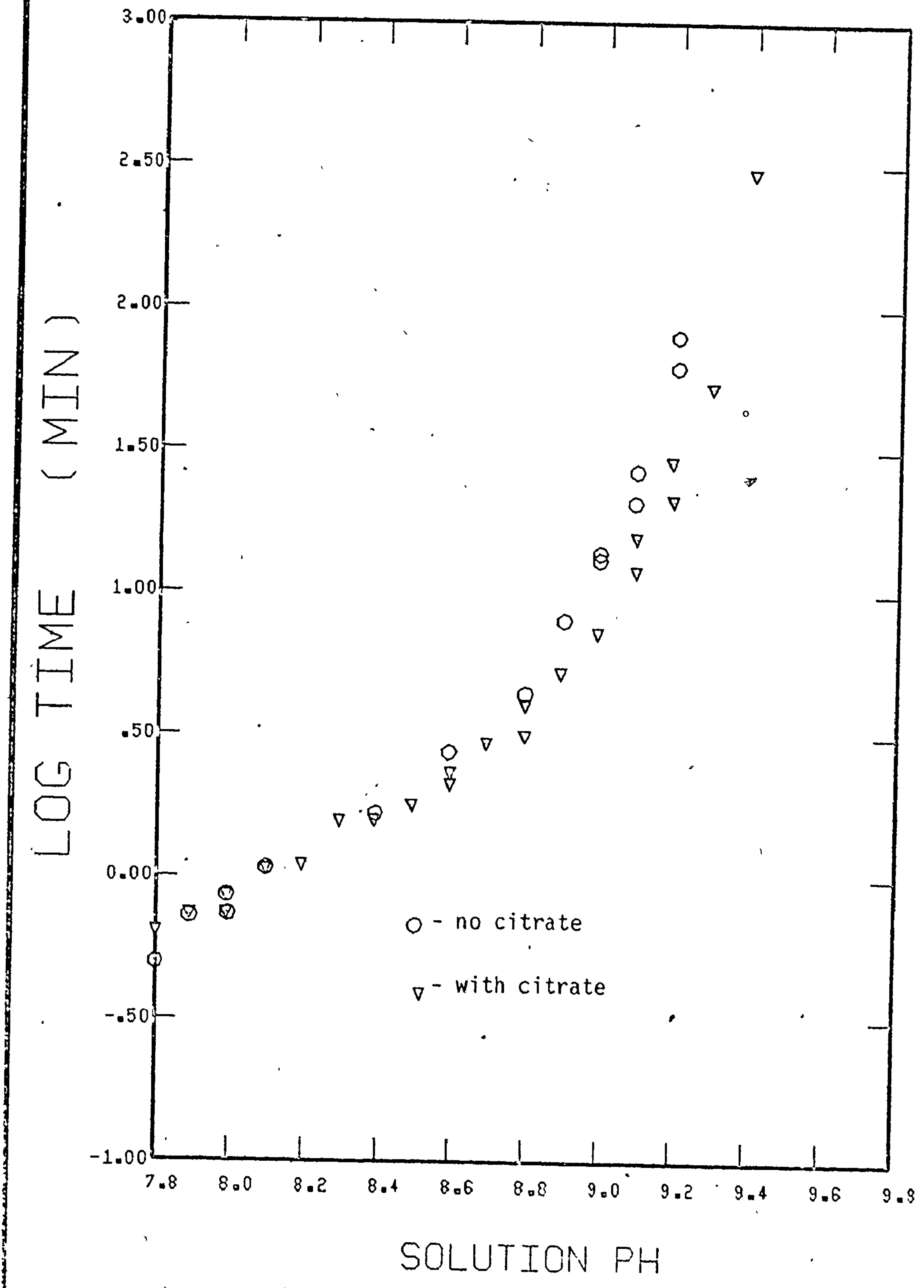

RED FILTER
PHOTO-RESISTOR
LASER
STRIP CHART RECORDER
+
−
VARIABLE BUCKING POTENTIAL

FIGURE 24. Plot of Log Time to Sulfur Precipitation vs. Solution pH


LOG TIME (MIN)
3.00
2.50
2.00
1.50
1.00
.50
0.00
-.50
-1.00
7.8
8.0
8.2
8.4
8.6
8.8
9.0
9.2
9.4
9.6
9.8
SOLUTION PH
○ - no citrate
▽ - with citrate

During the course of the reaction between V^{5+} and H_2S, the concentration of V^{4+} increases, thus one might expect that V^{5+}/V^{4+} interactions would become an important consideration, and indeed different reaction solution colours are observed with and without citrate present. When the concentration of polysulfide (brown/orange solution; $\varepsilon \sim 2000$) decreases to a point where the absorbance of vanadium 4+ ($\varepsilon \sim 50$) becomes important, the solution appears green. At a later point in time - at lower polysulfide concentrations - both solutions appear blue, with the familiar blue colouration of V^{4+}/citrate/carbonate solutions in the presence of citrate and with the citrate-free solution showing at higher pH's a much "darker" blue colouration (i.e., broader and more intense visible absorption). At lower pH, early precipitation of sulfur masks the solution colourations. The blue colouration in citrate-free solutions at pH > 7.4 may be due to V^{4+}/V^{5+} interactions, since at these pH's V^{4+} anions and polysulfides would be expected to impart a brown colouration. This effect does not seem to be accompanied by significant differences in overall rate, since the time to precipitation is not significantly effected by the presence of citrate.

Further investigation into this effect is warranted since it may give insight into the rate and extent of V^{4+}/V^{5+} interactions in systems which are deficient in citrate. Some possible explanations may be that:

1) the formation constant of the V^{4+}/V^{5+} complex may be small so that only a small fraction of the unreacted V^{5+} is associated with the V^{4+} during the course of the reaction, or,

2) the rate of reaction of the complex with H_2S is near that of the uncomplexed V^{5+}, or,

3) the rate of formation of the V^{4+}/V^{5+} complex may be sufficiently slow that during the course of the experiment only a small fraction of the V^{5+} becomes associated with V^{4+}.

3.3.2.2 The Effect of pH on the Reaction of H_2S with V^{5+}

As can be seen from Fig. 24 the time to precipitation of S produced by the V^{5+}/H_2S reaction increases dramatically from ∿ 0.5 min to > 200 min over the pH range 8-9.5. The simple model on which the experiment was designed is inadequate to handle the large increases in time observed. The results do, however, suggest the direction that future experiments should take. Firstly, since the absence of citrate as a complexing agent does not appear to change the results, it should be possible to determine the extent of reaction directly by titration of an acid quenched reaction aliquot for V^{4+}/V^{5+} ratio as per the method described in Appendix III. This is far superior to monitoring the time to precipitation as a measure of reaction rate, since the latter may or may not occur at the same percent oxidation at all pH levels.

Secondly, since determination of the V^{4+}/V^{5+} ratio allows an unambiguous measure of the extent of the reaction, this can be used to study the behaviour of polysulfide solutions in carbonate buffer, and especially the conditions under which sulfur will be precipitated from Stretford-like solutions.

3.4 Future Work on the Vanadium/Sulfur Chemistry of Stretford Solutions

3.4.1 Introduction

It has become obvious that the understanding of the V^{5+}/H_2S chemistry in Stretford solution requires an understanding of the nature of aqueous polysulfide solutions as a function of solution pH and degree of oxidation ($S°/S^=$ ratio, chain length, etc.). Because of very recent reports on the speciation in polysulfide solutions and the apparent lack of influence of citrate on the V^{5+}/H_2S reactions, this promises to be a very fruitful area of investigation in Stretford chemistry, and one which can have practical benefits in the design and optimization of process plant operations. For example, if the kinetics were known, one could optimize the delay time between absorber and oxidizer with respect to sulfide/polysulfide reaching the oxidizer and could conceivably reduce the rate of sulfur fixation. This increase in the efficiency of performance would reduce liquor disposal and replacement requirements of the plant, providing both economic and environmental benefits.

To this end, background information on polysulfide solutions has been collected which should allow the design of experiments that will yield maximum information.

3.4.2 The Nature of Polysulfide Solutions

Elemental sulfur can exist in many catenated or polymeric forms with the thermodynamically most stable allotrope at STP being a rhombic molecular lattice of S_8 rings. In addition to the crystalline modifications of S_8 and S_6 rings, sulfur can exist as linear polymers of divalent atoms, $S_x^°$, in both solid and liquid states.[29]

Liquid sulfur exhibits a maximum in viscosity as a function of temperature that is explained on the basis of linear chain formation from S_8 rings followed by chain length reduction as the boiling point is reached. The maximum is presumed to occur near the point of maximum average chain length. Sulfur vapour in equilibrium with the liquid is a mixture of linear chains of S_8, S_7, S_6, etc., with the average chain length decreasing with increasing temperature.[30]

In these cases, linear chains are formed by the homolytic cleavage of an S-S bond, giving the polymer a diradical character. These radicals can attack other ring structures enlarging the chain, or can undergo ring closure by reaction within the chain, producing an S_x ring (usually with $x = 8$) and a shortened chain. At any temperature, an equilibrium will be established, the rate of reaction being determined by the rate of fission of S-S bonds. This is observed to increase with increasing temperature consistent with an increase in steady state concentration of sulfur radicals. The enthalpy of formation is estimated to be 3.2 kcal/gmole of S_8 incorporated into the chain. This change is quite low because a polymeric bond similar to the S_8 bond is formed giving a small net change in energy.[31]

Ionic species are not considered to be of importance in elemental sulfur where all atoms have formal zero oxidation state. If, however, the end group of a catenated specie is not a sulfur atom, ionic species can be formed via heterolytic cleavage of the S-X or S-SX bond. The primary example of these are the polysulfanes of the form HS_xH. These molecules are stable in aqueous alkaline solution only as an anion and decompose to H_2S and the element on acidification. The acid/base characteristics of the polysulfanes are summarized in Table 5.

The existence of ionic species in polar media allows equilibration among sulfur species by nucleophilic displacement of an S-S- bond

Table 5

pK Values of the Polysulfanes*

Sulfane		T°C	pK_1	pK_2	Ref.
H_2S †	0	25°	7.0 6.83	17.1 14.0	37 39
H_2S_2	0.1(KCl)	25	5.0	9.7	38,39
H_2S_3	0.1	20	4.2	7.5	38,39
H_2S_4	0.1	20	3.8	6.3	38,39
H_2S_5	0.1	20	3.5	5.7	38,39

† pK_2 ranges $12.2 < pK_2 < 15$

* from Hoffman[34]

as illustrated in reaction 31.

(31) $-S-Sx-S-S-S-S^{-} + S^{=} \longrightarrow -S-Sx-S^{-} + {}^{-}SSSS^{-}$

Systems such as CH_3-S_x-CH_3 that exclude $S^{=}$ and nucleophiles are observed to achieve equilibrium among x values in ∿ 1300 hours, with x taking the values 1, 2, 3, 4, 5 and possibly higher.[32] This time requirement is reduced to about 10 hours by the addition of a stable free radical or an organic peroxide. At higher temperatures the equilibration rate is increased, again consistent with increased concentration of sulfur radicals from thermal equilibration with the surroundings. By comparison, Na_2S_2 was observed to equilibrate in aqueous solution within 0.01 seconds to give mono-, tetra-, and penta-sulfides as the only detectable products.[33] This was rather a significant finding since the di- and tri-polysulfides were not detected in the equilibrium mixture, and the rate of equilibration was at least 6 orders of magnitude faster than in the non-aqueous systems. It is difficult to rationalize a kinetic model that allows only medium length polymers via a chain buildup process without giving a distribution among shorter and longer chains. Up to this time, the concept of a distribution in x values had inherently supposed that significant amounts of all possible molecules were present at all times. Discussions of sulfur formation made reference to distributions in terms of short and long chains. The criteria for sulfur production was then assumed to be that the average chain length be large enough that a significant fraction of the polysulfide have chain lengths > 8, since only they could ring close to eliminate S_8 rings. As recently as 1977, kinetic schemes that involve all polysulfides in stepwise reactions, as shown below, have been suggested on the literature, however, it is pointed out that "since the stoichiometric coefficients of H_2O_2 and H_2S exceed their kinetic orders in the fitted rate equation there may be several other intermediates after the rate determining step".[34] These reaction schemes can only be considered to be a convenient representation that fits the overall stoichiometry. Like a balanced redox equation, they cannot be supposed to be a statement of mechanism.

$$H_2S \rightarrow H^+ + SH^-$$
$$HS^- + H_2O_2 \rightarrow HSOH + OH^-$$
$$HS^- + HSOH \rightarrow HS_2^- + H_2O$$
$$HS_2^- + HSOH \rightarrow HS_3^- + H_2O$$

•

•

•

$$HS_9^- + HSOH \rightarrow S_8 + HS^-$$

More than 10 years after the original work by Swarzenbach,[33] some of the equilibrium distributions in polysulfide solutions were described by Giggenbach.[35] He attempted to resolve the UV-VIS spectra of equilibrated solutions into the bands due to the individual polysulfide ions in the pH range 7-14 and in [NaOH] to 18 M. Equilibrium was obtained very rapidly even in the most concentrated hydroxide solutions (ca. saturated @ 20°C) in which no spectral changes were observed five minutes after preparation.

The equilibrium distributions are plotted vs a normalizing expression log β where

$$\beta = \frac{[SH^-][OH^-]}{[S(0)]} = \frac{P}{[S(0)]}$$

$[S(0)] \equiv$ concentration of zero-valent sulfurs

$\equiv \bar{n}[S_nS^=]$

where $\bar{n} \equiv$ avg. chain length

based on the equilibrium between adjacent polysulfides (i.e., $S_3S^=$ and $S_4S^=$).

$$(a-1)S_aS^= + SH^- + OH^- \rightleftarrows aS_{(a-1)}S^= + H_2O$$

$$\frac{K_{a-1}}{a} = \frac{[S_{a-1}S^=]^a}{[S_aS^=]^{a-1}[SH^-][OH]} = \frac{[S_{a-1}S^=]^a}{[S_aS^=]^{a-1}P}$$

The parameter β is somewhat empirical and is introducted to express the fraction of zero-valent sulfur in any particular polysulfide unit.

$$U_{a-1} = \frac{[S_{a-1}S^=]_n}{S(0)}$$

$n \equiv$ no. zero-valents sulfur in a polysulfide ($n = 2$ for $^-S\text{-}S\text{-}S^-$).

The equilibrium expression can be re-written then as:

$$K_{a-y_a} = \frac{m^{a-1}U_n^a}{n^aU_m^{a-1}} \times \frac{1}{\beta}$$

This relationship then predicts that the polysulfide distribution should be fixed at fixed values of $\beta = \frac{[SH^-][OH^-]}{S(0)}$. The results obtained by Giggenbach are reproduced as Figure 25. It should be noted that these

FIGURE 25. Polysulfide Speciation in Aqueous Solution from Giggenbach[35]

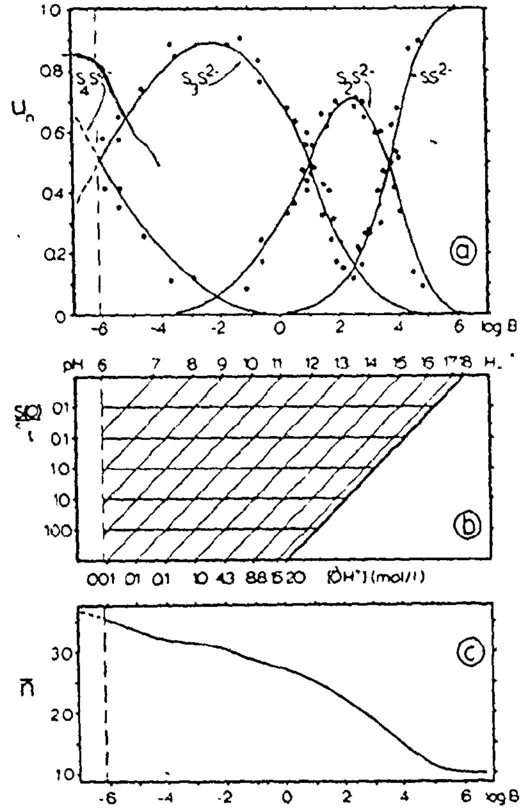


Figure 5 —Equilibrium distribution of polysulfide ions S_nS^{2-} as a function of log B. Circles in part a represent experimental values of u_n as calculated from eq 30, whereas solid lines were calculated by use of the experimental values for $K_{n/m}$. Part b represents the relationships among log B, $S(0)/S_t$, and solution pH. Part c gives $\bar{n}$, the average number of atoms of zerovalent sulfur per polysulfide ion, as a function of log B.

Figure shows the equilibrium distribution of polysulfide ions as a function of log B = log([SH⁻]·[OH⁻]/S(0)). In order to facilitate the determination of log B, a diagram taking into account changes in [SH⁻] due to the formation of H_2S in the acidic range and those due to the formation of S^{2-} and the increase in OH^- activity at extremely high pH's is added. Thus for a given ratio $S(0)/S_t$, with S_t the total concentration of free monosulfide sulfur as given by $[H_2S] + [SH^-] + [S^{2-}]$, values for log B are obtained by following the horizontal line for a given $S(0)/S_t$ ratio to the 45° line representing the solution pH

At low pH's the amount of zerovalent sulfur present in solution is determined by its solubility as given by

$$K_s = \frac{S(0)}{[SH^-][OH^-]\bar{n}} = \frac{1}{B\bar{n}}$$

with $K_s = (3.3 \pm 0.7) \times 10^5$ at 20°. With a value for $\bar{n}$ of 3.65 at 25° as extrapolated from the data given for 25 and 50° in 0.1 M Na_2S solution, log B for a solution saturated in zerovalent sulfur is found to be -6.1 + 0.1. With the experimental values for ε_3' and ε_4' and the resulting value for $K_{3/4}$, however, approximately equal amounts of tetra- and pentasulfide are calculated to be present at this B value. This small discrepancy in n is probably due to the considerable uncertainty in the value of ε_4' and that of $K_{3/4}$ derived from it. On the other hand, considering the large differences in experimental conditions employed in determining the values for n in these saturated solutions, the agreement is satisfactory and would indicate that any aqueous polysulfide solution saturated with zerovalent sulfur at 20° contains approximately equal amounts of tetrasulfide and pentasulfide ions, with $n = 3.6 \pm 0.1$.

