THE ABSORPTION AND ELECTROLYSIS OF HYDROGEN SULPHIDE IN A RECIRCULATED ALKALINE LIQUOR CONTAINING THE VANADIUM (IV/V) REDOX COUPLE

*Any-one who has common sense will remember that the bewilderments of the eyes are of two kinds, and arise from two causes, either from coming out of the light or from going into the light, which is true of the mind's eye, quite as much as of the bodily eye, and he who remembers this when he sees any one whose vision is perplexed and weak, will not be too ready to laugh, he will first ask whether that soul of a man has come out of the brighter life, and is unable to see because unaccustomed to the dark, or having turned from darkness to the day is dazzled by excess of light. And he will count the one happy in his condition and state of being, and he will pity the other, or if he have a mind to laugh at the soul which comes from below into the light, there will be more reason in this than in the laugh which greets him who returns from above out of the light into the den.

That, he said, is a very just distinction.

But then, if I am right, certain professors of education must be wrong when they say that they can put a knowledge into the soul which was not there before, like sight into blind eyes.

They undoubtably say this, he replied.

Whereas, our arguement shows that the power and capacity of learning exists in the soul already, and that just as the eye was unable to turn from darkness to light without the whole body, so too the instrument of knowledge can only by the movement of the whole soul be turned from the world of becoming into that of being, and learn by degrees to endure the sight of being, and of the brightest and best of being, or in other words, of the good.

* Book VII

For my sister and my parents,

You bring light into my life.

THE ABSORPTION AND ELECTROLYSIS OF HYDROGEN SULPHIDE IN A RECIRCULATED ALKALINE LIQUOR CONTAINING THE VANADIUM (IV/V) REDOX COUPLE

by

David E. Prosser

A Thesis
Submitted to the Faculty of Graduate Studies
In Partial Fulfillment of the Requirements
for the Degree
Master of Science

McMaster University
June, 1985.

MASTER OF SCIENCE (1985)

McMaster University
Hamilton, Ontario

TITLE: THE ABSORPTION AND ELECTROLYSIS OF HYDROGEN SULPHIDE IN A RECIRCULATED ALKALINE LIQUOR CONTAINING THE VANADIUM (IV/V) REDOX COUPLE

AUTHOR: David Eric Prosser, Hons. B.Sc. (McMaster University)

SUPERVISOR: Dr. O.E. Hileman Jr.

NUMBER OF PAGES: xvi, 207.

ABSTRACT

The vanadium mediated electrolysis of hydrogen sulphide has been demonstrated in a bench top pilot plant. The first step in the process is the absorption of hydrogen sulphide from a sour gas stream into an carbonate buffered liquor, pH 9. In the presence of citrate ion, the vanadium (V) in the liquor is reduced to vanadium (IV) by (hydro) sulphide ion, which is oxidized to yellow elemental sulphur. The vanadium (IV) rich solution is then pumped to an electrolysis cell where the vanadium (IV) is reoxidized to vanadium (V) and protons are reduced to elemental hydrogen. The reoxidized liquor is then returned to the absorber.

The oxidation of vanadium (IV) to vanadium (V) in the liquor was found to be electrochemically irreversible. The current efficiency for vanadium (IV) oxidation exceeded 90 percent. The voltametric half-wave potential, at platinum, was 0.34 v (vs Ag/AgCl, sat. KCl). With the slippage of sulphide or polysulphide ion into the electrolysis cells, the electrodes became passivated with electrodeposited sulphur. This resulted in an increased anode potential demand which may promote the electrosynthesis of oxygen and sulphate ion.

The oxidation of vanadium (IV) at the anode releases 4 protons and acidifies the solution adjacent the electrode surface. This may induce carbon dioxide evolution and inhibit the discharge of vanadium (IV). The inhibition appears as a suppressed current and an anodic shift in the voltametric half-wave potential. This inhibition can be minimized at high pH levels in the liquor, buffer capacity, and citrate concentration.

The irreversibility of the vanadium (IV/V) couple allows electrolysis cells to be constructed without a cell membrane. This is a significant advantage which will offset the cost of large electrolysis cells. Large cells will enable high energy efficiencies to hydrogen production to be realized. Energy efficiencies greater than 0.28 m^3/kwhr may be indicated.

This study features a critical review of sulphide electrooxidation, a factorial designed voltametric experiment, and a newly identified catalytic response in the polarographic analysis of sulphide ion.

ACKNOWLEDGEMENTS

I would like to take this opportunity to once again thank Dr. Hileman and Mike Malott for your invaluable contributions to my studies at McMaster. Your respective philosophies of education are most conducive to learning and to tolerating the πhoop jumping.π Thanks also to Dr. Hileman for the key to the lab, the roof, and your sense of directions.

I would like to thank Dennis Moore for the generous loan of undergraduate teaching instruments, and for your assistance in demonstrating.

I gratefully acknowledge the financial assistance of Dr. Hileman, the Chemistry department, and the School of Continuing Education.

A number of friends have provided support of one form or another. I would like to thank Eric and Gerda Prosser, Jen and Les, Mike and Erin-Blythe, Steven Zucker, Joseph and the pistanken (prosit). I would also like to thank C. Neske, D. Cooper, W. Bradnam, D. Didur, B. Ferroni, and K. Ashcroft.

For the most part the electrolysis of water is easy. We have only to provide an electrolyte between two electrodes. With the passage of current we observe gas evolution at both electrodes -hydrogen from the cathode and oxygen from the anode. Both gases are exceedingly pure and easily collected, but because much energy is consumed in their formation, they are expensive.

Ideally, we would like to produce hydrogen from readily available and/or less expensive feedstocks. Hypothetically, we could produce cheap hydrogen by:

a) tapping some cheap universal, previously unexploited energy source (e.g. sunlight),
b) using conventional resources with greater efficiency,
c) producing an anode product which does not consume as much energy as oxygen,
d) identifying a miracle.

In my third year as a undergraduate student, I was made aware of an industrial waste -hydrogen sulphide- and an industrial process used for its disposal-the Stretford process. Specifically I noticed a slightly different way of performing the process chemistry so that hydrogen gas could be obtained. Although exposed to knowledge of the public domain, I believe that I recieved special insights into desulphurization chemistry from O.E. Hileman Jr. during his instruction of the Industrial Chemistry course. It was through a certain rapport with the man that I consider the conceptualization of the modified process to be one of co-inventorship with him. In order to determine if c) and d) apply, I undertook the task of evaluating the modified process as the topic of this my Master's thesis.

During the summers of 1979, 1980, and 1981 I was fortunate to have worked in the Research department of Dofasco, Inc., a major Canadian steel producer and a company using the Stretford process. For the two summers after the conceptualization of the modified process at McMaster, I was almost totally oblivous to the Stretford plant at Dofasco, although I was familiarized with the chemistries of producing blast furnace and coke oven hydrogen sulphide. During the summer of 1981, I consulted informally with members of the Research department and was allowed access to their Stretford files. I believe that I learned no hidden or privileged information about the Stretford process from this freedom.

I am eternally grateful to Dofasco for the privilege of working with their Research staff, the intellectual freedom given to me in contributing to their on-going projects, those long contemplative nights sampling coke and liquid metals, and finally for the stink of the industry's metalwinning.