With increasing pH the tetrasulfide ion remains the predominant species for log B up to +1.0, whereas log B values between 1.0 and 4.0 most of the zerovalent sulfur is present as trisulfide. The disulfide ion is formed only in highly alkaline solutions or in solutions with extremely low ratios $S(0)/S_t$. In systems where virtually all free sulfide S_t is present in the form of the sulfide ion S^{2-}, the distribution of polysulfides becomes independent of [OH⁻] and is only determined by $S(0)/S_t$. For aqueous solutions this conditions is reached for H^- values above 18, in systems with low H^+ activities, e.g., nonaqueous solvents or salt melts, however, the formation of disulfide ion can be expected to be quite common.

results are not rigorous and represent the first major work in sulfur polyanion speciation. The approximations and assumptions made in the development of theory and treatment of data are extensive, however, the end result gives insight into the behaviour of aqueous polysulfide solutions. His discussion (refer to Figure 25) has serious and hitherto unconsidered ramifications with respect to the solution oxidation of sulfide to sulfur that are worthy of immediate investigation. For example, it was confirmed in the laboratory that the average chain length in sulfur-saturated sulfide solutions (Na_2S) was ∿ 3.6. This was performed by the precipitation of sulfur from a sulfur-saturated Na_2S solution (pH > 12 ± ?) of known total sulfide concentration by addition to acid. The average chain length is then calculated as:

$$\bar{n} = \frac{\text{moles of sulfur precipitated}}{\text{moles of sulfide in the sample volume}} = 3.6$$

The results of Giggenback, using the procedure outlined in his discussion (refer to Figure 25) would predict the ratio of $S(0)/S_t > 1000$. To good approximation, all the sulfide is involved in polysulfide formation, and the calculation of average chain length as performed in the lab would be a valid estimation. If, however, the experiment were performed at pH 8.0, these results would predict that at sulfur saturation ($\log \beta = 6.1$, pH = 8.0) $S(0)/S_t \sim 1.5$. Only $(1.5/1.5 + 3.6) \times 100 \sim 30\%$ of all sulfide is involved in polysulfide formation, although the average chain length of those molecules formed is still ∿ 3.6. The chain length determined by the precipitation procedure would give an average chain length of ∿ 1.1.

$$\bar{n}^* = \frac{S(0)}{S_t + S_xS^-} = \frac{S(0)}{S_t + (1/\bar{n})S(0)} = \frac{\bar{n}(S(0)/S_t)}{\bar{n} + (S(0)/S_t)} = \frac{3.6(1.5)}{3.6 + 1.5} \approx 1.1$$

Another way of looking at this in terms of sulfide oxidation would be that at pH 12, (3.6/4.6) x 100 $\sim$ 78% of all sulfide must be oxidized before precipitation can occur, whereas at pH 8, sulfur precipitation could occur at only (1.1/2.1) x 100 = 52% of sulfide oxidized. At pH 7, ($S(0)/S_t \sim 0.09$) this is reduced to $\sim$ 10%.**

** These results should, in principle, allow the estimation of the overall second order rate constant (if it exists) for the reaction A + 2B → C using the data in Fig. 24 and 25. One could consider the conversion at precipitation to be a pH dependent parameter, treated as a constant for any one run at a fixed pH. Substitution of this and the measured time to precipitation into the integrated form of the differential rate expression 32 allows calculation of k.

$$(32) \qquad -r_A = \frac{-dC_A}{dt} = kC_AC_B = k\overset{\circ}{C}_A{}^2(1-X_A)\left(\frac{\overset{\circ}{C}_B}{\overset{\circ}{C}_A} - 2X_A\right)$$

where $X_A = \dfrac{\overset{\circ}{C}_A - C_A}{\overset{\circ}{C}_A}$

Note, however, that $\overset{\circ}{C}_B/\overset{\circ}{C}_A = 2$ gives a special case of this differential equation giving a different integrated form.

$$(33) \qquad \overset{\circ}{C}_B/\overset{\circ}{C}_A \neq 2 \qquad \ell n \frac{\overset{\circ}{C}_A C_B}{\overset{\circ}{C}_B C_A} = \ell n[(\overset{\circ}{C}_B/\overset{\circ}{C}_A - 2X_A)/(\overset{\circ}{C}_B/\overset{\circ}{C}_A(1-X_A)) = \overset{\circ}{C}_A\left(\frac{\overset{\circ}{C}_B}{\overset{\circ}{C}_A} - 2\right)kt$$

$$(34) \qquad \overset{\circ}{C}_B/\overset{\circ}{C}_A = 2 \qquad 1/C_A - 1/\overset{\circ}{C}_A = 1/\overset{\circ}{C}_A[X_A/1-X_A] = 2kt$$

The inherent sensitivity of these equations near $\overset{\circ}{C}_B/\overset{\circ}{C}_A = 2$ to parameter errors (i.e., $\overset{\circ}{C}_B/\overset{\circ}{C}_A$, X_A, t) make the data unsuitable for the estimation of rate constants. In general, shoichiometric ratios of reactants should be avoided.

These results, if correct, have direct and profound effects on our current understanding of the chemical and physical characteristics of liquid redox plants. Chemically, they help explain the variability of measurable parameters such as acid precipitated sulfur and total sulfide reaching the oxidizer since they will be functions of pH. This also might explain the physical phenomena of loss of sulfur froth with the addition of caustic to the process liquor (essentially a step increase in pH) or the appearance of a sulfur "bloom" with a decrease in pH (for example during start-up) as changes in $S(0)/S_t$ resulting from the pH change.

CHAPTER 4

SUMMARY AND CONCLUSIONS

This work has touched on a wide variety of subjects associated with vanadium process chemistry in Stretford solutions. In the course of these investigations the author has made several noteworthy contributions.

1) During preliminary experiments, it was found that solution pH had a marked effect on the air oxidation of V^{4+}/citrate solutions. An apparatus to maintain a setpoint pH in carbonate buffers while allowing control of gas flows and composition through the solution was designed and constructed.

2) Studies of the uncatalysed air oxidation of carbonate buffered V^{4+}/citrate solutions as a function of pH produced a baseline suitable for the evaluation of potential catalysts for the reoxidation of Stretford solutions.

3) Studies of unbuffered and carbonate buffered V^{4+}/citrate solutions clarified vanadyl speciation in Stretford solutions and identified pH ranges in which the different forms are stable with respect to plant operation.

4) Studies have shown the effect of V^{4+}/V^{5+} ratio, pH, buffer concentration, and citrate concentration on vanadyl vanadate precipitation from Stretford-like soluti[illegible].

5) Preliminary studies have demonstrated that pH is an important parameter in the production of sulfur in Stretford-like solutions.

A large portion of the information collected from literature sources, presented in chapter 1 and appendix II, form the basis of a paper presented at the McMaster Symposium on Iron and Steelmaking No.5.

APPENDICES

APPENDIX I

PHYSICAL PLANT DATA

DESIGN BASIS: 0.6 mscf/hr COG
8 psig
38°C (gas)
3.5 grain/cu ft (~ 8.1 gm/NM^3)
2-4% vol CO_2
0.5% vol O_2
500 ppm sulfide loading in solution (~ 0.5 gm/ℓ $S^=$)

PLANT DIMENSIONS:

Absorption tower: 10' diameter x 97' - 12' bottom holdup
- 4 x 12' splash plate packing
- top demister

Delay tank: Not used
Oxidizers (4): 10' dia x 27' - airblowers (4) 20000 cuft/hr
Pumping tank: 13' dia x 25'
Slurry tank: 13' dia x 25'

Total volume liquor: 85000 Imp. gal.
Circulation rate: 60000 Imp. gal/hr.

APPENDIX II

A SUMMARY OF CURRENT AND POTENTIAL COKE OVEN GAS DESULFURIZATION PROCESSES WITH EMPHASIS ON BASIC PROCESS CHEMISTRY

DATA IS COLLECTED FROM TRADE, RESEARCH AND PATENT LITURATURE, AND FROM COMPANY PUBLICATIONS. CRITICAL APPRAISALS OF INDIVIDUAL PROCESSES, OR INTER-PROCESS COMPARISONS ARE NOT ATTEMPTED, ALTHOUGH KNOWN INTERFERENCES ARE NOTED WHERE POSSIBLE.

PROCESSES ARE CATEGORIZED ACCORDING TO MAJOR COMMON CHARACTERISTICS AND WITHIN EACH CATEGORY PROCESSES ARE DESCRIBED SEPARATELY. A DESCRIPTION CONSISTS OF A SIMPLIFIED FLOW DIAGRAM AND AN OUTLINE OF UNIT OPERATIONS WITH EMPHASIS ON THE PHYSICAL AND/OR CHEMICAL EVENTS TAKING PLACE WITHIN EACH STAGE.

ABSORPTION / REGENERATION PROCESSES

CARBONATE BASED PROCESSES

THE PROCESSES ARE BASED ON ABSORPTION OF ACID GASES INTO AN AQUEOUS ALKALINE SOLUTION OF POTASSIUM CARBONATE. THE RICH SOLUTION IS HEATED UNDER REFLUX RELEASING CO_2 AND H_2S AS UNCONDENSABLE OVERHEAD. REGENERATED SOLUTION IS RETURNED TO THE ABSORBER. COS IS HYDROLYSED TO CO_2 AND H_2S WHILE CS_2 IS UNREACTIVE AND APPEARS IN THE OFF GAS.

INCREASING SALT CONCENTRATION IN SOLUTION FROM A SLOW BUILDUP OF SULFATES AND FORMATES IS USUALLY CONTROLLED BY BLOWDOWN AND DILUTION OR BY CRYSTALLIZATION OF A SLIPSTREAM. SOME NAMED PROCESSES AND THEIR DISTINGUISHING FEATURES ARE NOTED BELOW.

SEABOARD - A HOT GAS STREAM IS UTILIZED AS THE STRIPPING GAS.

CATACARB, BENFIELD - NITROGEN CONTAINING ABSORPTION CATALYSTS ARE ADDED TO ENHANCE THE RATE OF ACID GAS REMOVAL FROM COG. IT IS SUGGESTED THAT THE REACTION OF CO_2 IS FASTER WITH THESE COMPOUNDS THAN WITH H_2O, INCREASING THE MASS TRANSFER OF CO_2 INTO SOLUTION. THE EQUILIBRIUM SOLUBILITIES ARE UNCHANGED. AMMONIUM BORATE IS ADDED IN THE CATACARB PROCESS; DIETHANOLAMINE TO THE BENFIELD PROCESS. THE CATACARB PROCESS UTILIZES A LEAN/SEMI LEAN SPLIT STREAM ARRANGEMENT OF THE SAME SOLVENT.

HIPURE - THE PROCESS UTILIZES A SPLIT STREAM ABSORPTION AND REGENERATION. THE FIRST SCRUB IS WITH A NORMAL BENEFIELD MIXTURE. THE SECOND IS TAILORED TO THE OUTPUT REQUIREMENTS. THE TWO SOLUTIONS ARE NON-MIXING.

VACUUM CARBONATE - THE REGENERATOR IS OPERATED AT REDUCED PRESSURE.

REFERENCES 1; 2,3,4; 5; 6,7,8,9.

ALKANOLAMINE BASED PROCESSES

SOUR GAS IS CONTACTED IN COUNTER CURRENT FLOW WITH AN AQUEOUS ALKALINE SOLUTION OF AN ALKANOLAMINE. THE ACIDIC COMPONENTS (H_2S, HCN, CO_2) ARE ABSORBED INTO SOLUTION AND UNDERGO REACTIONS (2) (3) (4). THIS RICH SOLUTION IS HEATED UNDER REFLUX. CONDENSABLE OVERHEAD IS RETURNED TO THE SYSTEM WHILE UNCONDENSABLE OVERHEAD (H_2S, CO_2) PROCEEDS TO THE NEXT PROCESS. REGENERATED SOLUTION IS DRAWN FROM THE REBOILER AND RETURNED TO THE ABSORBER. NONVOLATILE BYPRODUCTS WHICH COLLECT IN SOLUTION ARE REMOVED BY BATCH RECLAIMING OR BLOWDOWN AND DILUTION.

(2) $H_2S + RNH_2 \rightleftharpoons HSH_3NR$

(3) $CO_2 + 2RNH_2 \xrightleftharpoons{H_2O} (RNH_3)_2CO_3 \rightleftharpoons RNHCOONH_3R$

(4) $COS, CS_2, HCN + RNH_2 \longrightarrow$ DEGRADATION PRODUCTS.

SNP·DEA: UTILIZES HIGHER DEA CONCENTRATIONS AND H_2S LOADING.
A LEAN SOLUTION SLIPSTREAM IS TREATED (ACTIVATED CARBON FILTER?)
TO REMOVE SOLIDS, HYDROCARBONS AND CORROSIVE BYPRODUCTS

ADIP: UNSPECIFIED ALKANOLAMINE - FACILITIES FOR COS REMOVAL.

FLUOR ECONAMINE: DIGLYCOLAMINE ($HOCH_2CH - OCH_2CH_2 - NH_2$) (DGA)

SULFIBAN: AQUEOUS MEA, PROVISIONS FOR CATALYTIC HCN DESTRUCTION AND NH_3 DECOMPOSITION PRIOR TO FEED TO A CLAUS PLANT.

AMMONIA BASED PROCESSES

H_2S AND CO_2 ARE ABSORBED INTO AN AQUEOUS AMMONIA SOLUTION. THIS RICH SOLUTION IS FED TO THE TOP OF A REGENERATION TOWER AND IS THEN HEATED UNDER REFLUX TO RELEASE ACID GASES AND SOME AMMONIA. NONVOLATILE AMMONIUM SALTS ARE RECOVERED BY TITRATION WITH BASE WHILE UNDER REFLUX OR BY BATCH RECLAIMING.

DIAMOX: PROGESS NH_3 IS OBTAINED FROM AN UPSTREAM WATER WASH.

FIRMACARL STILL: PROCESS AMMONIA IS OBTAINED FROM THE COKE-OVEN GAS IN A DOWNSTREAM WATER WASH.

OTTO-SULFAMMON: PROCESS NH_3 IS OBTAINED FROM A DOWNSTREAM WATER WASH.

COLLIN: DATA NOT AVAILABLE.

REFERENCES 10, 11; 12; 13; 14, 15, 16 / 17, 18, 19; 20, 21.

METHANOL BASED PROCESSES

WATER AND ACID GASES ARE ABSORBED INTO A METHANOL SOLUTION OF AN ALKANOLANINE. PLANT DESIGN IS SIMILAR TO THAT OF AN ALKANOLANINE PLANT. THE REGENERATOR OVERHEAD IS WATER WASHED AND IS THEN REDISTILLED TO RECLAIM METHANOL FOR RECYCLE. BYPRODUCTS FORMED FROM THE REACTIONS OF HCN CO_2, COS AND CS_2 WITH THE ALKANOLANINE ARE REMOVED BY BATCH RECLAIMING.

AMISOL: METHANOL, DEA, AND AN UNSPECIFIED ABSORPTION ACTIVATOR.

RECTISOL; METHANOL

SPECIALTY SOLVENT / SOLUTE PROCESSES

ALKAZID DIK:

THE PROCESS IS BASED ON SELECTIVE ABSORPTION OF H_2S INTO AN AQUEOUS SOLUTION OF POTASSIUM DIMETHYLAMINO ACETATE (NN-DIMETHYL GLYCINE). LOW SOLUTION VAPOUR PRESSURES AND HYDROCARBON SOLUBILITIES ARE CLAIMED AS ADVANTAGES FOR CERTAIN APPLICATIONS. PROCESS UNITS ARE ANALOGUS TO THOSE FOR ALKANOLAMINE PLANTS. BYPRODUCT FORMATION DATA IS NOT AVAILABLE ALTHOUGH TOLERENCE TO SMALL AMOUNTS OF CS_2 AND HCN IS CLAIMED.

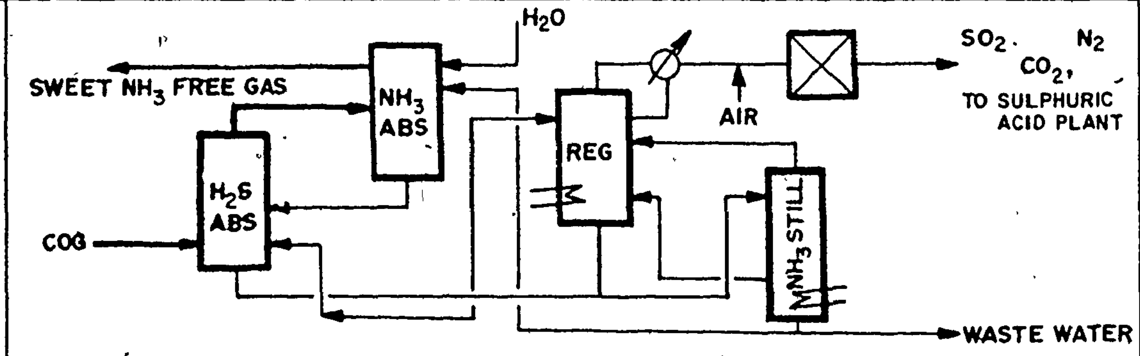
SULFINOL:

THE PROCESS IS BASED ON A COMBINATION OF PHYSICAL AND CHEMICAL ABSORPTION OF H_2S INTO A SULFOLANE ($CH_2 - CH_2 - CH_2 - CH_2 - SO_2$). ALKANOLAMINE AND WATER SOLUTION. PLANT DESIGN IS ANALOGOUS TO THAT OF AN ATMOSPHERIC ALKANOLAMINE PLANT. THE PHYSICAL ABSORPTION CHARACTERISTICS OF THE SOLVENT MIXTURE ALLOWS INCREASED H_2S LOADING AT HIGHER PARTIAL PRESSURES OF H_2S. FOR HIGHER PRESSURE APPLICATIONS RICH SOLVENT CAN BE FLASHED TO SEPARATE ABSORBED HYDROCARBONS BEFORE REGENERATION. COS IS ABSORBED AND IS THEN RELEASED INTO THE OVERHEAD. INSOLUBLE SALTS FORMED AS BYPRODUCTS ARE REMOVED BY BATCH RECLAIMING.

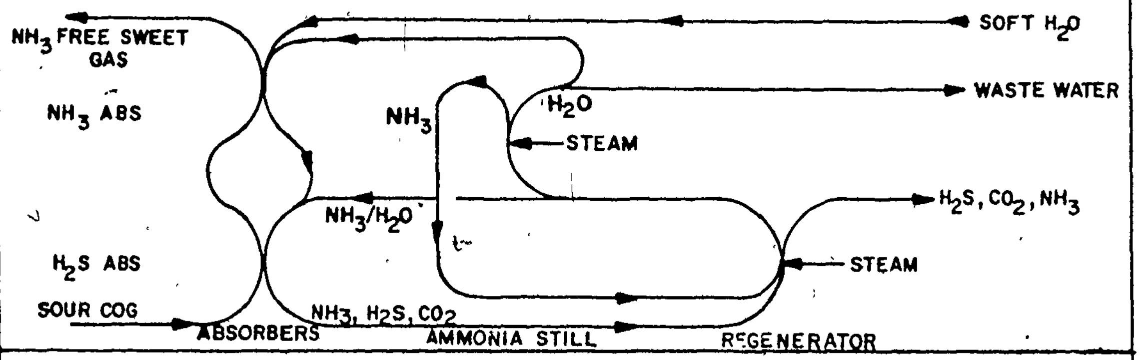
REFERENCES 22; 23,24,25; / 26,27; / 28,29,30,31.