TABLE OF CONTENTS

CHAPTER 3 -- EXPERIMENTAL

CHAPTER 4 -- RESULTS AND DISCUSSION

4.1 The Oxidation of Vanadyl ion

4.2 Pilot Plant

4.3 Current Efficiency Measurements

4.3.3 Results

Appendix 3 -- The Development of the Polarographic Techniques

A3.1 Aim of Analysis

A3.2 Sulphide Polarography

A3.3 Vanadium (V) Polarography

Appendix 4 -- The Determination of Vanadate by Coulometric Titration

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

1.1 Setting

In the years immediately prior to undertaking this project, the public became aware of a serious North American enviromental problem - acid rain [1]. It seemed that the decades of releasing carbon, nitrogen, and sulphur oxide gases into the atmosphere through the burning of fossil fuels was having a noticeable effect in the enviroment. These acid gases disperse in the atmosphere and combine with moisture to form acids (equations 1.1 through 1.4). Through the action of the wind and the rain, these acids wash over the land.

$$CO_2 + H_2O = H_2CO_3 \qquad (1.1)$$

$$SO_2 + H_2O = H_2SO_3 \qquad (1.2)$$

$$SO_3 + H_2O = H_2SO_4 \qquad (1.3)$$

$$N_2O_5 + H_2O = 2HNO_3 \qquad (1.4)$$

The acid rain creates problems when contaminated air masses are slow to disperse and when the contaminant deposition is localized over certain geological formations. In areas where sedimentary rocks predominate, there is enhanced erosion. The erosion of sedimentary rocks liberates carbonates which partially protect soil and water by neutralizing these acids. Regions that predominate in granites, quartzites, and other siliceous types of bedrocks [1] are not afforded such protection from acid rain and are more adversely affected. Hardest hit in central Canada is an extensive and delicate ecosystem of Canadian Shield lakes lying close to industrial centers. The Canadian Shield is predominant in siliceous bedrocks. As a result, lakes in these areas are reported to be suffering pH changes so large as to become hostile to the fish and algae in them. It has been estimated [2], that by the year 2000, 48,000 Ontario lakes will be rendered lifeless by acid rain. Forest soils sensitive to pH shifts become incapable of sustaining tree growth. The economic losses associated with the loss of forest and wildlife resources, the decline of tourism in affected areas, and potential adverse health effects are staggering.

Many industrial activities have been implicated as the source of acid rain pollutants: metal smelting, petroleum refining, and coal fired electricity generation are the largest producers. Indeed many industrial dollars have been directed toward reducing sulphur emissions. One can expect that there will be increased dependancy on wood, peat, biomass, and high sulphur lignite coals in the future. A switch to such alternate fuels will compound the acid rain problem through increased sulphur emissions per BTU.

Desulphurization research has been steadily advancing to cope with the problems of sulphur emissions, and has resulted in a great selection of economically viable desulphurization processes [3]. With few exceptions these processes operate through a controlled oxidation of hydrogen sulphide producing water and sulphur or sulphur oxides. If a process could be developed which was capable of producing hydrogen from hydrogen sulphide there would be a considerable economic incentive to desulphurize.

The present and future value of hydrogen in our economy cannot be over-emphasized. Of the virtually unlimited array of hydrogen consuming enterprises there exists one industry in Canada which would benefit significantly from such technology, the upgrading of the Athabasca tar sands.

Briefly, the tar sands development process involves the extraction of heavy (low hydrogen content) bitumen from mined tar sand. During upgrading, the heavy bitumen is coked to produce a char and an enriched hydrocarbon stream. The hydrocarbon stream is thermally cracked with hydrogen to increase the H:C ratio and to remove sulphur to produce a transportable product. Since the sulphur is removed primarily as hydrogen sulphide, which is processed using existing desulphurization technologies, valuable hydrogen is discarded. The Syncrude operation at Fort MacMurray looses nearly one million scf of hydrogen in this manner every hour. The planned expansion of the operations hydrogen producing capacity from 8 to 10 million scf hydrogen per hour will increase these losses to 2.2 million scf per hour. The recovery of hydrogen on this scale would clearly be an economic boost to the industry.

1.2 Stretford Process Chemistry and its Limitations

The Stretford process was developed jointly in 1957 by the North Western Gas Board and the Clayton Analine Co. Ltd. The process performance was significantly improved in 1967 by W.C. Holmes Ltd., in conjunction with Dofasco and O.E. Hileman's research group an McMaster. The improvements [4] consisted of:

i) replacing tartrate and EDTA (ethylenediaminetetraacetate) with citrate;

ii) lowering the ADA concentration to a catalytic value;

iii) not adding ferrous or ferric ion to the liquor;

iv) increasing the vanadium concentration to maintain a stoichiometric equivalence with hydrogen sulphide in the absorber; and

v) removing the delay tank.

The Holmes-Stretford process differs from the Stretford process by the addition of a Fixed Salt Recovery unit, which incinerates a liquor slipstream and returns sodium carbonate and sodium vanadate to the process [3]. These processes are recognized as a viable desulphurization process -viability is based on a maximum plant size. Although initially intended for the removal of hydrogen sulphide from coal gas and coke oven gas (COG), they have shown promise in hydrogen sulphide removal from other gas streams and solvents immiscible with water [5].

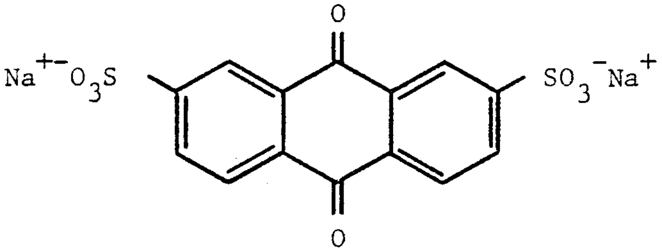
A typical Stretford process plant used to desulphurize coke oven gas is depicted in Figure 1.2.1. The process involves the absorption of oxygen and hydrogen sulphide gases into a recirculating alkaline absorber solution where they are catalytically reacted forming water and elemental sulphur. The intial composition [6] of Stretford liquor is listed in Table 1.2.1. An overview of the chemistry of the process is described below.

The gas stream containing hydrogen sulphide is contacted with oxidized Stretford liquor (pH 8.5 to 9.3), in a counter-current absorber. Hydrogen sulphide absorbs into the liquor, where it