THE PROCESS RELIES ON THE ABSORPTION OF ACID GASES FROM A COG STREAM INTO AN AQUEOUS AMMONIA SOLUTION (2.5% NH_3). A SUBSEQUENT WATER WASH OF THE SWEETENED GAS REMOVES NH_3. THE NH_3 WASTE WATER IS FEED TO THE TOP OF THE H_2S ABSORBER. H_2S RICH SOLUTION (2% NH_3, 0.7% H_2S) IS HEATED UNDER REFLUX IN A REGENERATION COLUMN RELEASING H_2S, CO_2 AND SOME NH_3 TO THE OVERHEAD. THE MAJOR FRACTION OF THE REGENERATOR BOTTOMS IS RETURNED TO THE H_2S ABSORBER WITH A MINOR STREAM PROCEEDING TO THE NH_3 STILL. THE NH_3/H_2O OVERHEAD FROM THIS STILL IS RETURNED TO THE REGENERATOR COLUMN AS REFLUX. STILL BOTTOMS (H_2O + NON-VOLATILE SALTS) ARE RETURNED TO THE NH_3 WASHES, WITH A SLIP STREAM PROVIDING OVERALL WATER BALANCE AND BLOWDOWN. THE ACID GAS STREAM IS OXIDIZED OVER A BAUXITE CATALYST TO N_2, CO_2 SO_2 AND H_2O PRIOR TO BEING FED TO A SULFURIC ACID PLANT.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(5) $H_2S + NH_3 \rightleftharpoons NH_4HS$

(6) $NH_4HS + NH_3 \rightleftharpoons (NH_4)_2S$

(7) $CO_2 + NH_3 + H_2O \rightleftharpoons NH_4HCO_3$

(8) $NH_4HCO_3 + NH_3 \rightleftharpoons (NH_4)_2CO_3 \rightleftharpoons H_2NCOOH_3N + H_2O$

(9) $HCN + NH_3 \rightleftharpoons NH_4CN$

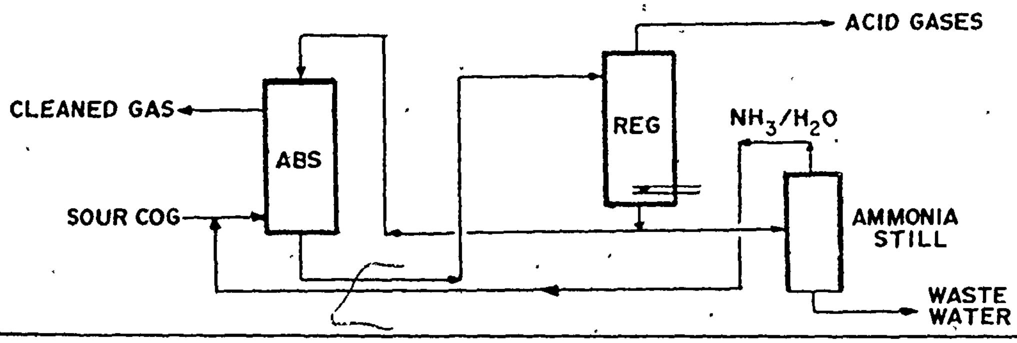
CYANIDE DESTRUCT REACTOR

(10) $NH_3.H_2S.HCN + O_2 \longrightarrow H_2O + SO_2 + CO_2 + N_2$

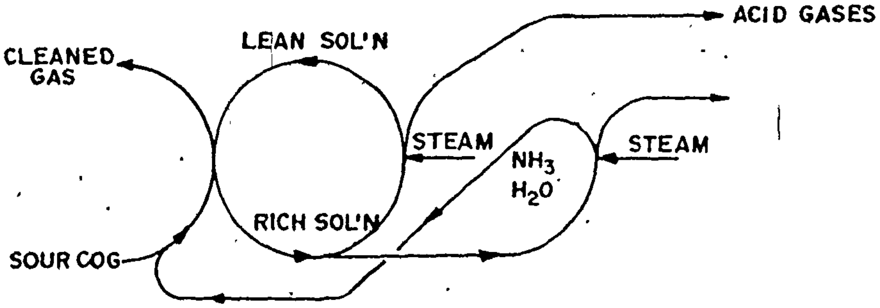
REFERENCES 32,33.

The process relies on absorption of acid gases into an aqueous ammonia solution (ca. 1 wt. % lean sol.) with subsequent regeneration under reflux. Included in the plant design is a napthalene scrubber upstream of the absorber and an ammonia recovery still to treat blowdown from the regenerator bottoms prior to activated sludge treatment. Overhead from the still (NH_3/H_2O) is added to COG upstream of the H_2S absorber. Makeup ammonia is from a water wash upstream of the plant. Nonvolatile salts formed from reactions of HCN, COS, CS_2 and small amounts of oxidative byproduct are removed in the blowdown.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(5) $H_2S + NH_3 \rightleftharpoons NH_4HS$

(6) $NH_4HS + NH_3 \rightleftharpoons (NH_4)_2S$

(9) $HCN + NH_3 \rightleftharpoons NH_4CN$

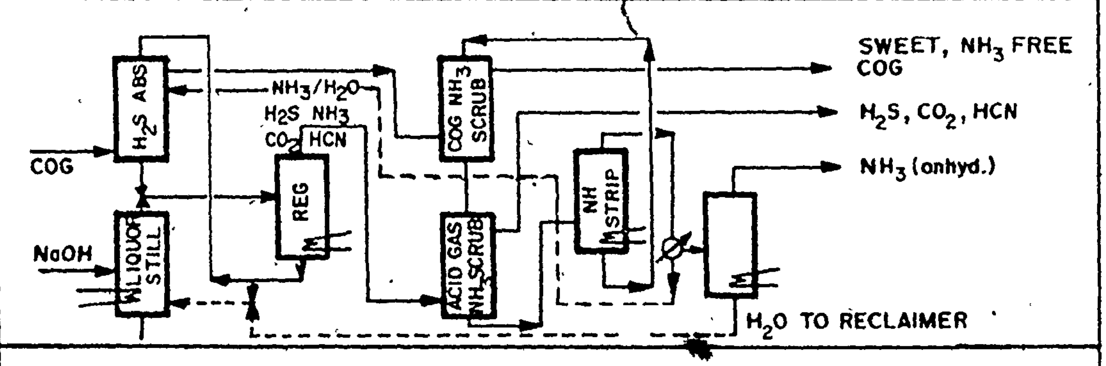
(7) $CO_2 + NH_3 + H_2O \rightleftharpoons NH_4HCO_3$

(8) $NH_4HCO_3 + NH_3 \rightleftharpoons (NH_4)_2CO_3 \rightleftharpoons H_2NCOONH_3 + H_2O$

References 17, 18, 19.

THIS PROCESS IS A COMBINATION OF THE STILL PROCESS FOR ABSORPTION OF ACID GASES IN AMMONIA SOLUTION WITH THE PHOSAM PROCESS FOR AMMONIA ABSORPTION AND RECOVERY. THE AMMONIA SOLUTION (1-2% NH_3) IS REGENERATED WITH STEAM IN THE DEACIFIER AND RECYCLED TO THE H_2S ABSORBER. THE SWEET COG AND THE DEACIFIER OVERHEAD VAPOR ARE SEPARATELY SCRUBBED WITH AMMONIUM PHOSPHATE SOLUTION TO REMOVE NH_3 AND THE PHOSPHATE SOLUTION IS REGENERATED IN A STRIPPER, PRODUCING NH_3-H_2O OVERHEAD (15% NH_3) WHICH IS SUBSEQUENTLY FRACTIONATED TO ANHYDROUS NH_3. PART OF THE 15% AMMONIA SOLUTION, FREE OF ACID GAS, MAY BE RETURNED TO THE H_2S ABSORBER TO INCREASE THE EFFICIENCY OF ABSORPTION.

FLOW DIAGRAM



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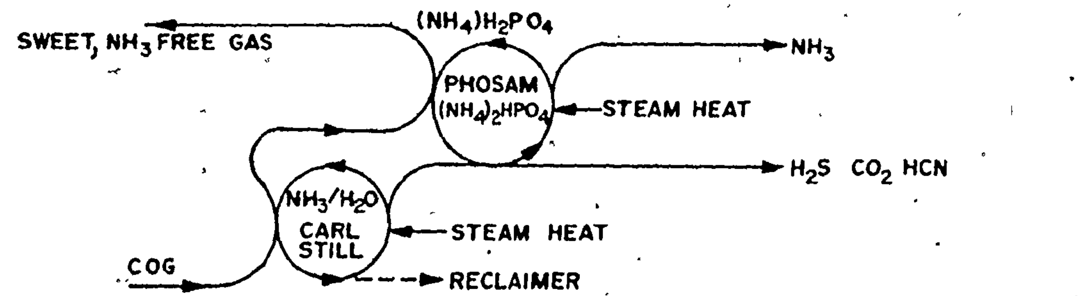


PROCESS CHEMISTRY

(5) $H_2S + NH_3 \rightleftharpoons NH_4HS$

(6) $NH_4HS + NH_3 \rightleftharpoons (NH_4)_2S$

(9) $HCN + NH_3 \rightleftharpoons NH_4CN$

(7) $CO_2 + NH_3 + H_2O \rightleftharpoons NH_4HCO_3$

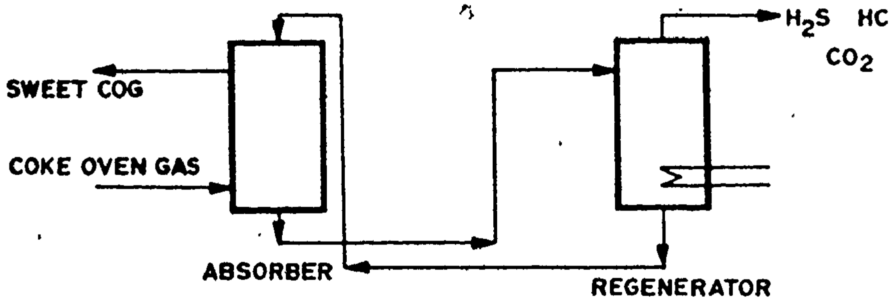
(8) $NH_4HCO_3 + NH_3 \rightleftharpoons (NH_4)_2CO_3 \rightleftharpoons H_2NCOOH_3N + H_2O$

(11) $NH_3 + NH_4H_2PO_4 \rightleftharpoons (NH_4)_2HPO_4 + H_2O$

REFERENCES 20, 21

THE PROCESS RELIES ON THE ABSORPTION OF ACID GASES INTO A 13 - 18% MEA SOLUTION AND SUBSEQUENT REGENERATION UNDER REFLUX. REBOILER BOTTOMS ARE RETURNED TO THE ABSORBER. NONCONDENSABLE REGENERATOR OVERHEAD IS HEATED TO 120°C (250°F) AND PASSED THROUGH A CYANIDE DESTRUCT REACTOR WHERE HCN, IN THE PRESENCE OF H_2S AND CO_2, IS CONVERTED TO NH_3, COS, CS_2, AND CO_2. AMMONIA IS DECOMPOSED TO N_2 AND H_2 BY MIXING OF THE 1/3 H_2S SPLITSTREAM AND THE POST COMBUSTION SO_2 STREAM WITH INDIRECT FUEL HEATING TO 1900°F. THE FIRST STAGE OF THE CLAUS REACTOR IS OPERATED AT ELEVATED TEMPERATURE TO DECREASE THE CONCENTRATION OF COS AND CS_2 IN THE FEED.

FLOW DIAGRAM



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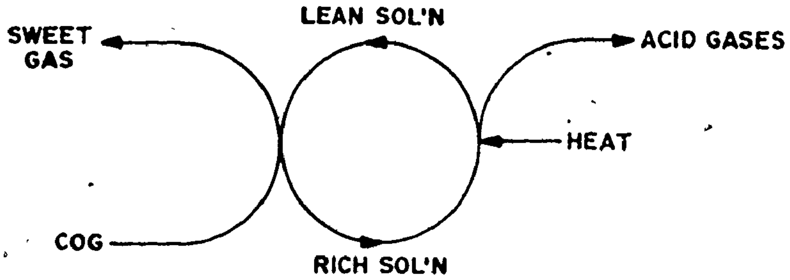


PROCESS CHEMISTRY

(12) $H_2S + HO-(CH_2)_2NH_2 \rightleftharpoons HO-(CH_2)_2NH_3HS$

(13) $HCN + HO-(CH_2)_2NH_2 \rightleftharpoons HO-(CH_2)_2NH_3CN$

(14) $CO_2 + HO-(CH_2)_2NH_2 + H_2O \rightleftharpoons HO-(CH_2)_2NH_3HCO_3 \rightleftharpoons HO(CH_2)_2NHCOOH_3N(CH_2)_2OH$

CATALYTIC CYANIDE OXIDATION PRIOR TO CLAUS UNIT

(15) $2HCN + H_2S + CO_2 \rightarrow NH_3 + COS + CS_2 + CO_2$

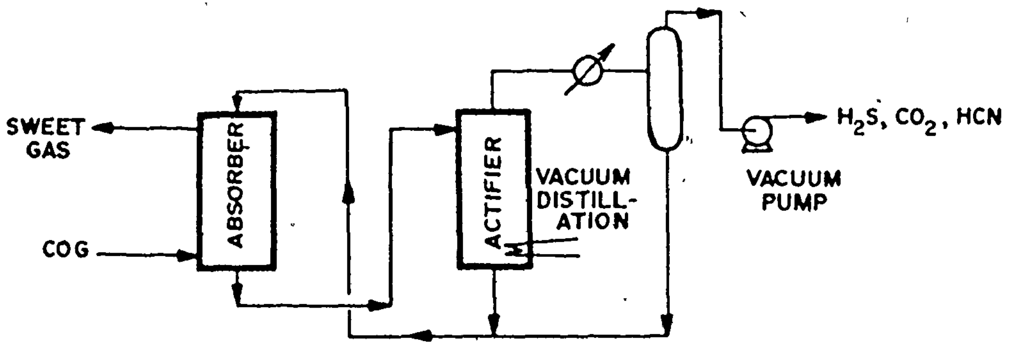
AMMONIA DECOMPOSTION

(16) $NH_3 + H_2S + SO_2 + O_2 + COS$ ETC. $\xrightarrow{900^\circ} N_2 + H_2 + H_2S + SO_2 + COS$ ETC

REFERENCES 14,15,16

THE PROCESS RELIES ON THE ABSORPTION OF ACID GASES INTO AN AQUEOUS CARBONATE SOLUTION (PH = 10) WITH SUBSEQUENT REGENERATION UNDER REFLUX AT REDUCED PRESSURE. THE CO_2 LOADING INCREASES WITH THE DEGREE OF DESORPTION OF CO_2 (FIG (2)) WHILE THE H_2S LOADING IS RELATIVELY INSENSITIVE TO THIS, THUSLY, ALLOWING SOME DEGREE OF SELECTIVITY. THE ADDED COST OF OPERATION AT 2 - 2.5 PSIA IS OFFSET BY LOWER STEAM REQUIREMENTS FOR REFLUX AT 140°F VS ~220°F FOR AN ATMOSPHERIC UNIT. THE CARBONATE SOLUTION IS UNAFFECTED BY HCN, NH_3, COS, AND CS_2 BUT OXIDATIVE BYPRODUCTS ($S_2O_3^{=}$, $SO_4^{=}$, SCN^-) BUILD UP IN SOLUTION AND MUST BE REMOVED BY PERIODIC BLOWDOWN. HCN AND NH_3 ABSORBED INTO THE SOLUTION APPEAR IN THE REGENERATOR OVERHEAD.

FLOW DIAGRAM



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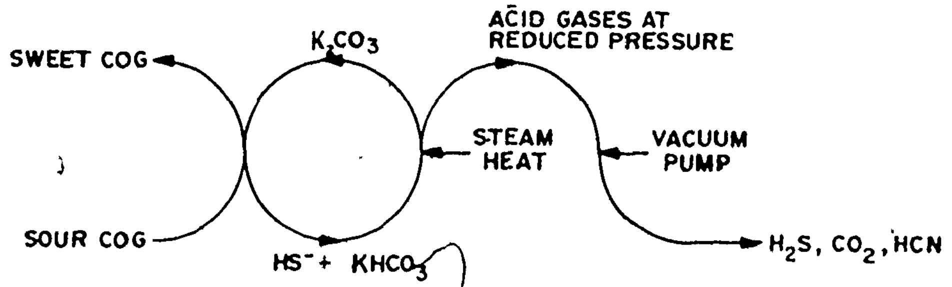


PROCESS CHEMISTRY

(17) $H_2S + K_2CO_3 \rightleftharpoons KHS + KHCO_3$

(18) $H_2S + KHCO_3 \rightleftharpoons KHS + H_2CO_3$

(19) $CO_2 + H_2O \rightleftharpoons H_2CO_3$

(20) $H_2CO_3 \xrightleftharpoons{K_{A1}} H^+ + HCO_3^- \xrightleftharpoons{K_{A2}} 2H^+ + CO_3^{=}$

(21) $COS + H_2O \rightleftharpoons CO_2 + H_2S$

(22) $CS_2 + 2H_2O \rightleftharpoons CO_2 + 2H_2S$

REFERENCES 6, 7, 8, 9.

CLAUS KILN

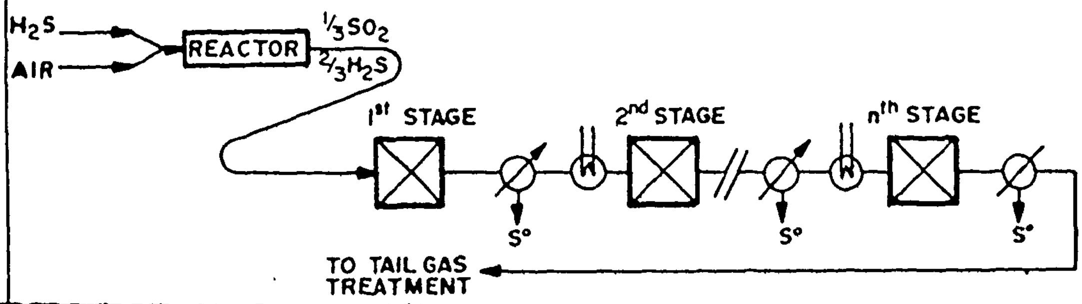
THE CLAUS KILN IS THE MOST COMMON PROCESS FOR THE PRODUCTION OF SULFUR FROM OFF GASES. IT RELIES ON THE DIRECT REACTION OF H_2S AND SO_2 ON A SOLID CATALYST AT ELEVATED TEMPERATURES (800 - 1100°F). ON COOLING, A LIQUID OR CRYSTALINE SULFUR PRODUCT IS DEPOSITED FROM THE VAPOUR.

THE REACTIONS OCCURRING ON THE CATALYST SURFACE ARE COMPLEX AND INVOLVE MANY OXYGEN, SULFUR AND OXYSULFUR INTERMEDIATES. THE NET EFFECT IS AN EQUILIBRIUM MIXTURE OF REACTANTS AND PRODUCTS OVER THE CATALYST THE COMPOSITION OF WHICH IS CONTROLLED BY THE H_2S/SO_2 RATIO, THE PERCENTAGE OF EACH IN THE FEED, THE FEED RATE, THE NATURE OF THE CATALYST AND THE TEMPERATURE. THIS EQUILIBRIUM BEHAVIOUR USUALLY NECESSITATES A MULTI-STAGED REACTION SEQUENCE WITH SULFUR PRODUCT REMOVAL AFTER EACH STAGE.

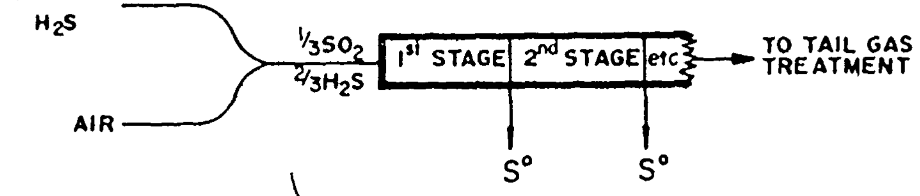
IN NORMAL COG APPLICATIONS THE FEED TO CLAUS PLANTS IS AN H_2S RICH $(>20\%\,^{V}/_{V})$ STREAM USUALLY FROM AN ABSORPTION/REGENERATION PLANT. AFTER PARTIAL OXIDATION, THE H_2S/SO_2 RATIO OF THIS STREAM USUALLY DETERMINES THE FINAL EFFICIENCY SINCE EXCESS OF EITHER REACTANT WILL APPEAR IN THE TAIL GASES. LARGE EXCESS OF H_2S CAN INTERFERE WITH THE SULFUR PRODUCT QUALITY BY INCREASING THE SULFANE (H_2S_x) CONTENT IN IT (DISSOLVED H_2S IN SULFUR PRODUCT). IF NO TAIL GAS CLEANUP STEP IS USED, IT IS INCINERATED TO SO_2 PRIOR TO VENTING. PRIMARY CONTAMINANTS IN THE TAIL GAS ARE COS AND CS_2 IN THE 200 - 5000PPMV CONCENTRATION RANGE. EACH ORIGINATES FROM EQUILIBRIUM REACTIONS WITH CO_2 AND/OR RESIDUAL HYDROCARBONS IN THE FEED WITH SULFUR SPECIES. CONTAMINANT CONCENTRATIONS DECREASE WITH INCREASING TEMPERATURES; WHERE AS, SULFUR YIELDS MAY DECREASE GIVING RISE TO A TRADE-OFF SITUATION. SOME PLANTS HAVE USED A HIGH TEMPERATURE AFTER COMBUSTION TO REDUCE THESE EMISSIONS.