Table 1.2.1

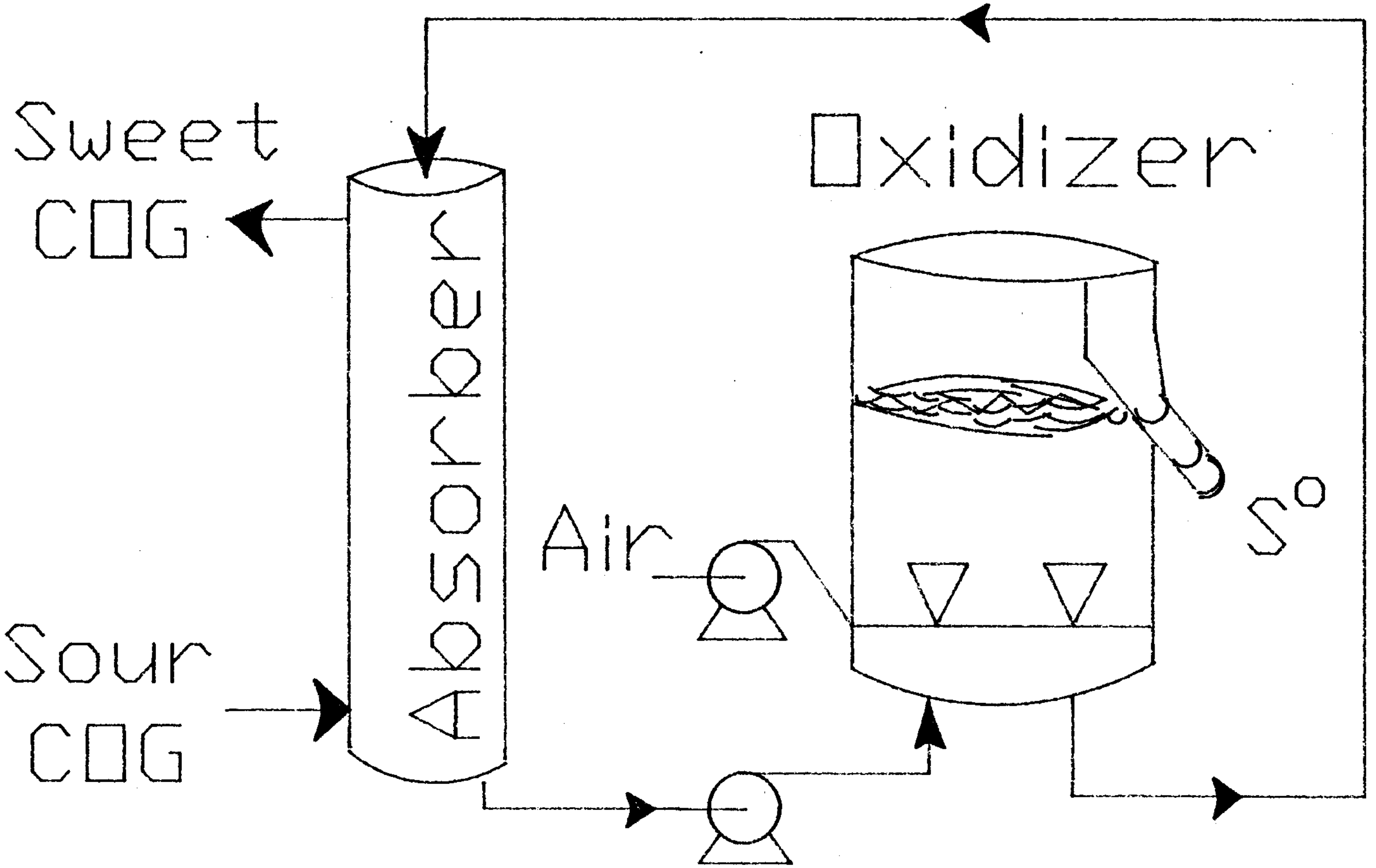
Initial Stretford Liquor Composition

Compound	Concentration (g/ℓ, M)
Sodium Carbonate, Na_2CO_3	25.0, 2.4×10^{-1}
Sodium Metavanadate, $NaVO_3$	1.5, 2.9×10^{-2} (as vanadium)
Trisodium Citrate-dihydrate, $Na_3C_6H_5O_7\cdot2H_2O$	10.0, 3.4×10^{-2}
Disodium-9,10-Anthraquinone-2,7-Disulfonate (ADA), $Na_2C_{14}H_6O_8S_2$	3.0, 7.3×10^{-3}



Disodium-9,10-Anthraquinone-2,7-Disulfonate

Figure 1.2.1
Stretford Process Flow Diagram



dissociates according to established acid/ base equilibria (equations 1.5 to 1.7).

$$H_2S(g) = H_2S(aq) \qquad K = 4.16\text{x}10^5 \text{ atm.} \qquad (1.5)$$

$$H_2S(aq) = H^+ + HS^- \qquad pKa = 7.04 \qquad (1.6)$$

$$HS^- = H^+ + S^{2-} \qquad pKa = (10.95) \qquad (1.7)$$

The sulphide may exist as hydrosulphide ion, which predominates at this pH, or may combine with elemental sulphur to form polysulphide ions (equation 1.8).

$$S^{2-} + xS(s) = S_{x+1}{}^{2-} \qquad (1.8)$$

The sulphide and polysulphide species are oxidized to sulphur and longer chain polysulphides in the liquor primarily by a solution redox reaction with vanadium (V) in the presence of citrate (equations 1.9 through 1.12). (It is important to note that the vanadium (V) mediated reactions consume more H^+ than the hydrogen sulphide releases.) The sulphide oxidation reactions are confined to the absorber and the pipes leading to the oxidizers. A delay tank, which was thought to be necessary to ensure complete sulphide oxidation, can be found in early plant designs.

$$HS^- + 2VO_3{}^- + 3H_2O = S^o + 2VO^{2+} + 7OH^- \qquad (1.9)$$

$$S_x{}^{2-} + S_y{}^{2-} + 2VO_3{}^- + 3H_2O = S_{x+y}{}^{2-} + 2VO^{2+} + 6OH^- \qquad (1.10)$$

$$HS^- + ADA = H_2ADA + S^o \qquad \text{(minor route)} \qquad (1.11)$$

$$\text{Activated oxygen} + HS^- = H_2O + S^0 \quad \text{(minor route)} \quad (1.12)$$

The reduced liquor, rich in vanadium (IV), passes into a co-current air blown oxidizer where vanadium (IV) is re-oxidized to vanadium (V). The oxidation of vanadium (IV) releases H^+ in the oxidizer (equation 1.13). The oxidized liquor is returned to the absorber to complete the cycle. The air blown through the solution serves as the source of dissolved activated oxygen, the primary oxidant. The blown air is often used to generate some frothing action in the oxidizers to remove elemental sulphur from the liquor.

$$2VO^{2+} + 6OH^- + 1/2\ O_2 = 2VO_3^- + 3H_2O \quad (1.13)$$

The oxygen is 'activated' in solution through interaction with the reversable di-hydroquinone/quinone forms of 2,7-anthroquinone disulphonic acid (H_2ADA/ADA) and several of its isomers. The mechanism of this interaction is not clearly understood. Indeed much research is being directed within our research group towards the elucidation of this mechanism.

The speciation of the vanadium ions in the Stretford liquor (and in alkaline solutions in general), is most complicated and has not been clearly established. It appears that pH, vanadium, carbonate, citrate, and ADA concentrations may all influence the vanadium speciation. (The vanadyl ion, VO^{2+}, and the meta-vanadate ion, VO_3^-, are satisfactory for use in reaction book-keeping.) Vanadium can be lost from solution as sodium vanadyl vanadates which precipitate in the pipes and process tanks. The solubility of this and other vanadyl salts can be enhanced in the presence of tartrate ion (which is rapidly oxidized), or citrate ion.

Citrate ion is added to the process as trisodium citrate. This salt dissociates completely (equations 1.14 to 1.17) but does not contribute any buffering action to the liquor above pH 7.5.

$$Na_3Cit = 3Na^+ + Cit^{3-} \qquad (1.14)$$

$$H_3Cit = H^+ + H_2Cit^- \qquad pKa = 3.15 \qquad (1.15)$$

$$H_2Cit^- = H^+ + HCit^{2-} \qquad pKa = 4.77 \qquad (1.16)$$

$$HCit^{2-} = H^+ + Cit^{3-} \qquad pKa = 6.39 \qquad (1.17)$$

The distribution of sulphur species in the Stretford liquor is varied. The oxidized sulphide appears primarily as elemental sulphur. The formation of the cyclo-octa sulphur allotrope in solution, is thought to be mediated by long chain polysulphide anions [7,8]. These long chain polysulphides eliminate sulphur rings according to equation 1.14.

$$S_x^{2-} = S_8(s) + S_{x-8}^{2-} \qquad (1.18)$$

Stretford liquors are buffered to pH values near 9 with carbonate/ bicarbonate salts. The equilibria associated with carbonate solutions is well known (equations 1.19 to 1.21 and 1.1).