HCN AND NH_3 PRESENT IN THE FEED MAY DEACTIVATE CLAUS CATALYSTS AS WELL AS CONTRIBUTE TO TAIL GAS EMISSIONS. THEY MAY BE REMOVED THROUGH CATALYTIC REACTION PRIOR TO THE CLAUS UNIT OR, IN THE CASE OF HCN, IN THE INITIAL STAGES OF THE CLAUS ITSELF.

FLOW DIAGRAM



PROCESS CYCLES



REFERENCES 35,36,37,38,39,40,41,42,43.

THIS PROCESS IS NOT OF CURRENT COMMERCIAL IMPORTANCE BUT MUST BE REGARDED AS BEING ONE WITH LONG TERM POSSIBILITIES. IT IS BASED ON THE DISPROPORTIONATION REACTION (24), AND CAN BE CONSIDERED TO BE THE "FIRST HALF" OF THE OVERAL CLAUS REACTION (23).

(24) $H_2S \rightleftharpoons H_2 + S$ $\quad \Delta H^\circ_R = +5$ KCAL/GM MOLE

(25) $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ $\quad \Delta H^\circ_R = -68$ KCAL/GM MOLE

(23) $H_2S + \frac{1}{2}O_2 \rightleftharpoons H_2O + S^\circ$ $\quad \Delta H^\circ_R = -63$ KCAL/GM MOLE

AS CAN BE SEEN FROM THE HEATS OF REACTION, DISPROPORTIONATION IS A NET ENERGY CONSUMER UNLIKE THE CLAUS WHICH IS A NET ENERGY PRODUCER. THE PROCESS IS ATTRACTIVE, HOWEVER, BECAUSE OF THE POSSIBLE PRODUCTION OF H_2 AT A LOWER COST RELATIVE TO SOME OTHER SOURCES.

A) <u>FORCED EQUILIBRIUM IN RECYCLE.</u>

REMOVE H_2 OR S AND RECYCLE.
(ONE PASS YIELDS 5% AT 1100°K WITH NO CATALYST)
(ONE PASS YIELDS 8% AT 900°K WITH CATALYST)

$$H_2S \rightleftharpoons H_2 + S^\circ \qquad \Delta H^\circ_R = +5 \text{ KCAL/MOLE}$$

B) <u>SUCCESSIVE REACTION</u>

$$H_2S + X \rightleftharpoons XS + H_2$$
$$XS + \text{HEAT} \rightleftharpoons X + S^\circ$$

C) <u>CO-REACTION WITH COMPATIBLE EXOTHERMIC REACTION.</u>

$$CH_4 + 2H_2S \rightleftharpoons CS_2 + 4H_2$$
$$CS_2 + SO_2 \rightleftharpoons CO_2 + 3S$$
$$S + O_2 \rightleftharpoons SO_2$$

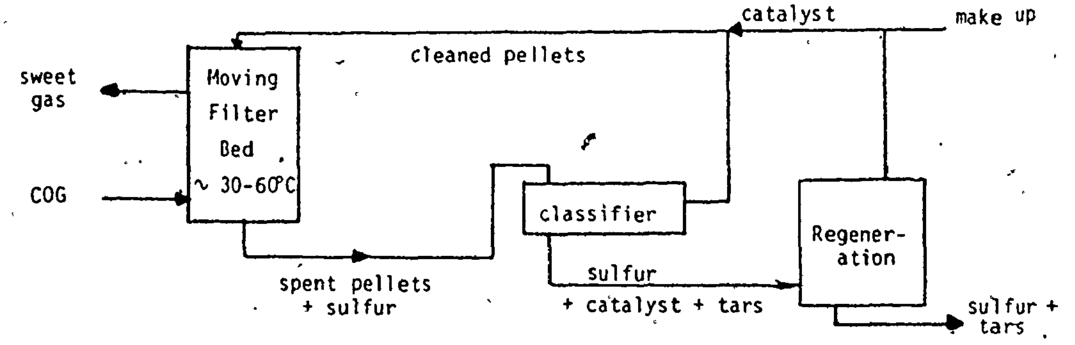
OVERALL

$$2H_2S \rightleftharpoons 2H_2 + 2S^\circ \qquad \Delta H^\circ_R = +5 \text{ KCAL/MOLE}$$
$$CH_4 \rightleftharpoons 2H_2 + CO_2 \qquad \Delta H^\circ_R = -75 \text{ KCAL/MOLE}$$

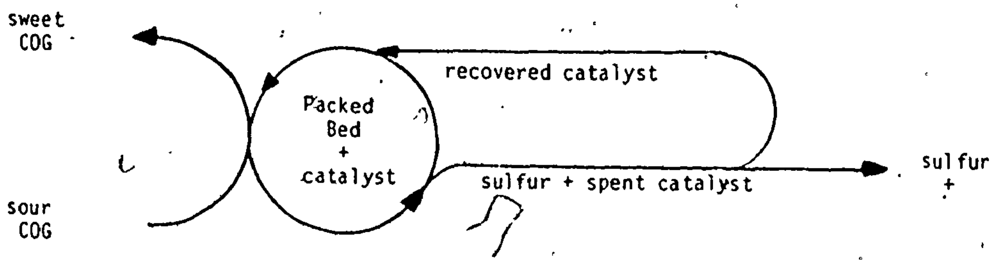
REFERENCE 44

THE IRON OXIDE PROCESS RELIES ON THE REACTION OF AN IRON OXIDE CATALYST WITH H_2S PRODUCING IRON SULFIDE. THIS SUBSEQUENTLY REACTS WITH OXYGEN TO EFFECT THE OVERALL OXIDATION OF H_2S TO ELEMENTAL SULFUR AND WATER. THE CHEMISTRY IS DESCRIBED BY EQUATIONS (26) AND (27). THESE REACTIONS CAN BE CAUSED TO OCCUR SIMULTANEOUSLY BY A CONTROLLED AIR INJECTION TO THE FEED GAS. THE SOLID SULFUR DEPOSITED ON THE BED MUST BE SEPARATED FROM IT OUTSIDE THE REACTOR. THE PROCESS IS NOT CONSIDERED VIABLE FOR HIGH OUTPUT SOURCES - SUCH AS COKE OVENS - UNLESS THE SULFUR PRODUCT IS OF SALABLE QUALITY AND THE CATALYST SUITABLE FOR RECYCLE.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(26) ABSORPTION + REACTION $3H_2S + Fe_2O_3 \rightleftharpoons Fe_2S_3 + 3H_2O$

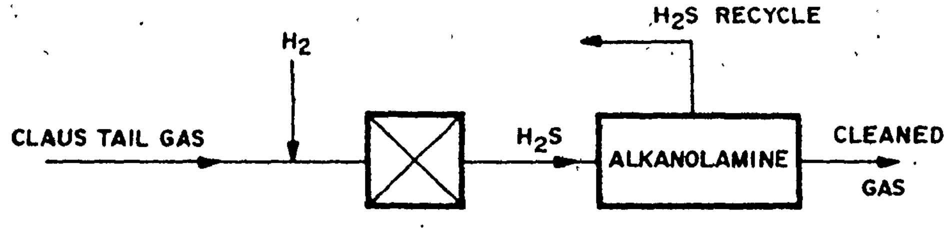
(27) REGENERATION $Fe_2S_3 + 1\frac{1}{2}O_2 \rightleftharpoons Fe_2O_3 + 3S°$

REFERENCES 45,46,47,48.

THRENTHAM TRENCOR-M

THE PROCESS IS SIMILAR TO THE SCOT PROCESS. CLAUS TAIL GASES ARE REACTED WITH H_2 OVER A PACKED BED CATALYST TO REDUCE ALL SULFUR COMPOUNDS TO H_2S BEFORE TREATMENT IN AN ALKANOLAMINE PLANT. THE METHYLDIETHANOLAMINE (MDEA) CONTAINS UNSPECIFIED INORGANIC SALTS WHICH ALLOW SELECTIVE ABSORPTION OF H_2S. THE REGENERATOR OVERHEAD IS RECYCLED TO THE CLAUS FEED.

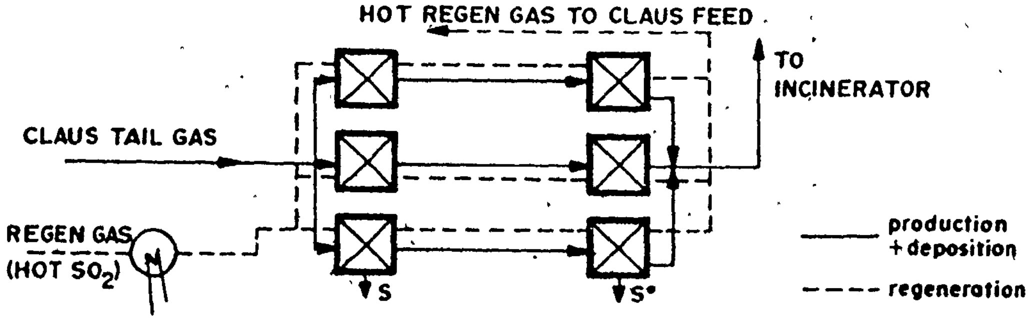
FLOW DIAGRAM



AMOCCO CBA (COLD BED ABSORPTION)

THE PROCESS IS SIMILAR TO THE SULFREEN PROCESS. IT RELIES ON THE COMPLETION OF THE CLAUS REACTION AT LOWER TEMPERATURES (260 -300°F) OVER A STANDARD CLAUS CATALYST. THE DEPOSITED SULFUR IS REMOVED BY VAPOURIZATION WITH A HOT STRIPPING GAS, NECESSITATING AT LEAST TWO REACTORS OPERATING ON SWING. THE STRIPPING GAS IS ONE OF THE CLAUS FEED OR OFF GASES AND NOT A SEPARATE INERT GAS AS IN THE SULFREEN PROCESS. SULFUR IS CONDENSED FROM THE STRIPPING GAS PRIOR TO VENTING (TAIL GAS STRIP) OR RECYCLE TO THE CLAUS FEED (FEED GAS STRIP).

FLOW DIAGRAM

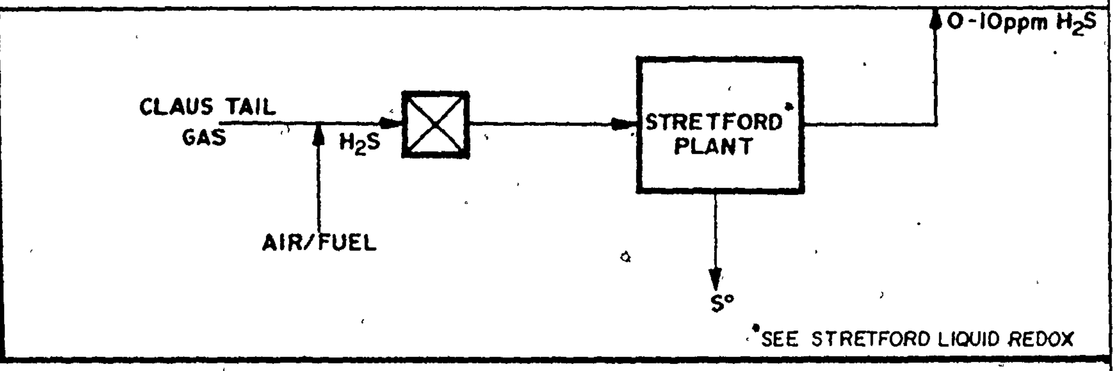


REFERENCES 51; 52.

BEAVON

CLAUS TAIL GAS CONTAINING SULFUR COMPOUNDS IS REDUCED WITH H_2 OVER A PACKED CATALYST BED AT 550 -750°F. THE GAS IS COOLED TO 70 - 120°F AND FED TO A STRETFORD PLANT. (SEE LIQUID REDOX: STRETFORD).

FLOW DIAGRAM

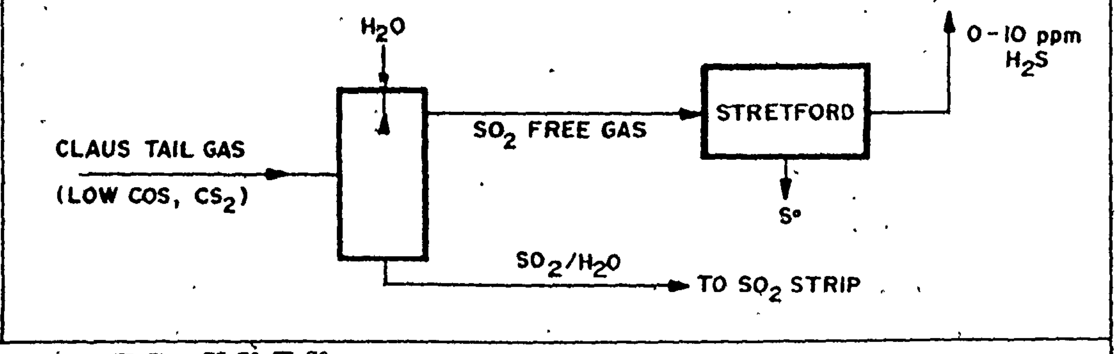


*SEE STRETFORD LIQUID REDOX

CLEANAIR

THIS THREE STAGE PROCESS IS COMPRISED OF A CLAUS KILN OPERATED AT ELEVATED TEMPERATURES TO REDUCE CS_2 AND COS, AN AQUEOUS SCRUBBER AND COOLER TO REMOVE SO_2 AND A STRETFORD UNIT FOR H_2S REMOVAL AND OXIDATION. THE NAMED PROCESSES ARE DESCRIBED ELSWHERE IN THE PAPER.

FLOW DIAGRAM

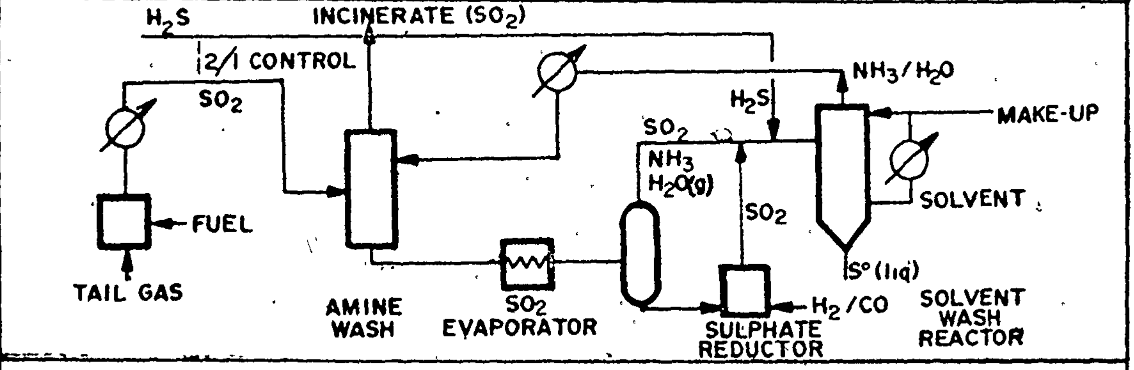


REFERENCES 53,54; 55,56,57,58.

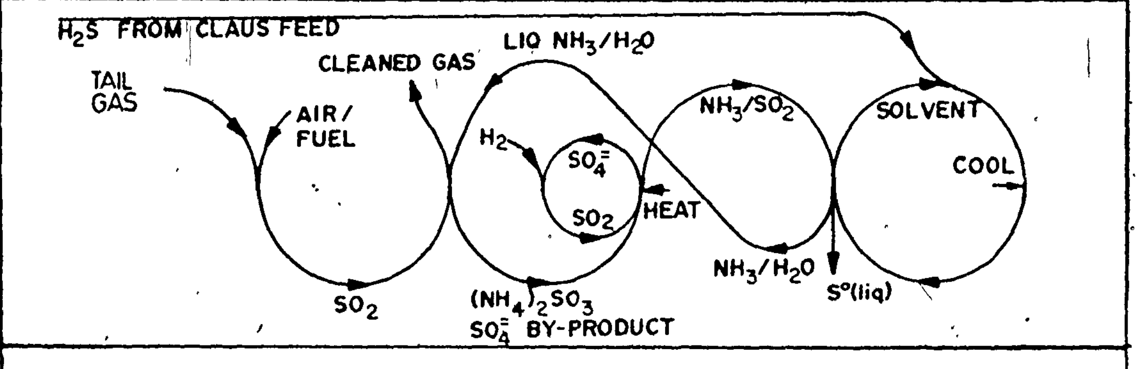
SO_2 IS ABSORBED INTO AN AQUEOUS ALKALINE AMMONIA SOLUTION TO GIVE $(NH_4)_2SO_3$. THIS RICH SOLUTION IS EVAPORATED TO GIVE A NH_3 / SO_2 / H_2O GAS MIXTURE WHICH IS FED ALONG WITH STOICHIOMETRIC H_2S TO A SPECIALTY SOLVENT CATALYTIC REACTOR. THE NONVOLATILE SULFATE IN THE EVAPORATOR BOTTOMS IS REDUCED TO SO_2 WITH H_2 AND RETURNED TO THE EVAPORATOR OVERHEAD. THE SPECIALTY SOLVENT REACTOR CONTAINS A POLYETHYLENE GLYCOLSOLVENT AND AN UNSPECIFIED CATALYST AT 250-280°C. THE INSOLUBLE LIQUID SULFUR FORMED IS WITHDRAWN AT THE REACTOR BOTTOM; THE NH_3/H_2O OVERHEAD IS CONDENSED AND RETURNED TO THE ABSORBER.

COS AND CS_2 ARE UNREACTIVE IN THE IFP UNIT AND THEIR AMOUNTS MUST BE CONTROLLED BY CLAUS TEMPERATURE CONTROL OR INCINERATION.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(28) $SO_2 + NH_3 + H_2O \rightleftharpoons NH_4HSO_3$

(29) $NH_4HSO_3 + NH_3 \rightleftharpoons (NH_4)_2SO_3$

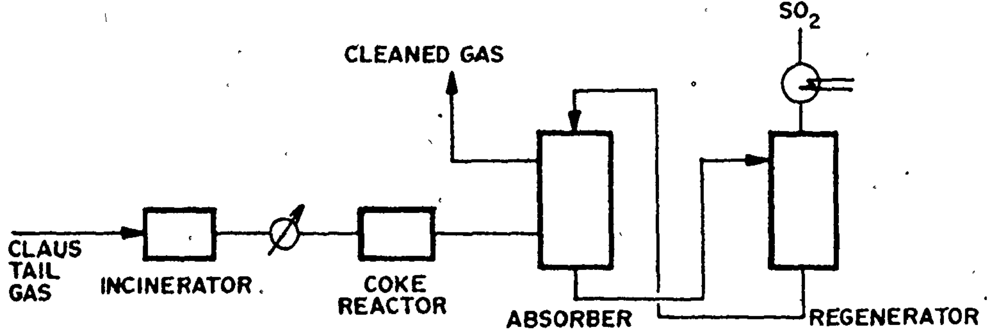
(30) $SO_2 + 2H_2S \xrightarrow[250°C]{\text{CATALYST}} 3S^\circ_{(l)} + 2H_2O$

REFERENCES 59, 60, 61, 62.