$$CO_2(g) = CO_2(aq) \qquad K = 1.61x10^3 \text{ atm.} \qquad (1.19)$$

$$CO_2(aq) + H_2O = H_2CO_3 \qquad (1.1)$$

$$H_2CO_3 = H^+ + HCO_3^{2-} \qquad pKa = 6.37 \qquad (1.20)$$

$$HCO_3^{2-} = H^+ + CO_3^{2-} \qquad pKa = 10.25 \qquad (1.21)$$

The chemistry of the Stretford process is depicted in Figure 1.2.2 and can be summarized in equations 1.6, 1.9, 1.22 and 1.23.

$$H_2S + OH^- = HS^- + H_2O \qquad (1.6)$$

$$HS^- + 2VO_3^- + 3H_2O = S^o + 2VO^{2+} + 7OH^- \qquad (1.9)$$

$$2VO^{2+} + 6OH^- + 1/2\ O_2 \underset{H_2ADA}{\overset{ADA}{=}} 2VO_3^- + 3H_2O \qquad (1.22)$$

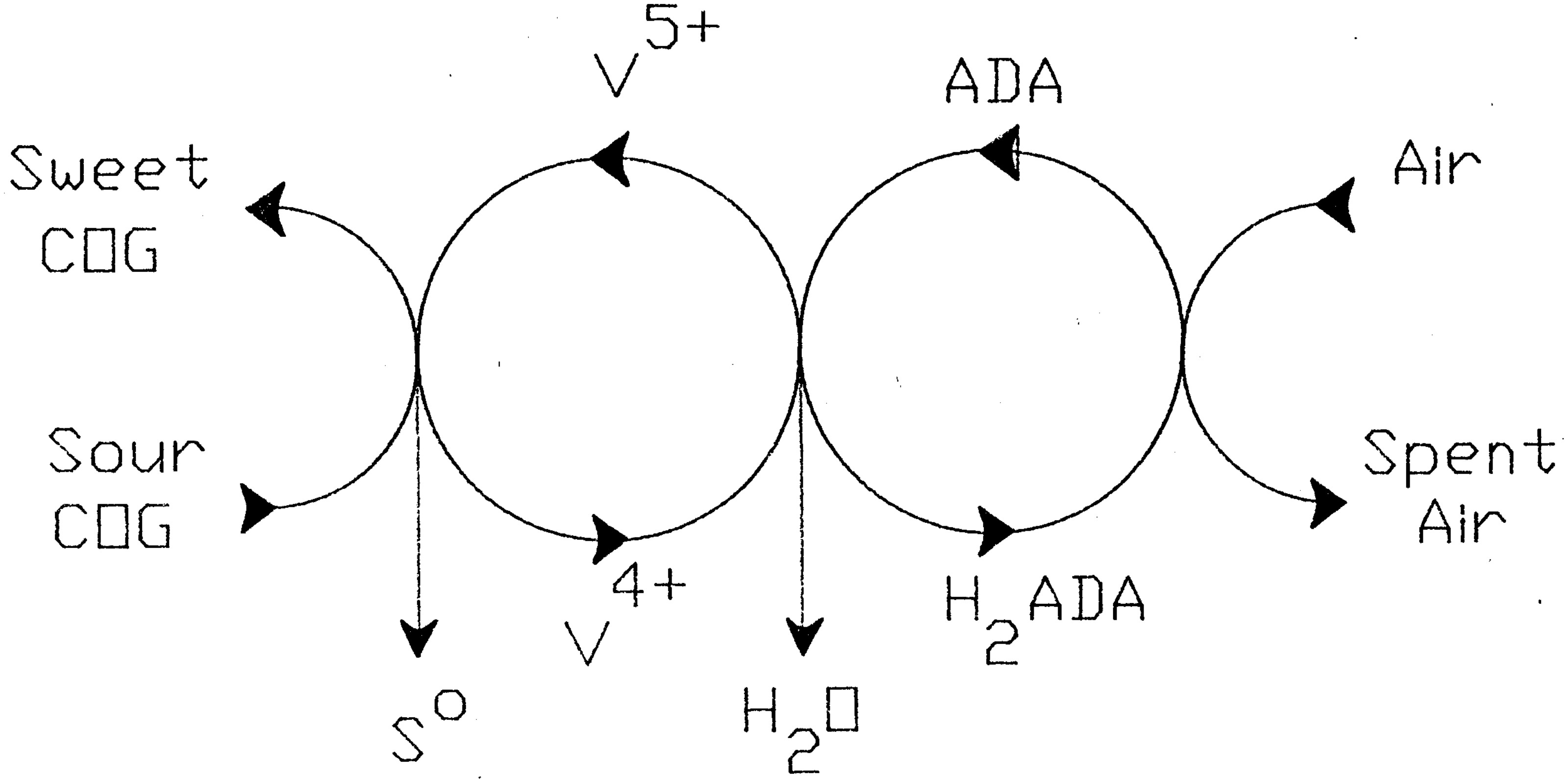
$$H_2S + 1/2\ O_2 = S^o + H_2O \qquad (1.23)$$

A major limitation associated with the Stretford process, past and present, can be attributed to the use and control of oxygen as an oxidant. As a reagent, oxygen is only slowly absorbed, activated, and reacted in the aqueous liquor. The need to activate the oxygen makes the Stretford process dependent upon ADA. The ADA is a good oxygen activator and an efficient frothing agent, but it is expensive. Once produced as a by-product of an industrial organic synthesis now falling into disuse, a secure supplier and its future price is uncertain.

Once activated, oxygen is a non-specific oxidant for vanadium (IV) ion and is capable of oxidizing sulphide to elemental sulphur and to stable oxysulphur compounds -fixed salts- that accumulate in the liquor. The fixed salts are known to be sulphate and thiosulphate, but their

Figure 1.2.2

Stretford Process Cycle [3]



formation is not completely understood. Although the prolonged saturation of the liquor with oxygen is a factor, the role of the soluablized or 'activated' forms of elemental sulphur (i.e. polysulphide or thiosulphate) in fixed salt formation has not been established. An overview of fixed salts formation is described below.

The sulphite ion may be an intermediate produced from the reactions of a sulphur containing species with activated oxygen (equations 1.24, 1.2, and 1.25).

$$'S' + 'O' = SO_2(aq) \qquad (1.24)$$

$$SO_2(aq) + H_2O = H_2SO_3 \qquad (1.2)$$

$$2OH^- + H_2SO_3 = 2H_2O + SO_3^{2-} \qquad pK_2 = 7.3 \qquad (1.25)$$

It does not accumulate in the process liquor as it reacts quickly with elemental sulphur to form thiosulphate (equation 1.26).

$$SO_3^{2-} + S^o = S_2O_3^{2-} \qquad (1.26)$$

The formation of sulphate ion from a sulphur containing species and activated oxygen may be illustrated by equations 1.27, 1.3, and 1.28).

$$'S' + 'O' = SO_3(aq) \qquad (1.27)$$

$$SO_3(aq) + H_2O = H_2SO_4 \qquad (1.3)$$

$$2OH^- + H_2SO_4 = 2H_2O + SO_4^{2-} \qquad pK_2 = 1.9 \qquad (1.28)$$

The processing of gas streams containing hydrogen cyanide (HCN), intensifies the fixed salt problem. This gas is absorbed in the process liquor (equations 1.29 and 1.30) where it reacts with elemental sulphur, polysulphide or thiosulphate to form thiocyanate ion. The thiocyanate ion does not decompose chemically in the process liquor, but there is some evidence of its bacterial degradation [9]. Thiocyanate accumulation can be minimized by operating efficient cyanide scrubbers upstream of the sulphide absorber.

$$HCN(g) = HCN(aq) \qquad (1.29)$$

$$HCN(aq) = H^+ + CN^- \qquad pKa = 6.86 \qquad (1.30)$$

$$CN^- + 'S' = SCN^- \qquad (1.31)$$

The formation and accumulation of fixed salts in the Stretford liquor is undesireable. Since sulphate and thiosulphate are acid anions, their formation is associated with the release of protons which consumes alkali in the liquor. Alkali makeup is expensive. Increasing fixed salt levels increase the density, viscosity, and ionic strength of the liquor and decrease the ADA solubility. Thus, liquor dilution or fixed salt removal becomes necessary. The removal and treatment or disposal of fixed salts is expensive, technically challenging, and invariably leads to the loss of Stretford chemicals [5]. As a result, fixed salts formation significantly contributes to the overall operating costs of the Stretford process.