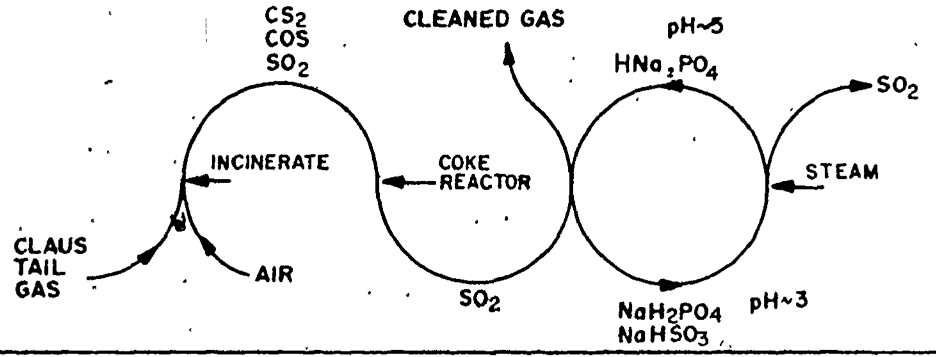
INCINERATED CLAUS TAIL GAS IS REACTED IN A HOT COKE BED AT 400°C WHERE REACTIONS (31), (32) (33) AND (34) OCCUR. SO_2 IS ABSORBED INTO AN AQUEOUS PHOSPHATE SOLUTION WHERE IT IS NEUTRALIZED TO GIVE BISULFITE. THIS RICH SOLUTION IS HEATED UNDER REFLUX TO GIVE AN SO_2/H_2O OVERHEAD SUITABLE FOR RECYCLE AND A REGENERATED NaH_2PO_4 SOLUTION FOR RETURN TO THE ABSORBER. FOR NON-CLAUS OPERATIONS, H_2 IS USED TO REDUCE THE SO_2 PRODUCT TO ELEMENTAL SULFUR.

COS, CS_2, AND NO_x ARE LARGELY CONVERTED TO SO_2, CO_2, AND N_2. EXCESS OXIDATION OF THE COKE IS DEPENDENT ON THE O_2 CONCENTRATION IN THE TAIL GAS.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(31) $CS_2 + 2O_2 \xrightarrow{COKE} CO_2 + 2SO_2$

(32) $COS + 3/2O_2 \xrightarrow{COKE} CO_2 + SO_2$

(33) $NO_x \xrightarrow{COKE} N_2 + CO_2$

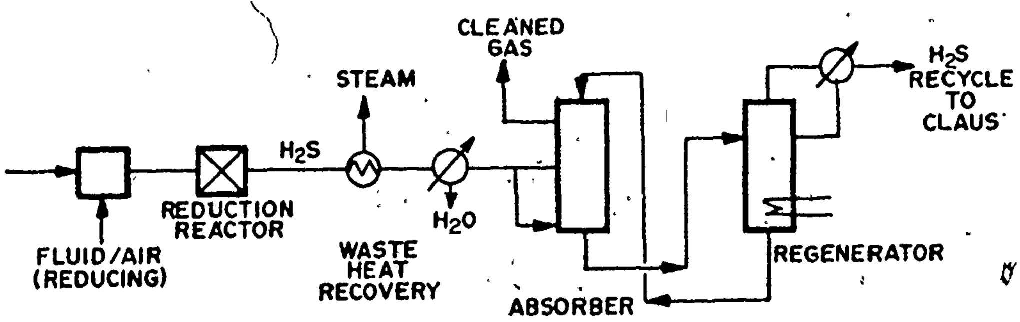
(34) $O_2 \xrightarrow{COKE} CO_2$

(35) $Na_2HPO_4 + H_2O + SO_2 \rightleftharpoons NaHSO_3 + NaH_2PO_4$

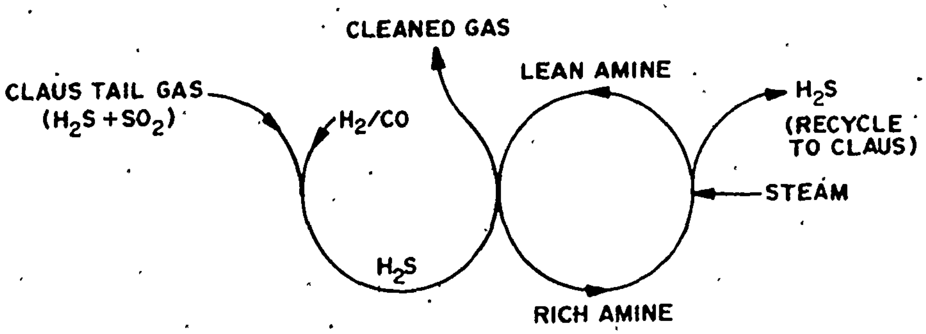
REFERENCES 63, 64

CLAUS TAIL GAS IS INCINERATED IN A REDUCING FLAME AND IS THEN PASSED OVER A FIXED BED CATALYST WHICH CONVERTS ALL SULFUR COMPOUNDS (INCL. COS, CS_2) TO H_2S. THE COOLED SOUR GAS STREAM IS FED TO THE ABSORBING TOWER OF AN ABSORPTION/REGENERATION SYSTEM. THE H_2S OVERHEAD FROM THE REGENERATION TOWER IS RECYCLED TO THE CLAUS. THE ABSORBER IS DESIGNED TO SELECTIVELY ABSORB H_2S IN THE PRESENCE OF EXCESS CO_2. THE ABSORBER OVERHEAD IS INCINERATED TO CONVERT ANY SLIPPED H_2S TO SO_2 PRIOR TO VENTING.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(36) $SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$

(12) $H_2S + HO\text{-}(CH_2)_2\text{-}NH \rightarrow HO\text{-}(CH_2)_2NH_3HS$

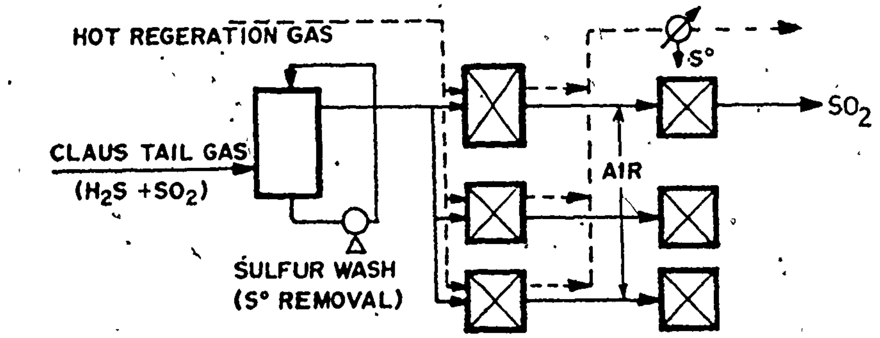
(37) $COS, CS_2 \xrightarrow{H_2/CO} CO_2 + H_2S$

REFERENCES 65, 66, 67, 68, 69, 70.

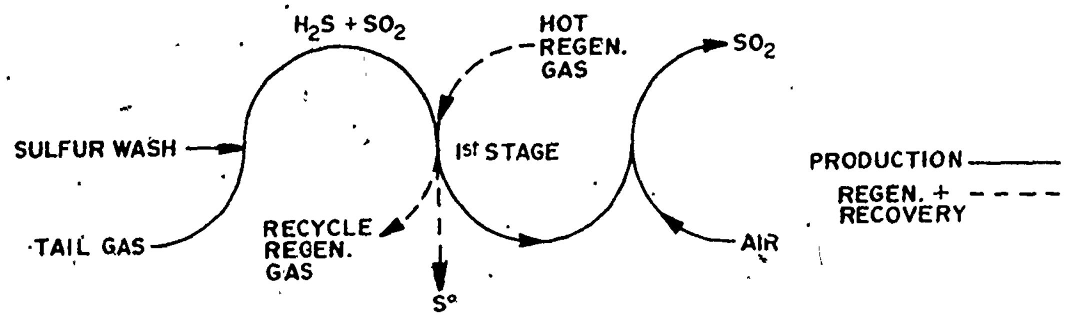
THE PROCESS IS BASED ON THE CLAUS REACTION BEING CARRIED OUT AT LOWER TEMPERATURES AND ON AN ALUMINA CATALYST. THE SULFUR PRODUCT AND ENTRAINED SULFUR IN THE FEED IS DEPOSITED ON THE CATALYST BED. PERIODIC REGENERATION WITH HOT INERT GASES IS REQUIRED. SULFUR PRODUCT IS CONDENSED FROM THE REGENERATION GASES BEFORE RECYCLE. AIR MAY BE FED TO THE LAST STAGE OF A REACTOR TO CONVERT ANY UNREACTED H_2S, CS_2, AND COS TO SO_2 PRIOR TO VENTING.

COS AND CS_2 ARE UNREACTIVE IN THE SULFREEN UNIT AND APPEAR IN THE OFF GAS UNLESS THE OXIDATION STEP IS INCLUDED. THE REGENERATION GAS IS CONTAINED IN A CLOSED LOOP AND IS NON-MIXING WITH THE CLAUS STREAMS.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(38) $2H_2S + SO_2 \xrightarrow{\text{PACKED BED}} S^\circ_{(s)} + H_2O$ (PRODUCTION & DEPOSITION)

(39) $S^\circ_{(s)} \xrightarrow{\text{HOT STRIPPING GAS}} S^\circ_{VAP}$ (REGENERATION)

(40) $COS + CS_2 \cancel{\xrightarrow{\text{PACKED BED}}}$

(41) $H_2S + COS + CS_2 + O_2 \longrightarrow H_2O + CO_2 + SO_2$ (LAST STAGE)

REFERENCES 71,72,73,74,75,76.

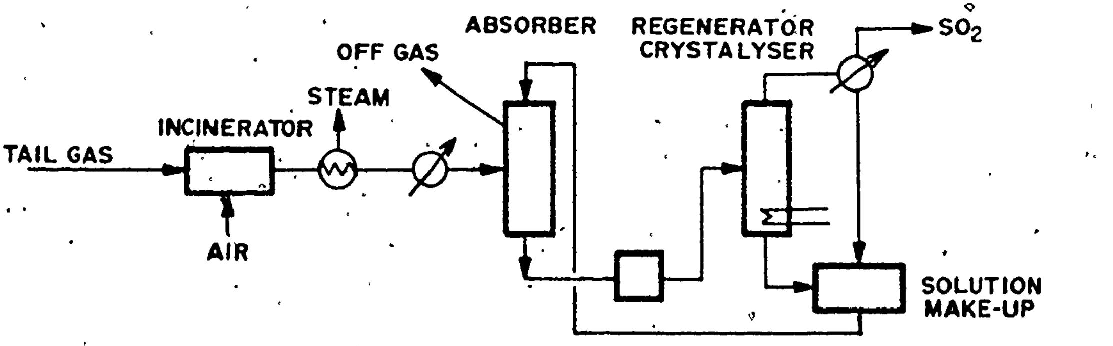
WELLMAN - LORD

Claus tail gas is incinerated converting all sulfur containing species (incl. COS, CS_2) to SO_2. The resulting gas mixture is cooled and SO_2 is removed by contact with an aqueous sodium sulfite solution to form a sodium hydrosulfite rich solution. Water is evaporated in a cystallizer producing a Na_2SO_3/H_2O slurry with a SO_2/H_2O overhead. Condensable overhead is mixed with crystallizer bottoms to dissolve the precipitated sulfite. This regenerated solution is returned to the absorber. The uncondensable SO_2 overhead is recyled to the feed of the Claus reactor. A substantial degree of evaporation must occur to minimize the formation of $Na_2S_2O_5$ (pyrosulfite). Recirculated pyrosulfite will not absorb an equivalent of SO_2.

Sulfate formed by the oxidation of sulfite by dissolved oxygen builds up in solution at an unspecified rate. SO_3 absorbed remains in solution as sulfate. The effect of COS and CS_2 is not specified.

The process has not been considered feasible for Claus plants of less than 50 tons/day S.

FLOW DIAGRAM



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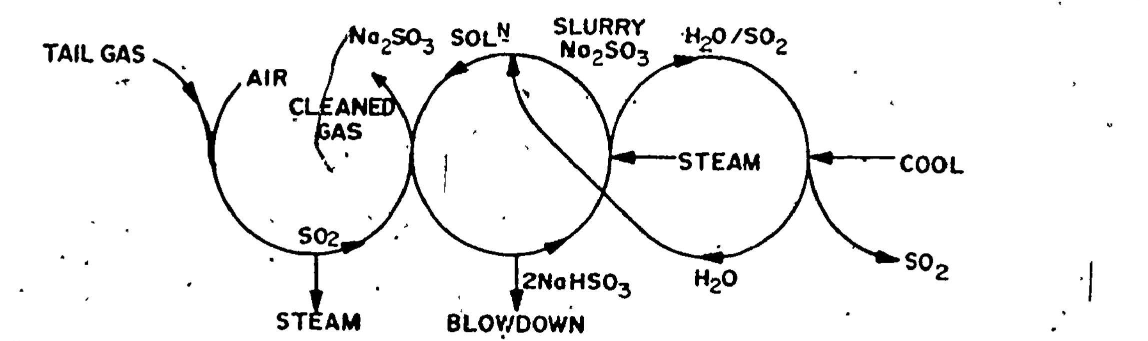


PROCESS CHEMISTRY

(42) $H_2S, COS, CS_2 + O_2 \longrightarrow SO_2 + CO_2 + H_2O$

(43) $SO_2 + Na_2SO_3 + H_2O \rightleftharpoons 2NaHSO_3$

(44) $4NaHSO_3 \xrightarrow{HEAT} Na_2SO_{3(SOLID)} + Na_2SO_{3(SOL^N)} + 2SO_2 + 2H_2O$

(45) $Na_2SO_{3(s)} + H_2O \rightleftharpoons Na_2SO_3(SOL^n)$

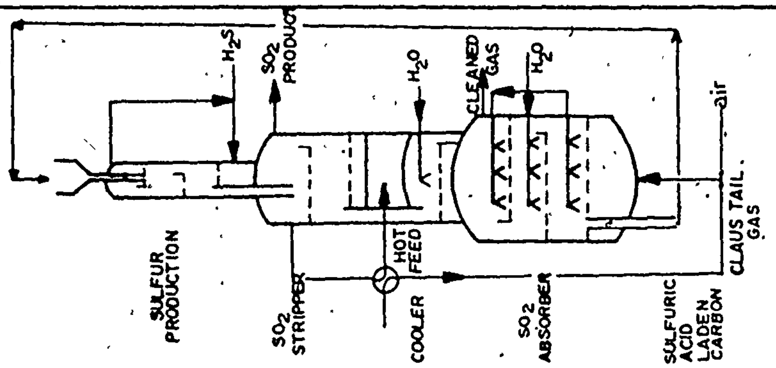
REFERENCES 77,78,79,80,81.

THE PROCESS USES A FLUIDIZED ACTIVATED CARBON TO EFFECT SO_2 ABSORPTION, OXIDATION TO H_2SO_4 AND ULTIMATE RE-REDUCTION TO EITHER SO_2 OR ELEMENTAL SULFUR.

IN THE PRESENCE OF O_2 AND H_2O, SULFUR COMPOUNDS IN THE FEED GAS ARE CATALYTICALLY CONVERTED TO H_2SO_4 WHICH REMAINS ADSORBED ON THE ACTIVATED CARBON. THIS IS CONTACTED WITH 1/9 STOICHIOMETRIC H_2S TO GIVE A STABLE $S°/H_2SO_4$ ADSORBED MIXTURE. ON HEATING WITH HOT SO_2 RECYCLE THIS IS CATALYTICALLY CONVERTED TO SO_2 AND STRIPPED FROM THE CARBON. AFTER COOLING, THE CARBON IS RETURNED TO THE ABSORBER SECTION. IF ELEMENTAL SULFUR PRODUCT IS DESIRED, 3 TIMES STOICHIOMETRIC H_2S IS REQUIRED.

THE PROCESS CHEMISTRY IS INTIMATELY RELATED TO THE EFFICIENT HEAT AND MASS TRANSFER PROPERTIES OF FLUIDIZED BEDS AND THE ABSORPTIVE AND CATALYTIC PROPERTIES OF ACTIVATED CARBON.

FLOW DIAGRAM



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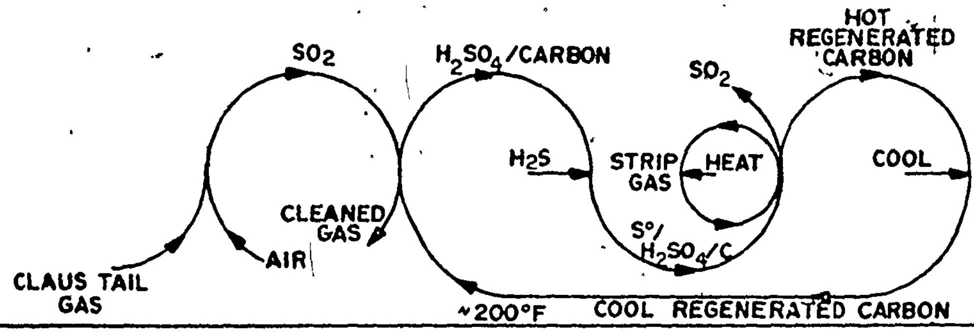


PROCESS CHEMISTRY

(46) $SO_2 + H_2O + {}^1/_2O_2 \xrightarrow{\text{CARBON}} H_2SO_4$ (CARBON)

(47) $9H_2SO_4$ (CARBON) $+ 3H_2S \rightleftharpoons (4S°/_8H_2SO_4)$(CARBON) $+ 4H_2O$

(48) $(4S°/_8H_2SO_4)/_{\text{CARBON}} \xrightarrow{\text{HEAT}} 12\ SO_2$ (SO_2 PRODUCT)

OR

(49) $(H_2SO_4)_{\text{CARBON}} + 3H_2S \rightleftharpoons (4S°)_{\text{CARBON}}$

(50) $(4S°)/_{\text{CARBON}} \xrightarrow{\text{HEAT}} 4S°_{(V)}$ (S° PRODUCT)

SO_2 PRODUCT $^1/_3$ MOLES H_2S/MOLE S IN FEED

S° PRODUCT 3 MOLES H_2S/MOLE S° IN FEED

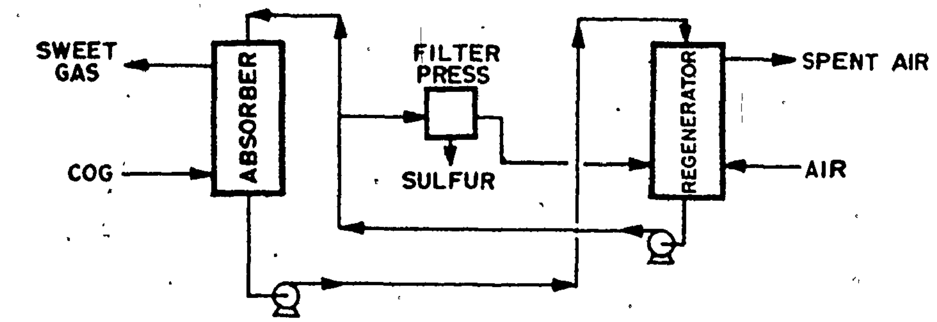
REFERENCES 82, 83, 84, 85, 86, 87.