It has been recently reported [9] that a large number of microorganisms can coexist and fluorish in process liquors. Of these, the slow growing Thiobacillus thioparus, T. neapolitanus, and possibly T. novellus gave been implicated in the oxidation of thiosulphate to sulphate. Pseudomonas species were found to metabolize organic substances while sulphate-reducing bacteria produce sulphide ion in the liquor. The bacterial blooms were reported to increase alkali consumption, decrease sulphur flotability, and cause foaming problems in the process plant. The bacterial degradation of citrate was not investigated in the report.

1.3 The Modified Process

A search of the history [5] surrounding the Stretford process reveals that the re-oxidation of vanadium (IV) ions with dissolved, activated oxygen followed naturally from the original intention to air oxidize absorbed hydrogen sulphide. It is not hard to imagine that at the time of Stretford process inception, other methods could have been considered including electrolysis. If it was considered it is likely that it would have been rejected on the grounds of expense. After all, why go to such extremes to treat an industrial waste that could be sent up a chimney? Besides sulphides foul up electrodes.

In the present setting, where enviromental and economic pressures dictate a different attitude, the electrolytic re-oxidation of vanadium (IV) with concurrent hydrogen evolution must be investigated. In such a case, the Stretford process would be formally modified through the replacement of the Stretford air blowers and oxidizer tanks by electrolysis cells. Hydrogen sulphide would then be up-graded by the vanadium mediated electro-oxidation of sulphide and the cathodic reduction of protons.

The solution chemistry of the modified process, based upon the electrolytic regeneration of the vanadium catalyst, is depicted in Figure 1.3.1 and summarized below:

$$H_2S + OH^- = HS^- + H_2O \quad (1.6)$$

$$HS^- + 2VO_3^- + 3H_2O = S^o + 2VO^{2+} + 7OH^- \quad (1.21)$$

$$2VO^{2+} + 8OH^- = 2VO_3^- + 4H_2O + 2e^- \quad (1.32)$$

$$2H^+ + 2e^- = H_{2(g)} \quad (1.33)$$

$$H_2S = H_{2(g)} + S^o \quad (1.34)$$

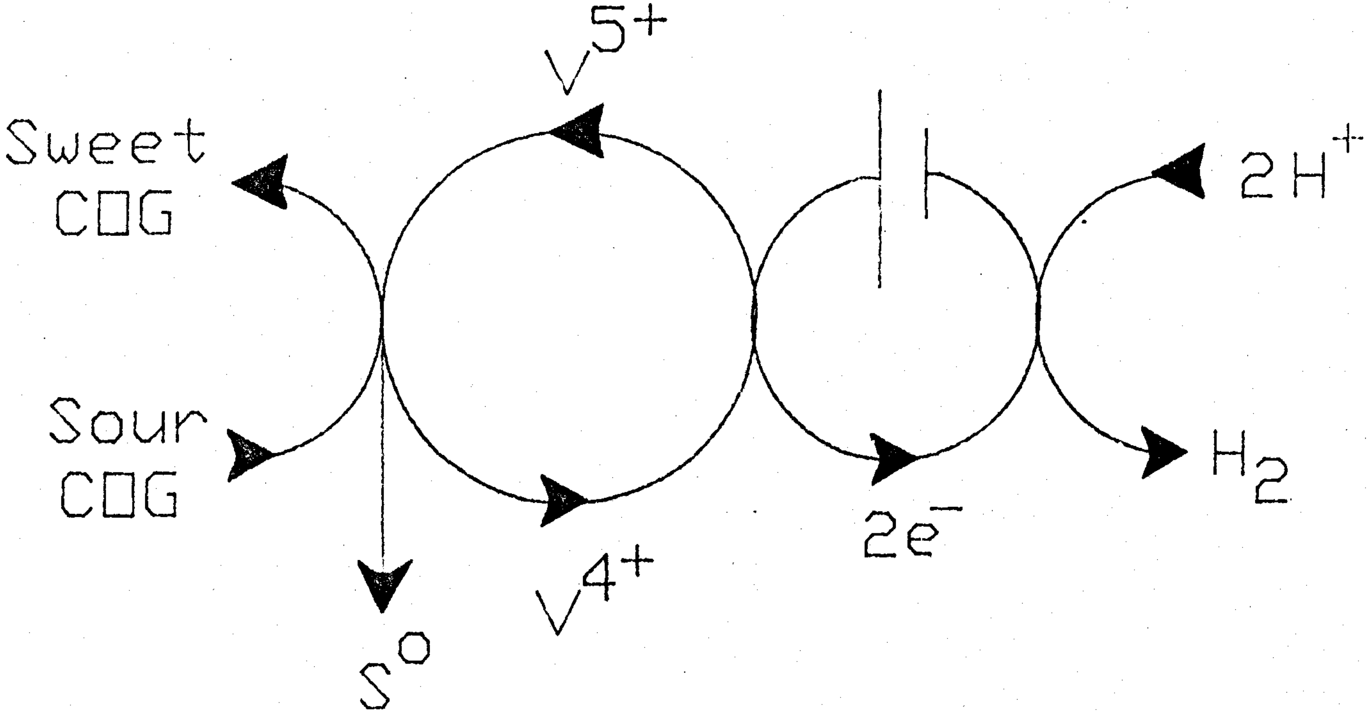
For the electrolytic process to be economically viable it must compete with the Stretford process. Specifically, the disadvantages of the large capital cost of the electrolyser units must be offset by significant advances in the process chemistry.

The first and foremost advantage of the electrolytic process would be a break from the need to saturate the liquor with oxygen and then to activate it with ADA. Since ADA is not required, it need not be purchased and added to the process liquor. In its absence, the oxygen introduced into the liquor will be unreactive towards fixed salt formation. Furthermore, without ADA, the process liquor will tolerate higher fixed salt loadings.

If the electrochemistry of the modified process is found to be selective, the fixed salts will be slow to accumulate. Low rates of fixed salt formation would result in real savings in decreased alkali consumption and relief from fixed salt recovery and treatment or

Figure 1.3.1

Modified Process Cycle



disposal.

Finally, the production and sale or utilization of hydrogen in industry is an increasingly significant bonus in the field of desulphurization.

1.4 Research Objective

The objective of this study is to evaluate the vanadium mediated electrolysis of hydrogen sulphide and its potential for use in industrial desulphurization. The first step in the evaluation will be to scrutinize the literature for prior development of the approach. A critical review the chemistry and electrochemistry of vanadium and sulphur in alkaline solutions will identify the chemical obstacles and advantages to be found with the new process. These criterian will aid in the investigation and evaluation of the process chemistry. The study will focus on those factors which have the greatest influence on the process chemistry and which are likely to be important in its optimization. The final objective will be to prepare a preliminary economic assessment of the process.

CHAPTER 2

LITERATURE REVIEW

CHAPTER 2

LITERATURE REVIEW

2.1 Vanadium Chemistry

2.1.1 General Chemistry

Vanadium, element 23, has an outer valence electron configuration of $3d^3\ 4s^2$. It is found in the expected oxidation states from 0 through +5. The upper oxidation states are usually stabilized by divalent oxygen or hydroxide (oxyvanadium ions) or complexing ligands that bind through oxygen, sulphur, or nitrogen. The oxyvanadium ions exhibit various pH properties, solubilities, and redox chemistries.

The important oxidation states of vanadium in the Stretford process are the tetra and pentavalent states. This selection appears to be determined by the oxidative and reductive strength of dissolved oxygen and hydrosulphide ion, respectively. In the absence of dissolved oxygen, and with the adoption of the electrolytic method, vanadium may not be confined solely to the tetra and pentavalent states. For this reason, it is necessary to review the chemical and electrochemical properties of aqueous vanadium species.

Pourbaix [10] lists the solubilities of the vanadium oxides. Vanadium (II) oxide, V_2O_2 (grey), and vanadium (III) oxide, V_2O_3 (black), do not dissolve in base, but, V_2O_3 can dissolve in alkaline media by oxidation. V_2O_2 is said to be unstable in water. The hydrate of vanadium (II), $V(OH)_2$, reacts with water to evolve hydrogen. Vanadium (IV) oxide, V_2O_4 (blue-black) and Vanadium (V) oxide, V_2O_5 (brick red) are amphoteric [11]. The vanadium (III) ion is known to precipitate quantitatively in base, a phenomenon which prevents its polarographic discharge [10]. Vanadium (IV) ions precipitate as the hydroxide, $VO(OH)_2$, from solutions more alkaline than pH 4, but this disolves in excess alkali to impart a red colour to the solution [12].

2.1.2 Electrochemistry

There is some information regarding the stability of tetra and pentavalent vanadium in the process liquors which can be discerned from the electrochemical studies reported in the scientific literature. The majority of these studies concern vanadium electrochemistry in acidic media. The study of alkaline electrochemical processes is complicated by the precipitation of hydrolysis products and the unresolved speciation of vanadium ions in alkaline solutions.

Bydon and Atkinson [13] attempted the coulometric generation of vanadium (II) and vanadium (III) from vanadium (IV) at platinum cathodes in a variety of media. They report that platinum is an unsatisfactory cathode material for the reduction of vanadium (IV). Reduction of vanadium (IV) to vanadium (II) was never observed. Reduction to vanadium (III) was observed in oxalate, sulfosalicylic acid, and kojic acid [5-hydroxy-2-(hydroxymethyl)-4-pyrone] solution, but current efficiencies never exceeded 10 percent. No reduction was observed at platinum in a 0.5 M EDTA / 0.05 M dipotasium sulphate solution at pH 9.5. The work of Bishop and Hitchcock [14] partially confirms the observations noted above. They found no evidence for reduction below vanadium (IV) in acidic media at platinum and report a low efficiency for the electro-oxidation of the vanadium (IV) ion (co-oxidized with the acidic solvent).

There is polarographic evidence to suggest that electro-reduction of vanadium (IV) at mercury proceeds below the tetravalent state, although there is some controversy in this respect. Brydon and Atkinson [13] have confirmed the electro-synthesis of vanadium (II) and (III) at mercury in various media. A survey of vanadium (IV) and vanadium (V) polarography can be found in Appendix A3.

Bard [10: reference 321], reports the anodic electrogeneration of vanadium (IV) from a vanadium metal anode with 100 percent current efficiency from 1 M sodium hydroxide. Bard also reported that the constant current electrogeneration of vanadium (V) from vanadium (IV) has never been reported.

Pourbaix [11] has compiled some standard potential data and equations pertaining to the vanadium (IV/V) couple. This information is shown in Table 2.1.1. Of particular interest is the standard potential expression corresponding to the oxidation of vanadyl ion to orthovanadate ion as shown in equation 2.35.

$$VO^{2+} + 3H_2O = H_2VO_4^- + 4H^+ + e^- \qquad (2.35)$$

Substituting a pH value of 9 and equimolar concentrations for the vanadium containing species, a standard potential of -0.81 volts can be calculated.

Working with equivalent amounts of vanadium (IV) and vanadium (V) in 1, 3, and 5 M sodium hydroxide, Willard and Manalo [15] observe

Table 2.1.1

The Standard Potentials of the Vanadium (IV/V) Redox Couple [11].

Couple	Standard Potential
$VO^{++} + H_2O = VO_2^{+} + 2H^{+} + e^{-}$	$E^{o} = 1.004 - 0.1182pH + 0.0591 \log C$
$2VO^{++} + 5H_2O = H_3V_2O_7^{-} + 7H^{+} + 2e^{-}$	$E^{o} = 1.096 - 0.2068pH - 0.0295 \log C$
$VO^{++} + 3H_2O = H_2VO_4^{-} + 4H^{+} + e^{-}$	$E^{o} = 1.314 - 0.2364pH + 0.0591 \log C$
$HV_2O_5^{-} + 2H_2O = H_3V_2O_7^{-} + 2H^{+} + 2e^{-}$	$E^{o} = 0.501 - 0.0591pH + 0.0295 \log C$
$HV_2O_5^{-} + 3H_2O = 2H_2VO_4^{-} + 3H^{+} + 2e^{-}$	$E^{o} = 0.719 - 0.0886pH + 0.0295 \log C$
$HV_2O_5^{-} + 3H_2O = 2HVO_4^{2-} + 5H^{+} + 2e^{-}$	$E^{o} = 1.281 - 0.1477pH + 0.0295 \log C$
$HV_2O_5^{-} + 3H_2O = VO_4^{3-} + 7H^{+} + 2e^{-}$	$E^{o} = 1.962 - 0.2068pH + 0.0295 \log C$

formal potentials of -0.74, -0.85, and -0.86 volts respectively. The authors also remark on the ease with which alkaline vanadium (IV) solutions are oxidized when exposed to air.

A number of Russian articles [Bard [10] references 56, 58, 176, and 177], have suggested the deposition of sparingly soluable vanadyl vanadates on platinum electrodes in sulphuric acid solutions. Selbin [9: references 231a-233, and 255] note similar problems associated with the formation of isopoly-vanadates and vanadylvanadates in solutions above pH 2.5. No reference to the electrochemical behaviour of the vanadium (IV/V) couple at platinum in the presence of citrate was found in the literature.

2.1.3 Vanadium Speciation

The literature survey of vanadium electrochemistry given in Section 2.1.2 revealed that vanadium will be confined to the tetra and pentavalent oxidation states in the modified process liquor. In this section a review the known aqueous speciation behaviours of these oxidation states will be presented. A brief discription of several vanadium (IV) and (V) species is given in Table 2.1.2.

2.1.3.1 Vanadium (V) Speciation

The speciation equilibria associated with aqueous vanadium (V) ions is fairly well understood. In 1966, Pourbaix [11] reported the equilibria given in equations 2.36 through 2.38.

$$2VO_2^+ + 3H_2O = H_3V_2O_7^- + 3H^+ \qquad (2.36)$$

$$H_3V_2O_7^- + H_2O = 2H_2VO_4^- + H^+ \qquad (2.37)$$

Table 2.1.2

Vanadium species in solution [11].