FUMAKS

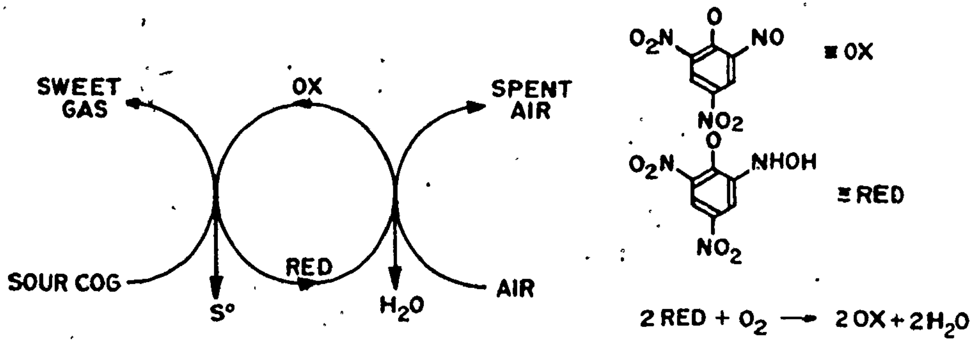
H_2S IS ABSORBED INTO AN AQUEOUS 2 - 3% CARBONATE OR AN AQUEOUS AMMONIA SOLUTION (BOTH OF UNSPEC. pH). THERE, IT REACTS WITH PICRIC ACID INITIALLY PRESENT IN SOLUTION TO FORM POLYSULFIDE AND THE REDUCED (HYDROXYLAMINO) COMPOUND. THE RESULTING SOLUTION IS AERATED IN A REGENERATION COLUMN WHERE THE HYDROXYLAMINO COMPOUND IS OXIDIZED TO THE NITROSO COMPOUND BY A RADICAL CHAIN MECHANISM. THIS REGENERATED SOLUTION IS RETURNED TO THE ABSORBING TOWER. PRECIPITATED SULFUR IS FILTERED OFF FROM A SLIP STREAM.

ANY HCN OR SO_2 ABSORBED WILL REACT WITH POLYSULFIDE AND WILL REMAIN IN SOLUTION AS THIOCYANATE AND THIOSULFATE. ALKALI MAKEUP DATA INDICATES AN OXIDATIVE BYPRODUCT (THIOSULFATE, SULFATE) FORMATION RATE OF 1 - 2% OF SULFUR PRODUCED.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(59) $H_2S \rightleftharpoons H^+ + HS^-$

(60) $2H_2S_{(x)} + OX \rightleftharpoons H_2S_{2x} + RED$

(56) $H_2S_{2x} \rightleftharpoons H_2S_{(2x-8)} + S_8$ (IF 2x>9)

(52) $RED + 1/2O_2 \rightleftharpoons OX + H_2O$

(61) $HCN \rightleftharpoons H^+ + CN^-$

(57) $CN^- + H_2S_x \rightleftharpoons SCN^- + H_2S_{x-1}$

(62) $SO_2 + H_2O \rightleftharpoons SO_3^= + 2H^+$

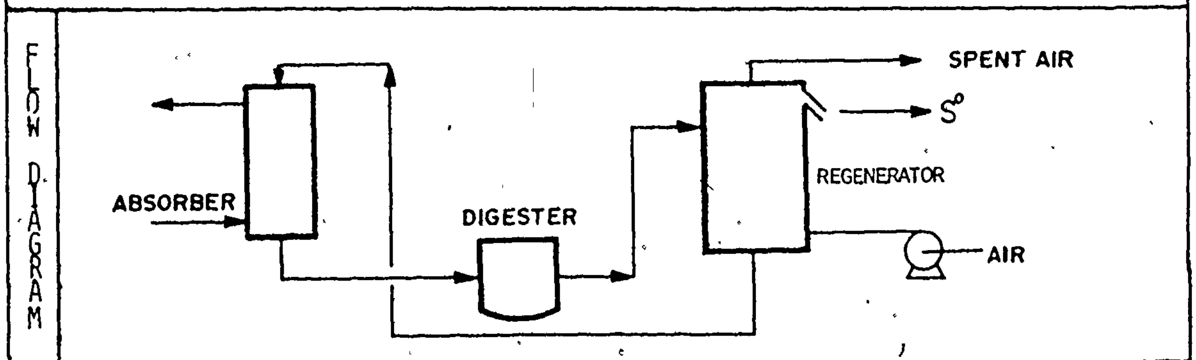
(63) $SO_3^= + H_2S_x \rightleftharpoons S_2O_3^= + H_2S_{x-1}$

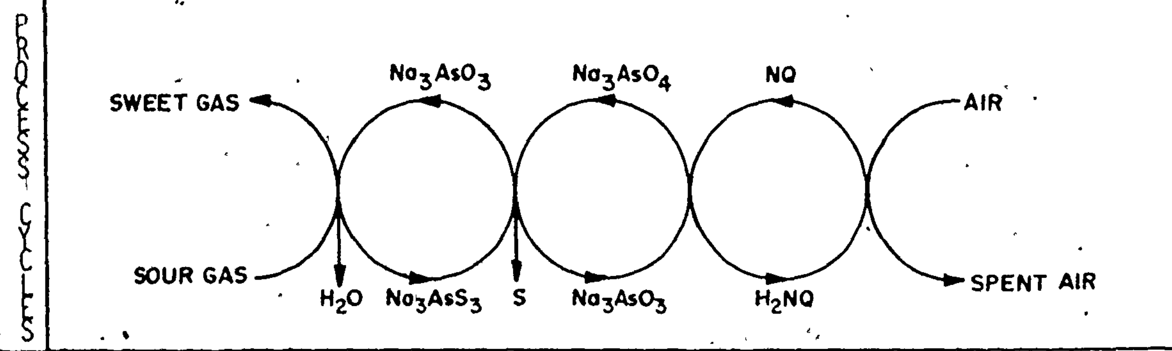
(64) $H_2S_x, S_2O_3^=, SO_3^= + O_2 \rightarrow SO_4^=$

REFERENCES 88,89.

H_2S IS ABOSRBED INTO AN AQUEOUS ALKALINE SOLUTION (UNSPECIFIED pH) OF SODIUM ARSENATE/ ARSENITE TO FORM SODIUM THIOARSENITE. AFTER ACIDIFICATION WITH CO_2, THE RESULTING SOLUTION ENTERS AN OXIDIZER/FROTH FLOTATION UNIT. REACTION BETWEEN ARSENATE AND THIOARSENITE PRODUCES MONOTHIOARSENATE WHICH SUBSEQUENTLY "DECOMPOSES" INTO ELEMENTAL SULFUR AND SODIUM ARSENITE. THE SODIUM ARSENITE IS AIR OXIDIZED IN THE PRESENCE OF A QUINONE BY A RADICAL CHAIN MECHANISM. THE EXISTANCE OF POLYSULFIDE INTERMEDIATES HAS NOT BEEN CONFIRMED BY THE AUTHORS.

HCN AND SO_2 ABSORBED INTO THE SOLUTION ARE PROBABLY FIXED AS THIOCYANATE AND THIOSULFATE. DETAILS ON OXIDATIVE BYPRODUCT FORMATION RATES (THIOSULFATE, SULFATE) ARE NOT AVAILABLE.





(65) $Na_3AsO_3 + 3H_2S \rightleftharpoons Na_3AsS_3 + 3H_2O$

(66) $Na_3AsS_3 + 3Na_3AsO_4 \rightleftharpoons 3Na_3AsO_3S + Na_3AsO_3$

(67) $Na_3AsO_3S \rightleftharpoons Na_3AsO_3 + S_x$

(68) $Na_3AsO_3 + 1/2\,O_2 \underset{RED}{\overset{OX}{\rightleftharpoons}} Na_3AsO_4$

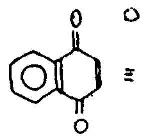
(61) $HCN \rightleftharpoons H^+ + CN^-$

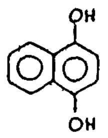
(57) $CN^- + H_2S_x \rightleftharpoons SCN^- + H_2S_{x-1}$

(62) $SO_2 + H_2O \rightleftharpoons SO_3^= + 2H^+$

(63) $SO_3^= + H_2S_x \rightleftharpoons S_2O_3^= + H_2S_{x-1}$

(64) $SO_3^=,\ S_2O_3^=,\ +O_2 \longrightarrow SO_4^=$


≡ OX

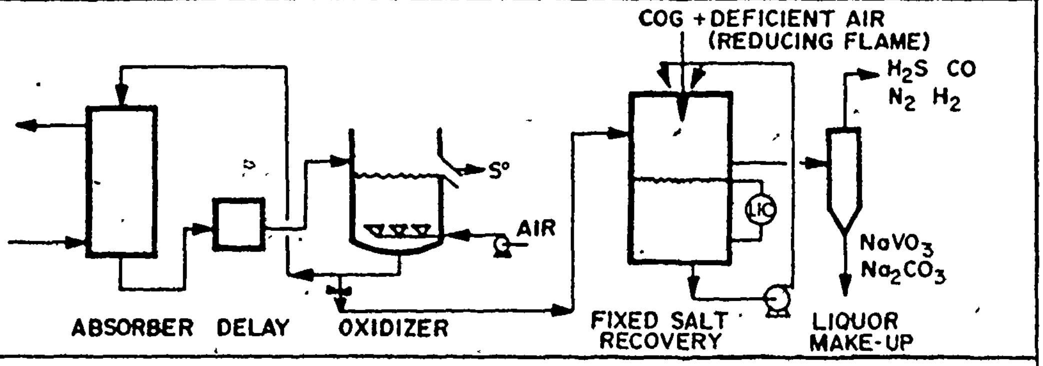

≡ RED

REFERENCES 90, 91, 92, 93.

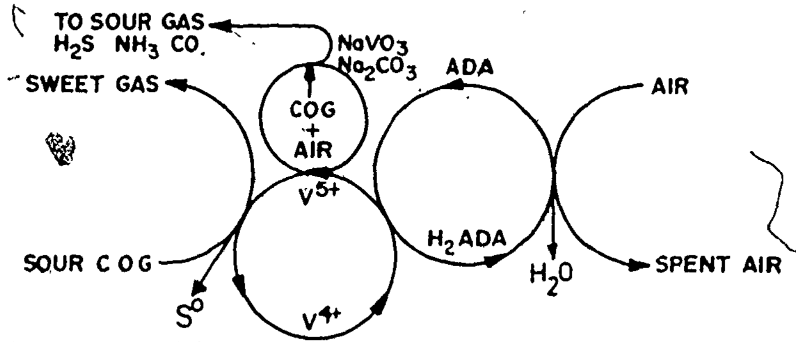
The solution chemistry is parallel to that of the Stretford process (Patent, British Gas Corp.). Additionally, a Fixed Salt Recovery unit is included (Patent: Peabody-Holmes Ltd.). It accepts a slipstream with byproduct flow rate equal to the fixed salt formation rate. This blowdown is incinerated and the products are recylced. The overall process is a closed system yielding sulfur, nitrogen and water as the only products.

Feed liquour to the FSR unit is first concentrated by injection into the partially cooled flame gases and is then recycled back into the hot combustion zone where the decomposition reactions occur. Gaseous and particulate products are venturi scrubbed, cyclone separated and recycled.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(69) $H_2S + Na_2CO_3 \rightleftharpoons NaHS + NaHCO_3$ (ABSORBER)

(70) $2H_2S_x + 2VO_3^- + 2H_2O \rightleftharpoons H_2S_{2x} + 2VO^{2+} + 6OH^-$ (DELAY TANK)

(71) $2VO^{2+} + 6OH^- + {}^1/_2O_2 \underset{H_2ADA}{\overset{ADA}{\rightleftharpoons}} 2VO_3^- + 3H_2O$ (OXIDIZER)

(72) $HCN + Na_2CO_3 \rightleftharpoons NaCN + NaHCO_3$

(57) $CN^- + H_2S_x \rightleftharpoons SCN^- + H_2S_{x-1}$

(73) $SO_2 + H_2O + 2Na_2CO_3 \rightleftharpoons Na_2SO_3 + 2NaHCO_3$

(63) $SO_3^= + H_2S_x \rightleftharpoons S_2O_3^= + H_2S_{x-1}$

(74) $HS^-, SCN^-, S_2O_3^=, SO_4^= + COG/_{AIR} \longrightarrow H_2S \& H_2 + H_2 + CO_3^=$

REFERENCES 94, 95, 96, 97, 98, 99, 100, 101.

H_2S IS ABSORBED INTO AN ALKALINE SOLUTION AT PH 9.5 (BUFFER UNSPECIFIED). IT IS CLAIMED THAT ELEMENTAL SULFUR PRODUCT IS FORMED FROM REACTION WITH FERRATE PRESENT IN SOLUTION. THE $FeO_2^{=}$ FORMED IS AIR OXIDIZED TO REGENERATE THE FERRATE.

REFERENCE 102.

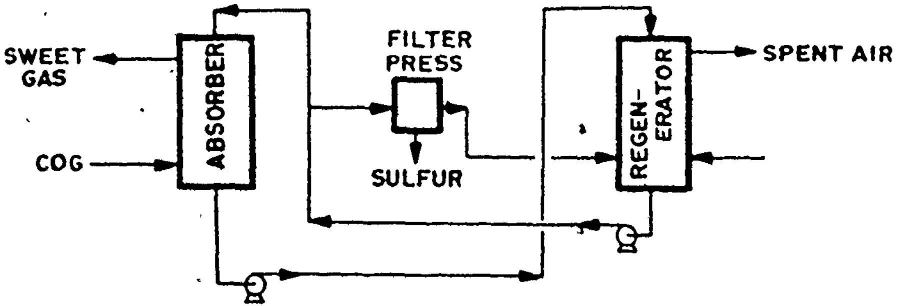
H_2S IS ABSORBED INTO AN AQUEOUS ALKALINE (pH 7.5 - 9.0) SOLUTION WHERE IT IS THEN OXIDIZED TO ELEMENTAL SULFUR BY THE Fe^{3+}/Fe^{2+} REDOX COUPLE. THE IRON IS COMPLEXED WITH AN ORGANIC OXYGEN AND/OR NITROGEN CONTAINING COMPOUND TO PREVENT THE PRECIPITATION OF MIXED IRON OXIDES, HYDROXIDES AND SULFIDES. THE Fe^{2+} COMPLEX IS AIR OXIDIZED BY A RADICAL CHAIN MECHANISM AND IS RETURNED TO THE ABSORBER. PRECIPITATED SULFUR CAN BE REMOVED BY CONVENTIONAL MEANS.

ANY HCN AND SO_2 ABSORBED WILL REACT WITH POLYSULFIDE AND WILL REMAIN IN SOLUTION AS THIOCYANATE AND THIOSULFATE. EXCESS CYANIDE MAY REACT TO FORM INSOLUBLE IRON-CYANIDE COMPOUNDS.

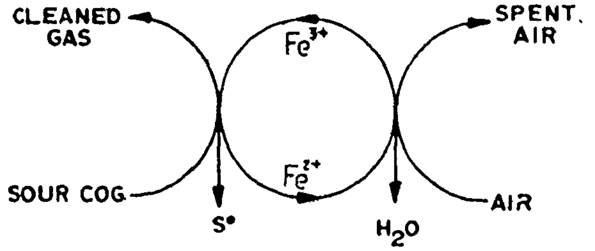
CATABAN: LOADING IS GIVEN AS 7000 PPM IN THE PROPRIETARY CATABAN CONCENTRATE (I.E., 350 PPM IN A 5% CATABAN SOLUTION). THIOSULFATE AND SULFATE ARE FORMED AS OXIDATIVE BYPRODUCTS AT A RATE OF 5% OF S PRODUCED.

LO - CAT: DATA NOT AVAILABLE.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(59) $H_2S \rightleftharpoons H^+ + HS^-$ (BUFFER?)

(75) $2H_2S_x + 2Fe^{3+} \rightleftharpoons 2Fe^{2+} + H_2S_{2x} + 2H^+$

(76) $Fe^{2+} + {}^1\!/_2O_2 + 2H^+ \rightleftharpoons Fe^{3+} + H_2O$

(57) $CN^- + H_2S_x \rightleftharpoons SCN^- + H_2S_{x-1}$

(63) $SO_3^{2-} + H_2S_x \rightleftharpoons S_2O_3^{2-} + H_2S_{x-1}$

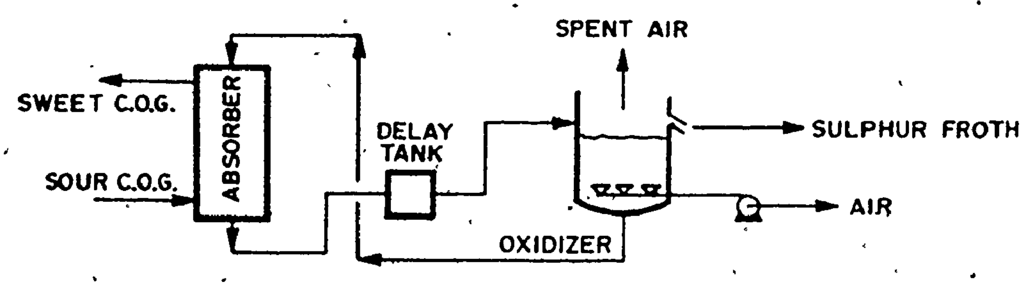
(77) $NCN^- + Fe^{2,3} \rightleftharpoons Fe(CN)_N^{2,3-N}$

REFERENCES 103; 104

H_2S IS SELECTIVELY ABSORBED INTO A CARBONATE SOLUTION BUFFERED AT PH 8.5 - 9.0 WHERE IT IS THEN OXIDIZED TO ELEMENTAL SULFUR BY THE VANADIUM 5+/4+ REDOX COUPLE. THE VANADIUM 4+ FORMED DURING POLYSULFIDE PRODUCTION IS COMPLEXED WITH AN ORGANIC CARBOXYLIC ACID TO PREVENT THE PRECIPITATION OF SODIUM VANADYL VANADATES. THE COMPLEX IS AIR OXIDIZED IN THE PRESENCE OF ANTHRAQUINONE DISULFONIC ACID (ADA) BY A RADICAL CHAIN PROCESS AND IS RETURNED TO THE ABSORBER. THE OXIDIZER DOUBLES AS A FROTH FLOATATION CELL THAT PRODUCES A SLURRY WHICH IS AUTOCLAVED YIELDING SULFUR OF SUFFICEINT PURITY FOR ANY COMMERCIAL USE.

SULFUR CHAIN BUILDUP IS BY THE POLYSULFIDE ROUTE. THEREFORE, THE SOLUTION FIXES ANY SO_2 AND CN^- AS THIOSULFATE AND THIOCYANATE. A SLOW BUILDUP OF NON-VOLATILE SODIUM SALTS (SULFATE, THIOSULFATE, THIOCYANATE) NECESSITATES A PERIODIC BLOWDOWN OR LIQUOR REPLACEMENT. THE BYPRODUCT FORMATION RATE IS APPROXIMATELY 1% BASED ON RECOVERED PRODUCT. AN OPERATING RANGE OF 500 - 1000 PPM H_2S (ONE HALF OF THE MOLAR VANADIUM CONCENTRATION) DETERMINES THE SIZE OF THE PLANT NECESSARY.