State	Species	Description
V(IV)	VO^{++}	vanadyl, blue
	HVO_2^+	limited stability at low V concentrations around pH 5
	$HV_2O_5^-$	hypovanadate, red-brown
V(V)	VO_2^+	pervanadyl or vanadic ion, lightyellow
	HVO_4^{-2}	*orthovanadate, colourless
	$H_2VO_4^-$	orthovanadate or metavanadate VO_3^-
	$H_3V_2O_7^-$	pyrovanadate orange

* The prefixes ortho- pyro- and meta- refer to anions with the ratio of negative charges to vanadium atoms (in the unprotonated anion) of 3(ortho), 2(pyro), and 1(meta). Metavanadate refers to the orthovanadate species when it is written with the exclusion of a water molecule in the inner coordination sphere [16].

$$VO_2^+ + 2H_2O = H_2VO_4^- + 2H^+ \qquad (2.38)$$

The understanding of aqueous vanadium (V) speciation was considerably advanced by Pope and Dale in 1968. Their review [16] of vanadium (V) chemistry further defined the pH domains of stability in terms of vanadium concentration, and drew attention to the presence of aqueous polymeric vanadate species. These polymeric species included the trimer ($V_3O_9^{3-}$), tetramer ($V_4O_{12}^{4-}$), and the decamer ($V_{10}O_{28}^{6-}$). The authors also report some controversy regarding the existance of the hexamer ($V_6O_{17}^{4-}$).

The use of ^{51}V nmr has been employed in our lab (Habayeb, Pitts) and by others to expand our understanding of vanadium (V) speciation in aqueous complexing media. Habayeb [17] employed ^{51}V nmr techniques to construct a distribution diagram [18] for 0.25 M sodium metavanadate as a function of pH. This diagram is reproduced in Figure 2.1.1. The work confirmed the existance of the hexamer.

A number of formation equilibria (equations 2.39 through 2.45), for the polymeric species were given by Habayeb [17]. The consideration of the acid/base behaviour of ortho- and pyrovanadates resulted in different versions of equations 2.39 and 2.40.

$$VO_4^{3-} + H^+ + 2H_2O = [VO_3\ (OH)\ (H_2O)_2]^{2-} \qquad (2.39)$$

$$*\ 2[VO_3\ (OH)\ (H_2O)_2]^{2-} = V_2O_7^{4-} + 5H_2O \qquad (2.40)$$

$$[VO_3\ (OH)\ (H_2O)_2]^{2-} + HV_2O_7^{3-} + 2H^+ = V_3O_9^{3-} + 4H_2O \quad (2.41)$$

$$HV_2O_7^{3-} + V_2O_7^{4-} + 3H^+ = V_4O_{12}^{4-} + 2H_2O \qquad (2.42)$$

$$2V_3O_9^{3-} + 2H^+ = V_6O_{17}^{4-} + H_2O \qquad (2.43)$$

$$V_4O_{12}^{4-} + HV_2O_7^{3-} + 3H^+ = V_6O_{17}^{4-} + 2H_2O \qquad (2.44)$$

$$V_6O_{17}^{4-} + V_4O_{12}^{4-} + 2H^+ = V_{10}O_{28}^{6-} + 2H_2O \qquad (2.45)$$

* Adam Habayeb's equations 3.35 through 3.38 do not balance, evidently due to a typographic error. The VO_2 in these equations should read VO_3. The corresponding equations in Steve Pitts' thesis were unsucessfully corrected.

In a related study, Habayeb studied the effects of various complexing agents on vanadium (V) speciation. He found that alpha or beta hydroxy-carboxylic acids prevented the formation of the decameric vanadate species and this resulted in the formation of a VO_2^+ complex. The ^{51}V-nmr evidence supportes the formation of a VO_2^+-citrate complex over the pH range 6 to 8. The equilibrium reaction given by Habayeb is shown by equation 2.46.

$$VO_2^+ + C_6H_5O_7^{3-} = [VO_2\ (C_6H_5O_7]^{2-} \qquad (2.46)$$

The pervanadyl ion was reported by Habayeb to be made available by the equilibria expressed in equations 2.47 through 2.50.

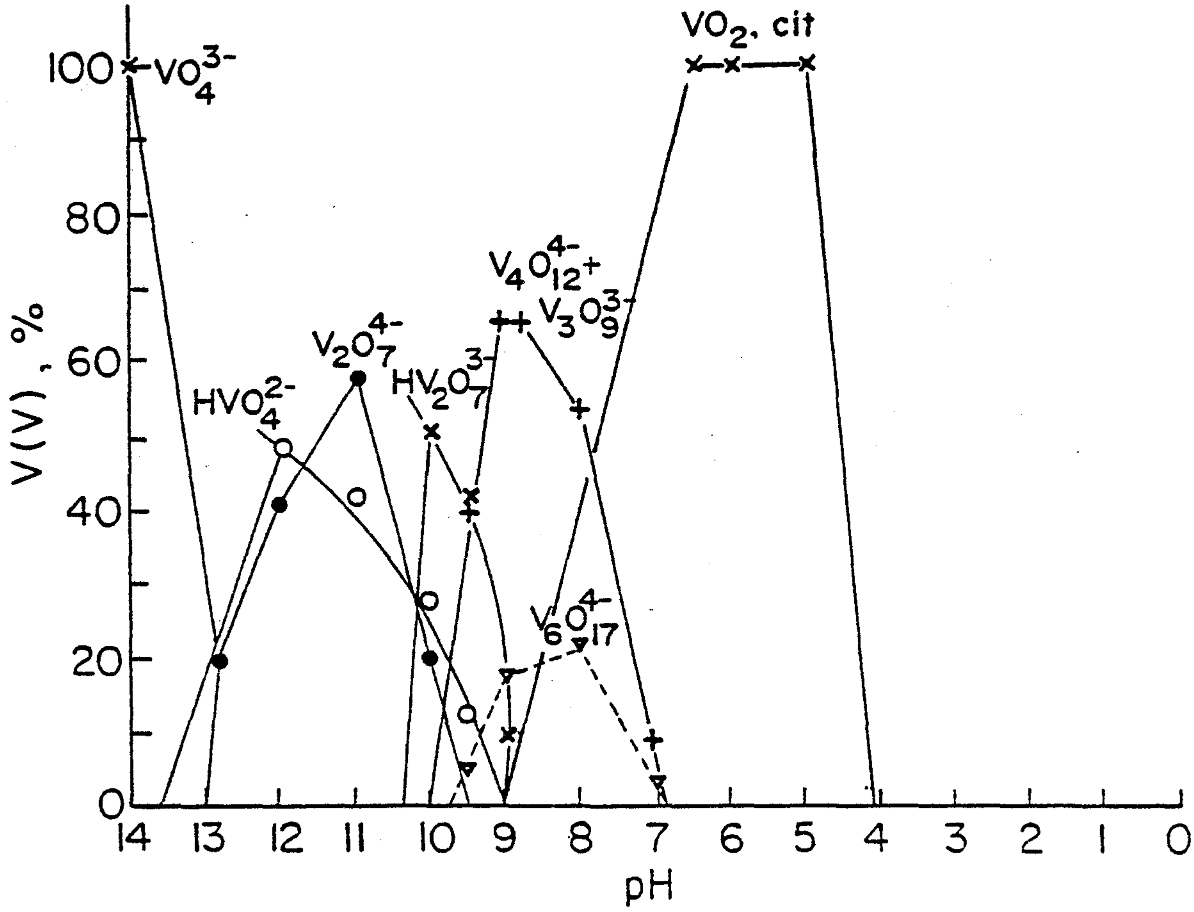
$$V_{10}O_{28}^{6-} + 16H^+ = 10VO_2^+ + 8H_2O \qquad (2.47)$$

$$V_3O_9^{3-} + 6H_3O^+ = 3VO_2^+ + 9H_2O \qquad (2.48)$$

$$V_4O_{12}^{4-} + 8H_3O^+ = 4VO_2^+ + 12H_2O \qquad (2.49)$$

$$V_6O_{17}^{4-} + 10H_3O^+ = 6VO_2^+ + 15H_2O \qquad (2.50)$$

Figure 2.1.1 The distribution of vanadium (V) species in solutions containing 1:1 metavanadate:citrate ion as a function of pH [17].