FLOW DIAGRAM



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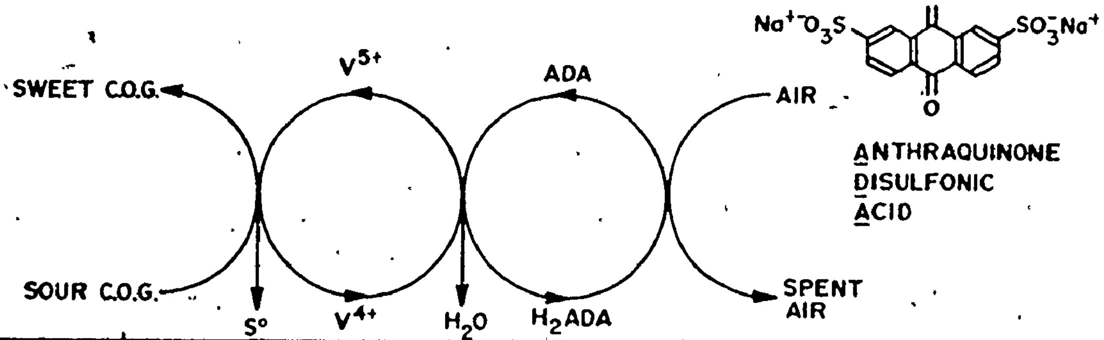


PROCESS CHEMISTRY

(69) $H_2S + Na_2CO_3 \rightleftharpoons NaHS + NaHCO_3$ ABSORBER

(70) $2H_2S_x + 2VO_3^- + 2H_2O \rightleftharpoons H_2S_{2x} + 2VO^{2+} + 6OH^-$ DELAY

(71) $2VO^{2+} + 6OH^- + {}^1/_2 O_2 \underset{H_2ADA}{\overset{ADA}{\rightleftharpoons}} 2VO_3^- + 3H_2O$ OXIDIZER

(72) $HCN + Na_2CO_3 \rightleftharpoons NaCN + NaHCO_3$

(57) $CN^- + H_2S_x \rightleftharpoons SCN^- + H_2S_{x-1}$

(73) $SO_2 + 2Na_2CO_3 + H_2O \rightleftharpoons Na_2SO_3 + 2NaHCO_3$

(63) $SO_3^{=} + H_2S_x \rightleftharpoons S_2O_3^{=} + H_2S_{x-1}$

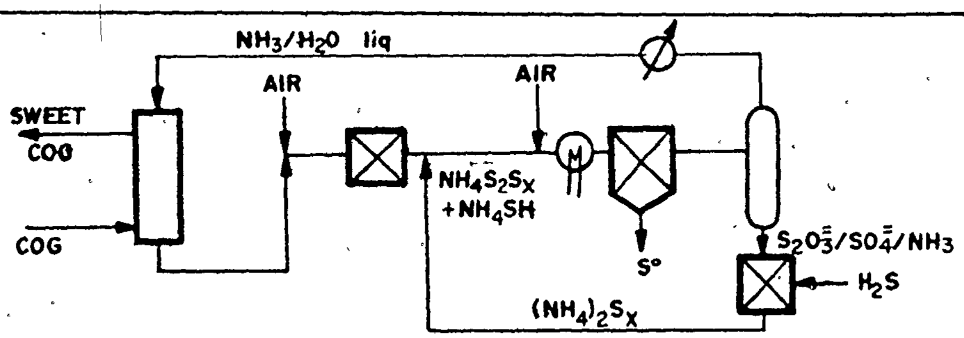
(64) $SO_3^{=}, S_2O_3^{=} + O_2 \rightleftharpoons SO_4^{=}$.

REFERENCES 94, 95, 96, 97, 98, 99, 100.

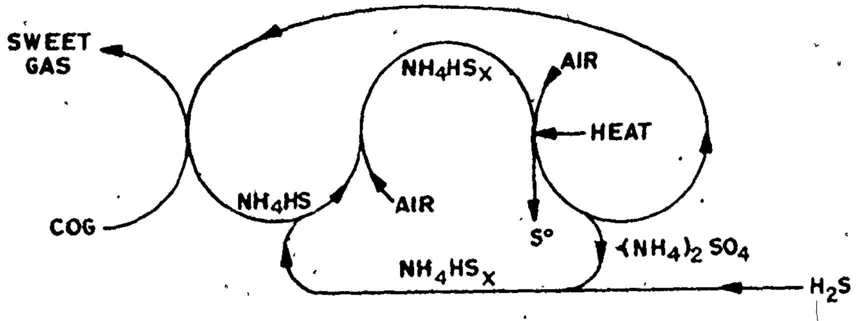
H_2S IS ABSORBED INTO AN AQUEOUS AMMONIA SOLUTION (PH OR % NH_3 UNSPECIFIED). THE STREAM IS MIXED WITH AIR, HEATED AND THEN PASSED THROUGH A PACKED CATALYST BED. PARTIAL OXIDATION OF THE HS^- YIELDS SULFUR AS POLYSULFIDES IN SOLUTION. THIS IS HEATED TO A TEMPERATURE ABOVE THE MELTING POINT OF SULFUR, AND A SUBSEQUENT AIR OXIDATION OVER A SECOND CATALYST BED CONVERTS ALL THE POLYSULFIDE TO INSOLUBLE MOLTEN SULFUR WHICH IS THEN WITHDRAWN.

THIOSULFATE FORMED AS A BYPRODUCT IS REACTED WITH EXCESS H_2S IN A SLIPSTREAM REACTOR TO GIVE A POLYSULFIDE SOLUTION WHICH IS RECYCLED. THE STOICHIOMETRY OF THIS REACTION IS NOT QUOTED. HCN ABSORBED WOULD BE CONVERTED TO THIOCYANATES. SULFATE IS FORMED AS AN OXIDATIVE BYPRODUCT AT A RATE OF 0.1% OF SULFUR PRODUCT AND MUST BE REMOVED BY PERIODIC BLOWDOWN.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(5) $H_2S + NH_3 \rightleftharpoons NH_4HS$

(78) $(N+1)NH_4HS + \frac{N}{2}O_2 \xrightarrow{\text{CATALYST}} H_2S_{N+1} + (N+1)NH_3 + NH_2O$ (1ST STAGE)

(79) $H_2S_{N+1} + \frac{1}{2}O_2 \xrightarrow[\text{HEAT}]{\text{CATALYST}} (N+1)\,S^\circ + H_2O$ (LAST STAGE)

(80) $H_2S_x, SO_3^{2-}, S_2O_3 \overset{O_2}{\rightleftharpoons} SO_4^{2-} + S_2O_3^{2-}$ (OXIDATIVE BYPRODUCT)

(81) $S_2O_3^{2-} + H_2S \underset{\text{EXCESS } H_2S}{\rightleftharpoons} H_2S_x + H_2O$ (THIOSULFATE REDUCTOR)

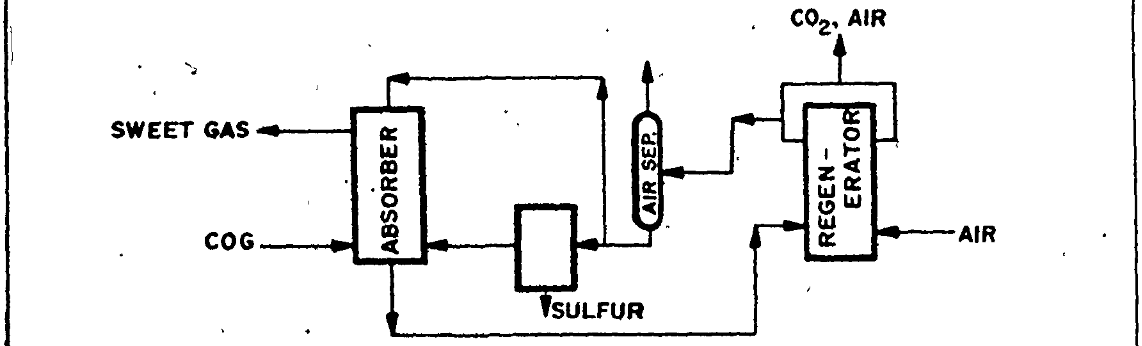
(57) $CN^- + H_2S_x \rightleftharpoons SCN^- + H_2S_{x-1}$

REFERENCES 105, 106, 107.

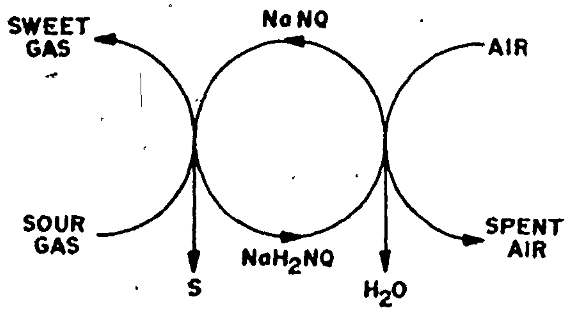
H_2S IS SELECTIVELY ABSORBED INTO AN AQUEOUS ALKALINE SOLUTION AT pH 8.0 - 9.0 WHERE IT REACTS WITH 1.4 NAPTHAQUINONE - 2 - SULFONATE TO FORM POLYSULFIDE CHAINS AND THE HYDROQUINONE. THE LATTER IS AIR OXIDIZED BY A RADICAL CHAIN MECHANISM AND THE REGENERATED SOLUTION IS RETURNED TO THE ABSORBER. SULFUR PRODUCT IS REMOVED BY FILTRATION OF A SLIPSTREAM.

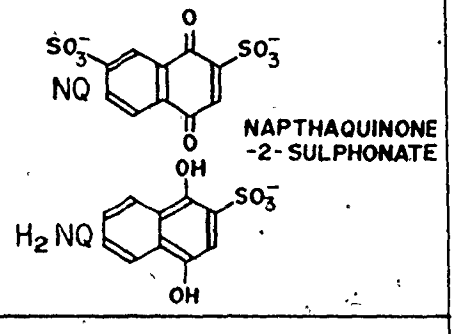
ANY HCN AND SO_2 ABSORBED WILL REACT WITH POLYSULFIDE AND WILL REMAIN IN SOLUTION AS THIOCYANATE AND THIOSULFATE. ADDITIONALLY, THIOSULFATE AND SULFATE ARE FORMED AS OXIDATION BY-PRODUCTS. REPORTED CARBONATE MAKEUP LEVELS OF 0.5 MOLE/KG S° WOULD INDICATE A FIXED SALT FORMATION RATE OF 2% OF SULFUR PRODUCT.

FLOW DIAGRAM



PROCESS CYCLES





PROCESS CHEMISTRY

$$H_2S + Na_2CO_3 \rightleftharpoons NaHS + NaHCO_3 \tag{69}$$

$$2HS_{2x} + NQ \rightleftharpoons H_2S_{2x} + H_2NQ \tag{82}$$

$$H_2S_x \rightleftharpoons S_8^{\circ} + H_2S_{x-8} \tag{56}$$

$$1/2\,O_2 + H_2NQ \rightleftharpoons H_2O + NQ \tag{83}$$

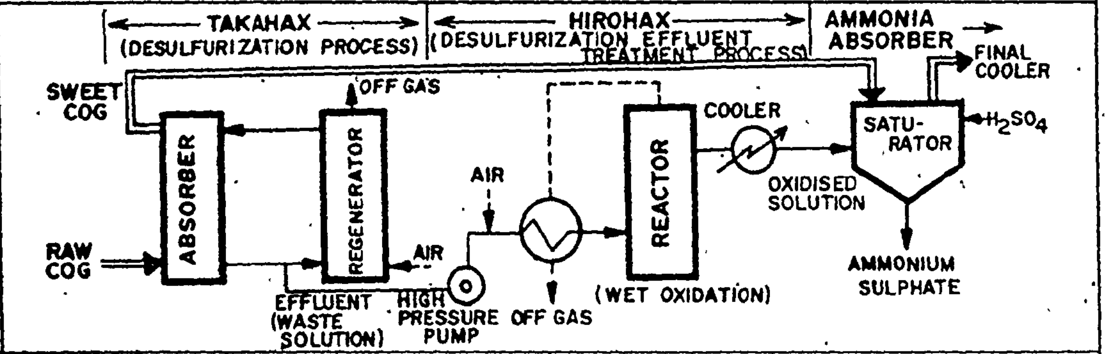
$$SO_3^{2-}, S_2O_3^{=} + O_2 \longrightarrow SO_4^{2-} \tag{64}$$

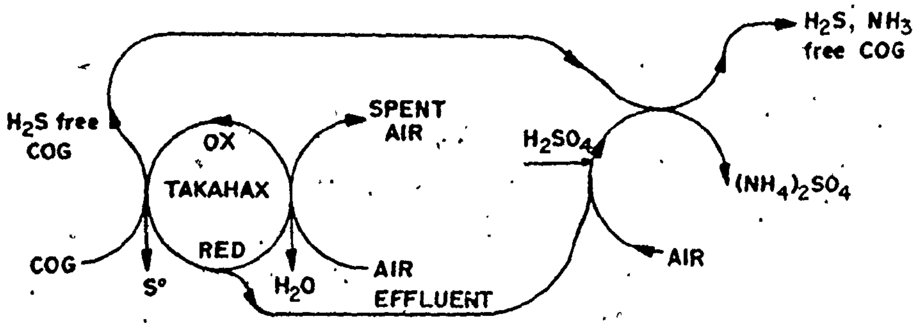
$$SO_3^{2-} + H_2S_x \rightleftharpoons S_2O_3^{2-} + H_2S_{x-1} \tag{63}$$

$$CN^- + H_2S_x \rightleftharpoons SCN^- + H_2S_{x-1} \tag{57}$$

REFERENCES 108, 109, 110, 111.

THE SOLUTION CHEMISTRY IS PARALLEL TO THAT OF THE TAKAHAX PORCESS BUT IS CARRIED OUT IN AN AMMONIA BASED SOLUTION. THE REDOX REACTIONS ARE INDEPENDENT OF THE BUFFER SYSTEM USED IN THE ABSORPTION PROCESS. ADDITIONALLY, A HIROHAX EFFLUENT TREATING PROCESS IS INCLUDED IT ACCEPTS A SLIPSTREAM WITH BYPRODUCT FLOW RATE EQUAL TO THE FIXED SALT FORMATION RATE. AFTER WET OXIDATION OF THE OXIDATIVE BYPRODUCTS TO SULFATE, NH_3 PRESENT IN THE COG IS ABSORBED TO FORM $(NH_4)_2SO_4$. THE OVERALL PROCESS IS A CLOSED SYSTEM YIELDING SULFUR, AMMONIUM SULFATE AND H_2O AS THE ONLY PRODUCTS.





(82) $2HS_x + NQ \rightleftharpoons H_2S_{2x} + H_2NQ$

(56) $H_2S_x \rightleftharpoons S_8^\circ + H_2S_{x-8}$

(83) $1/2\,O_2 + H_2NQ \rightleftharpoons H_2O + NQ$

(64) $SO_3^{2-}, S_2O_3^{=} + O_2 \longrightarrow SO_4^{2-}$

HIROHAX (50.- 90 ATM ; 250 - 280°C)

(84) $NH_4SCN + 2O_2 + 2H_2O \longrightarrow (NH_4)_2SO_4 + CO_2$

(85) $(NH_4)_2S_2O_3 + 2O_2 + H_2O \longrightarrow (NH_4)_2SO_4 + H_2SO_4$

REFERENCES 112,113,114

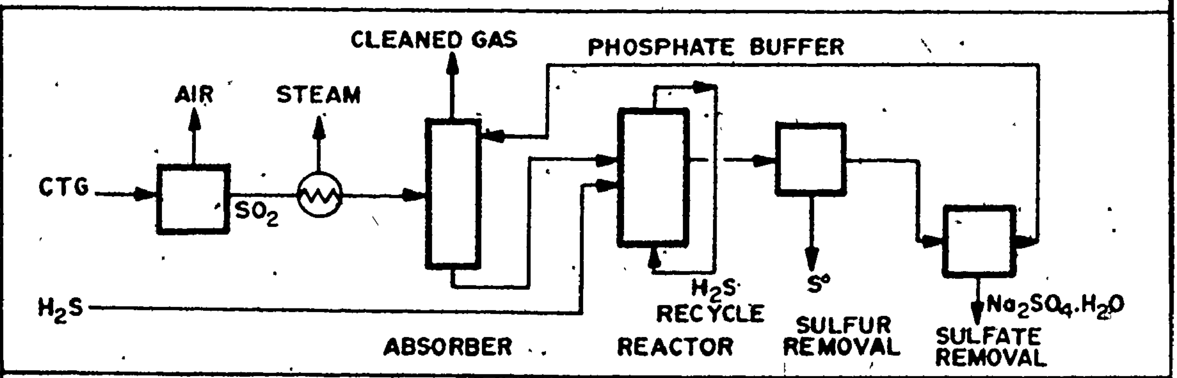
AQUACLAUS

THE AQUA CLAUS PROCESS RELIES ON THE UNCATALYSED REACTION OF H_2S AND SO_2 IN AQUEOUS ACIDIC SOLUTION (PH 2.5 - 5.0). SODIUM HYDROGEN PHOSPHATE PRESENT IN SOLUTION ACTS AS A PH BUFFER AND, THUS, ALLOWS A HEAVIER LOADING OF SO_2 (SEE FIG. (4)). THE NATURE AND RATES OF THE REDOX REACTIONS ARE INDEPENDENT OF THE PRESENCE OF PHOSPHATE.

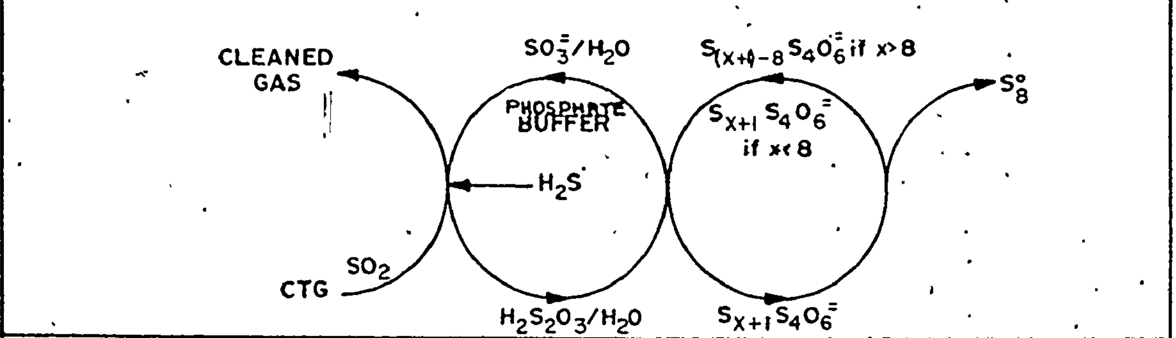
GASEOUS SULFUR BEARING FEED GAS IS INCINERATED TO CONVERT COS, CS_2 AND H_2S TO SO_2. THIS IS SCRUBBED FROM THE COOLED GAS STREAM WITH THE PHOSPHATESOLUTION. THE RESULTING $NaHSO_3$ SOLUTION IS PUMPED TO A REACTION VESSEL WHERE H_2S FROM THE CLAUS FEED OR ON SITE GENERATION IS ADDED, AND SULFUR PRECIPITATION OCCURS. ON HEATING, LIQUID SULFUR PRODUCT IS SEPARATED FROM THE REACTION MIXTURE.

SULFATE IS FORMED IN SOLUTION AS AN OXIDATIVE BY PRODUCT AND FROM SO_3 ABSORPTION AND IS REMOVED BY CRYSTALLIZATION OF $NaSO_4 \cdot 10H_2O$ FROM A SLIPSTREAM. SULFUR CHAIN BUILDUP IS BY THE POLYTHIONATE ROUTE. REACTIVE INTERMEDIATES INCLUDE H_2S, HSO_3^-, $S_2O_3^=$, AND $S_xO_6^=$.

FLOW DIAGRAM



PROCESS CYCLES



PROCESS CHEMISTRY

(92) $SO_2 + H_2O + NaH_2PO_4 \rightleftharpoons NaHSO_3 + H_3PO_4$

(93) $4HSO_3^{1-} + 2H_2S \rightleftharpoons 3S_2O_3^{2-} + 3H_2O + 2H^+$

(87) $S_2O_3^{2-} + S_xS_2O_6^{2-} \rightleftharpoons S_{x+1}S_2O_6^{2-} + SO_3^{2-}$

(88) $S_xS_2O_6^{2-} \rightleftharpoons S_8 + S_{(x-8)}S_2O_6^{2-}$

OVERALL

(23) $2H_2S + SO_2 \rightleftharpoons 3S^\circ + 2H_2O$

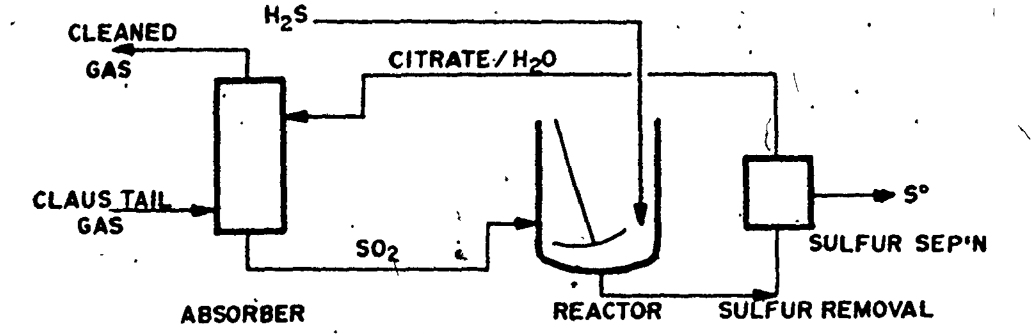
REFERENCES 117, 118, 119.

THE CITRATE PROCESS RELIES ON THE UNCATALYSED REACTION OF H_2S AND SO_2 IN AQUEOUS ACIDIC SOLUTION (pH 2.5 - 5.0). CITRIC ACID PRESENT IN THE SOLUTION ACTS AS A BUFFER AND THUS ALLOWS A HEAVIER LOAD OF SO_2 (SEE FIG. (3)). THE NATURE AND RATES OF THE REDOX REACTIONS ARE INDEPENDENT OF THE PRESENCE OF CITRATE.

GASEOUS SULFUR BEARING FEED GAS IS WATER WASHED AND COOLED AND THEN ABSORBED INTO THE CITRATE BUFFER SOLUTION. THE SOLUTION IS PUMPED TO A REACTION VESSEL WHERE H_2S IS ADDED, PRODUCING ELEMENTAL SULFUR VIA POLYTHIONATE FORMATION. PRECEPITATED SULFUR IS COLLECTED BY CONVENTIONAL MEANS.

THE EFFECTS OF COS AND CS_2 ARE NOT SPECIFIED. SULFATE IS FORMED AS AN OXIDATIVE BYPRODUCT AT A RATE OF 1% OF RECOVERED SULFUR PRODUCT. REACTIVE INTERMEDIATES INCLUDE H_2S, HSO_3^-, $S_2O_3^=$, AND $S_xO_6^=$.

FLOW DIAGRAM



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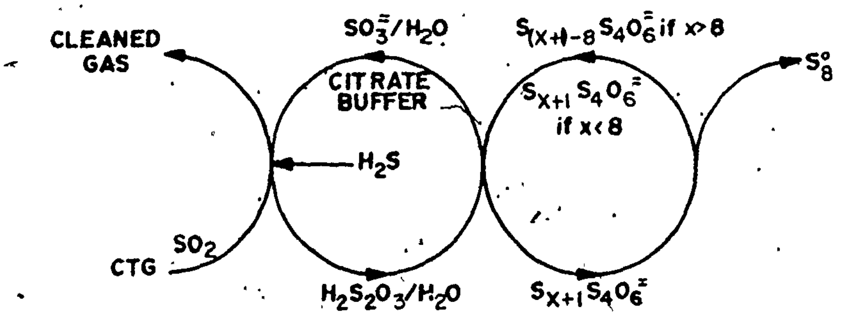


PROCESS CHEMISTRY

(94) $H_2O + SO_2 + Na_3Cit \rightleftharpoons NaHSO_3 + Na_2HCit$ pKA 6.4

(95) $H_2O + SO_2 + Na_2HCit \rightleftharpoons NaHSO_3 + NaH_2Cit$ pKA 4.8

(96) $H_2O + SO_2 + NaH_2Cit \rightleftharpoons NaHSO_3 + H_3Cit$ pKA 3

(93) $4HSO_3^- + 2H_2S \rightleftharpoons 3S_2O_3^{2-} + 3H_2O + 2H^+$

(87) $S_2O_3^{2-} + S_xS_2O_6^{2-} \rightleftharpoons S_{x+1}S_2O_6^{2-} + SO_3^{2-}$

(88) $S_xS_2O_6^{2-} \rightleftharpoons S_8 + S_{(x-8)}S_2O_6^{2-}$

OVERALL

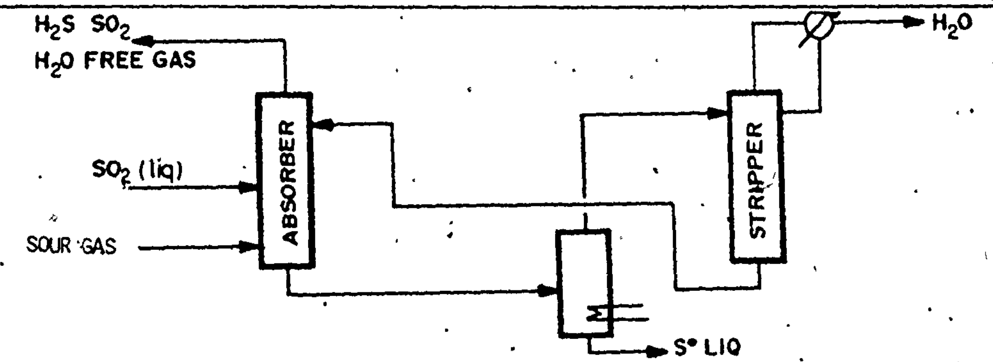
(23) $2H_2S + SO_2 \rightleftharpoons 3S° + 2H_2O$

REFERENCES 120, 121, 122

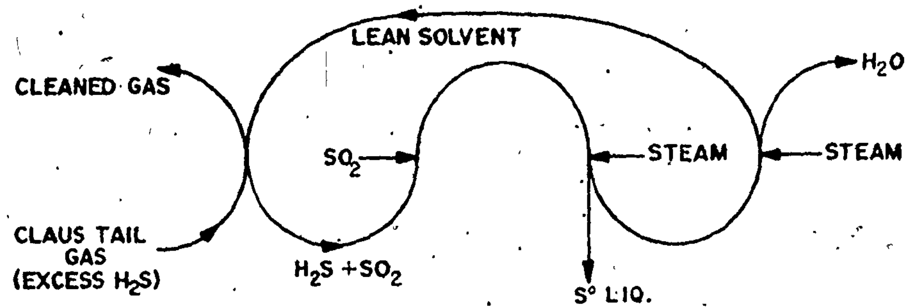
H_2S IS SELECTIVELY ABSORBED FROM A SOUR GAS STREAM INTO A TRIETHYLENE GLYCOL SOLVENT ($HO(CH_2CH_2O)_3H$) AT 250 - 270°F. ELEMENTAL SULFUR AND H_2O ARE PRODUCED BY THE REACTION BETWEEN THE H_2S IN SOLUTION AND ADDED LIQUID SO_2. THE INSOLUBLE LIQUID SULFUR IS SEPARATED, AND THE WATER IS REMOVED IN THE REGENERATOR REFLUX OVERHEAD. THE DRY GLYCOL IS THEN RETURNED TO THE ABSORBER. SO_2 IS PRODUCED ON SITE BY OXIDATION OF PART OF THE SULFUR PRODUCT.

THE EXISTANCE OF POLYSULFIDES OR POLYTHIONATES IN THE GLYCOL SOLUTION HAS NOT BEEN CONFIRMED BY THE AUTHORS. THE NATURE OF ANY BYPRODUCTS AND THEIR FORMATION RATES HAS NOT BEEN FOUND.

FLOW DIAGRAM



PROCESS CYCLES



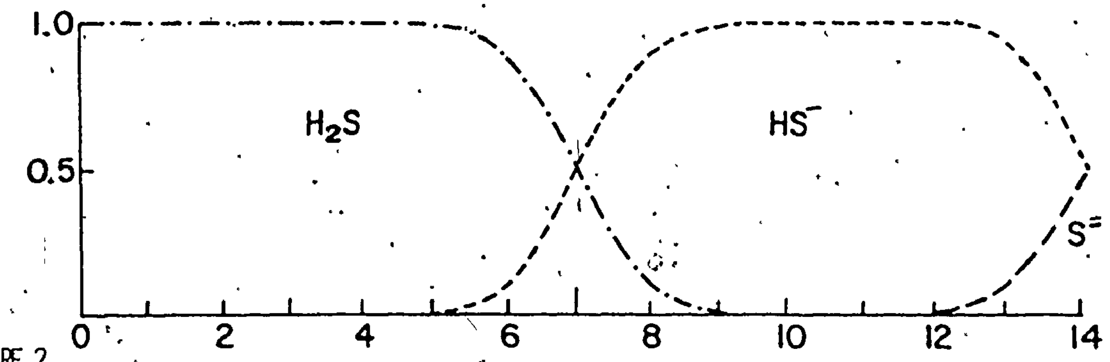
PROCESS CHEMISTRY

OVERALL REACTION

(23) $2H_2S + SO_2 \longrightarrow 3S° + 2H_2O$

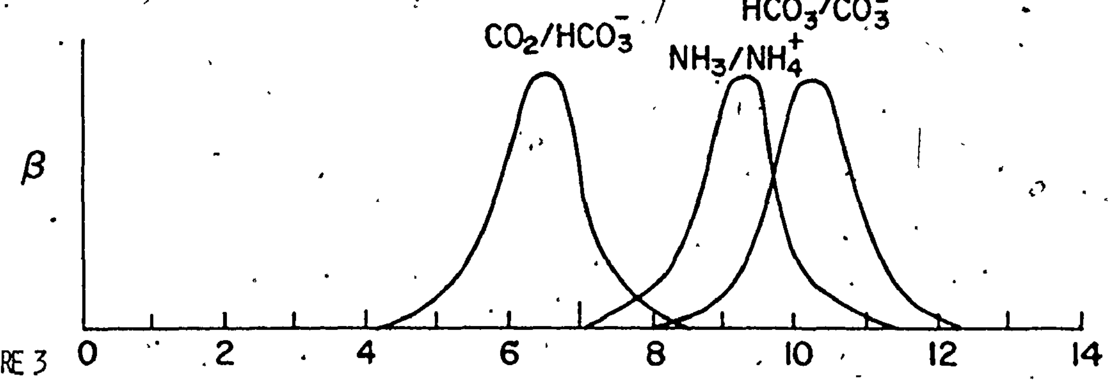
REFERENCES 123, 124, 125.

FIGURE 1



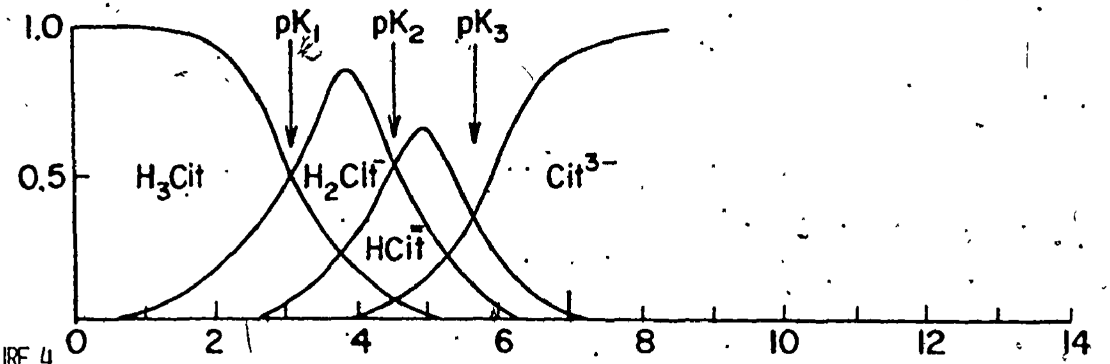
H$_2$S - IONIZATION CURVES

FIGURE 2



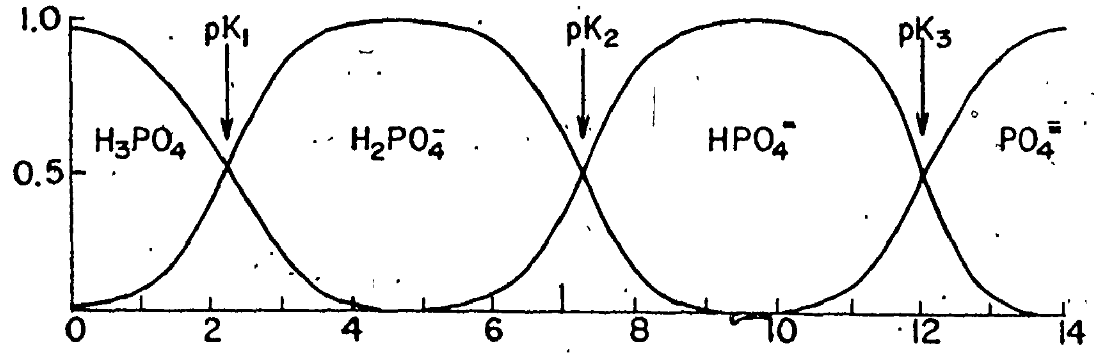
CARBONATE & AMMONIA BUFFER CURVES

FIGURE 3



CITRATE - IONIZATION CURVES

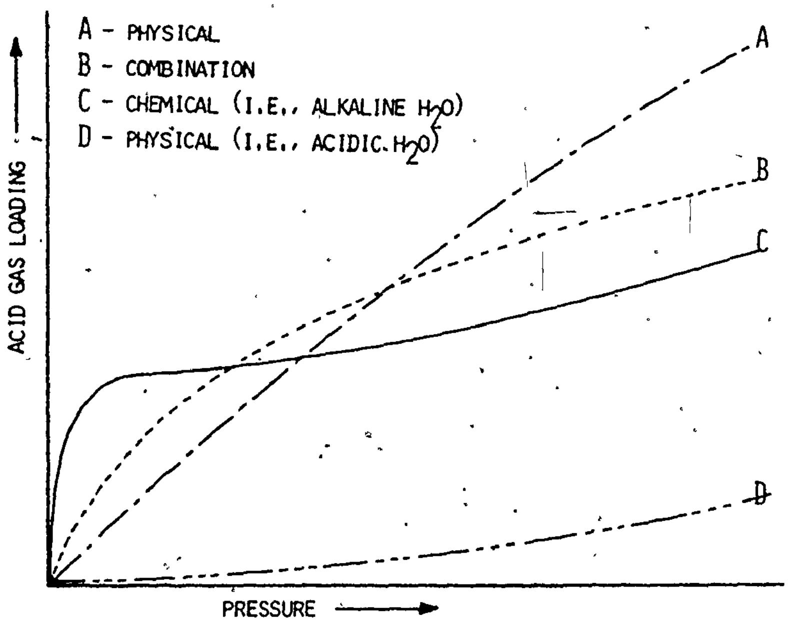
FIGURE 4



PHOSPHATE - IONIZATION CURVES

REFERENCE 126.

FIGURE 5


A - PHYSICAL
B - COMBINATION
C - CHEMICAL (I.E., ALKALINE H2O)
D - PHYSICAL (I.E., ACIDIC H2O)
A
B
C
D
ACID GAS LOADING
PRESSURE

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APPENDIX III

NON-STANDARD ANALYTICAL METHODS

1) Determination of V^{4+}/V^{5+} ratio (iodometric)

Fifteen (15) mls. of stock Na_2S (∿ 2.17 N) was diluted to one litre with water to give an ∿ .35 N working solution. To fifty mls of this solutionwere added 10 mls of 200 gm/l Na_2CO_3 at pH 8.3 and (e.g.) 25 ml of the V^{4+}/V^{5+} unknown. Under these conditions, V^{5+} reacts with sulfide to produce V^{4+} and elemental sulfur. After 10 minutes, the reaction mixture was added slowly to 25 ml of N/10 I_2 in 50 vol % H_2SO_4. This was backtitrated to a starch end point with N/10 $Na_2S_2O_3$. A blank with no vanadium present gave the sulfide normality. The equivalents of sulfide oxidized, therefore, gave the equivalents of V^{5+} present in the sample. Determinations were done in duplicate or triplicate if the difference in the first two was greater than 0.3 mls titrant added (minimum titrant was 15 mls). The average deviation from mean for 23 determinants was 0.29 ± .18% absolute; the method is precise, but it is tedious and time-consuming.

The method can be applied without modification to solutions which do not contain thiosulfate, sulfite or other species which will react with I_2 or $S_2O_3^{=}$. It is possible to correct for thiosulfate and/or sulfite by doing an additional basic $I_2/S_2O_3^{=}$ titration if their concentrations are not too high since differences must be taken. Citrate should not present a major interference since when acidified, all vanadium is as V^{4+} and will not react with the citrate. The method, therefore, has possible applications in studying V^{4+}/V^{5+} precipitation in citrate-deficient systems.

2) Determination of V^{4+}/V^{5+} ratio (potentiometric)

Solutions: All reagents are analytical grade

0.0500 NCr^{7+}	- prepared as per Vogel[36]
0.05 NFe^{2+}	- 19.6 gm ferrous ammonium sulfate was added to 2 ℓ 25% H_2SO_4 and standardized against dichromate as per Vogel.[36]
$KMnO_4$	- saturated aqueous solution

5% Sulfamic acid

0.5% $NaNO_2$

H_3PO_4 concentrated.

A) Precipitate analysis (no citrate present)

An accurately weighed (∿ 100 mg) sample of precipitate was added to an N_2 sparged background of 50 ml 50% vol H_2SO_4 and 10 ml concentrated orthophosphoric acid. This was titrated under N_2 atmosphere with an 0.005 N Fe^{2+} to a potentiometric endpoint. The equivalents of Fe^{2+} used gives the equivalents of V^{5+} present in the precipitate sample.

To determine the total vanadium, the sample is re-oxidized to V^{5+} and the titration is repeated. Addition of $KMnO_4$ (sat'd) dropwise converts all V^{4+} and Fe^{2+} to V^{5+} and Fe^{3+}. Excess $KMnO_4$ is destroyed with the addition of 0.5% $NaNO_2$ in 10 drop increments. Excess nitrite is destroyed with the addition of 10 mls of 5% sulfamic acid. A further 10 mls H_3PO_4 is added, and the solution is titrated to a potentiometric endpoint giving the equivalents of $V^{4+} + V^{5+}$. V^{4+} is found by difference.

B) Solution analysis (no citrate present)

Procedure is as part A above using a solution instead of a precipitate as the vanadium source. Titrant used is stock 0.05 N Fe^{2+} in 25% H_2SO_4.

C) Solution analysis (citrate present)

It is not possible to determine accurately the V^{4+}/V^{5+} ratio by this method in the presence of citrate since it will react with V^{5+} in acidic solution giving low results. If citrate is destroyed by oxidation, it is possible to determine total vanadium.

A sample of V^{n+}/citrate is added to 50 mls 50% H_2SO_4 and brought to a boil. $KMnO_4$ is added dropwise until the pink colour is stable for more than one minute. After cooling, the sample is worked up and titrated as in section A above. Note that pre-oxidation with $HNO_3.H_2SO_4$ affects the change in potential associated with the endpoint and was therefore not suitable.

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