VO2, cit
100
80
60
40
20
0
V(V), %
VO4 3-
HVO4 2-
V2O7 4-
HV2O7 3-
V4O12 4- +
V3O9 3-
V6O17 4-
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
pH

In vanadate-carbonate solutions in the pH range 7 to 9, Habayeb observed some stabilization of the tri and tetrameric species and also a ^{51}V-nmr resonance which was assigned to a VO_2^+-carbonate complex. Pitts [6] confirms the latter observation, but assigned the resonance to a bicarbonate complex. Habayeb constructed a distribution diagram for Vanadium (V) in a Stretford-like solution. This diagram is shown in Figure 2.1.2.

2.1.3.2 Vanadium (IV) Speciation

In contrast with Vanadium (V), the aqueous speciation of Vanadium (IV) is most complicated and unresolved. Vanadium (IV) solutions below pH 4 are blue attesting to the presence of the vanadyl ion, VO^{2+}. Vanadium (IV) solutions above pH 4 contain a grey-white to dark brown precipitate and assume the red colouration of the hypovanadate ion [12]. Pourbaix [11] presents equilibria involving these two species and a third un-named species, as shown in equations 2.51 through 2.53.

$$VO^{++} + H_2O = HVO_2^+ + H^+ \tag{2.51}$$

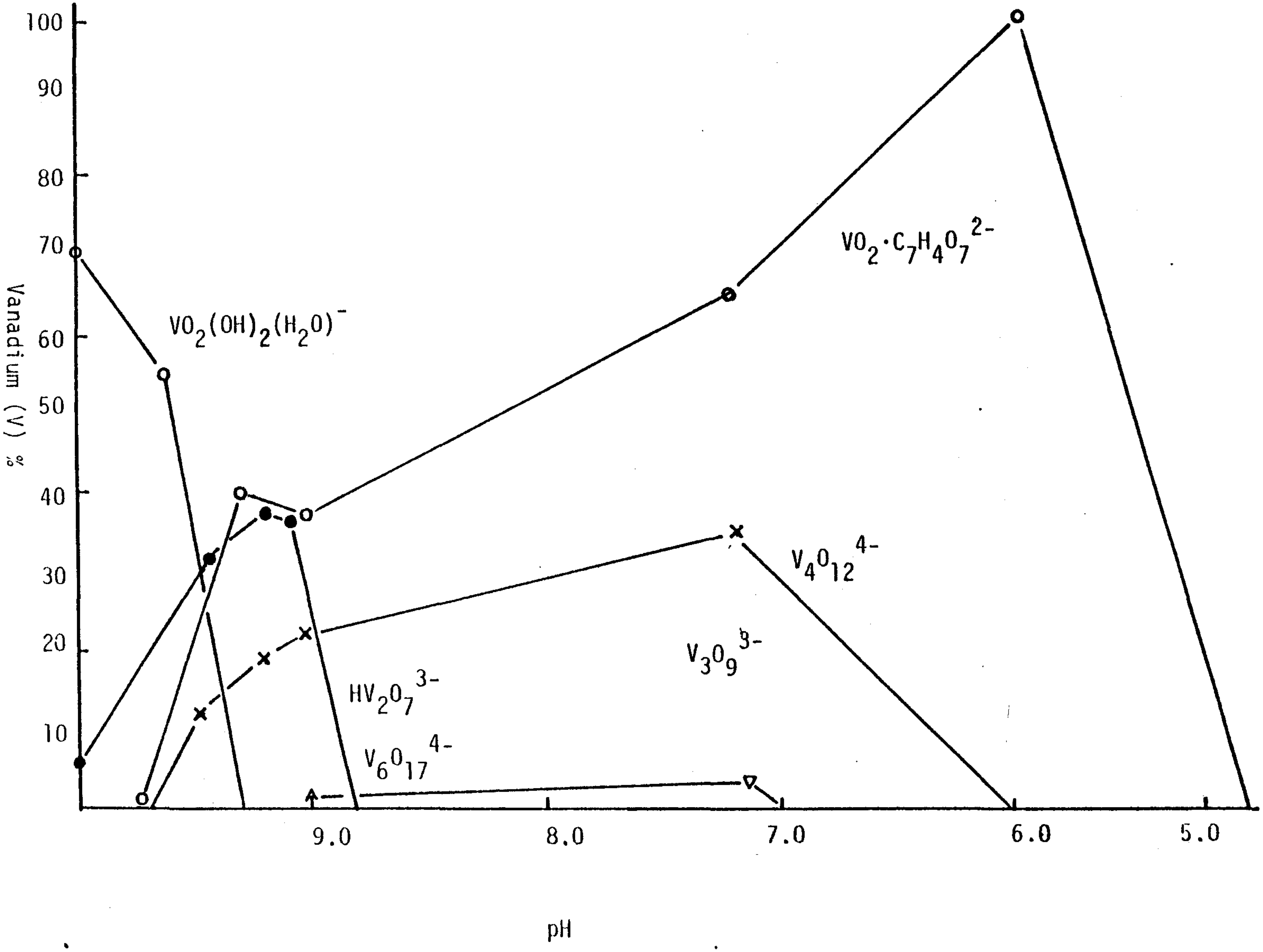
$$2HVO_2^+ + H_2O = HV_2O_5^- + 3H^+ \tag{2.52}$$

$$2VO^{++} + 3H_2O = HV_2O_5^- + 5H^+ \tag{2.53}$$

It is interesting to note that Pourbaix does not consider the Vanadium (IV) species, $V_2O_5^{2-}$ and $V_4O_9^{2-}$, as identified by Lingane and Meites in 1946 (20 years earlier).

The application of esr, nmr and UV spectroscopies to the elucidation of Vanadium (IV) speciation in aqueous complexing media is an active field of research. Studies of this type have been undertaken in

Figure 2.1.2 A distribution diagram of vanadium (V) species in Stretford-like solutions. (pH range 9.5-6.0, $[NaVO_3]$ = 0.034 M, $[Na_2CO_3]$ = 0.202 M and $Na_3C_6H_5O_7.2H_2O$ = 0.034 M) [17].


100
90
80
70
60
50
40
30
20
10
Vanadium (V) %
$VO_2(OH)_2(H_2O)^-$
$VO_2 \cdot C_7H_4O_7^{2-}$
$V_4O_{12}^{4-}$
$V_3O_9^{3-}$
$HV_2O_7^{3-}$
$V_6O_{17}^{4-}$
9.0
8.0
7.0
6.0
5.0
pH

our group by Walker [19] who identified a vanadyl-citrate complex in the pH range 2 to 12.5.

2.1.4 Summary

In summary, the chemistry of vanadium does not appear to be adversely affected by the introduction of the electrolytic method. Vanadium (IV) and (V) are expected to remain the active oxidation states in the process liquor. The speciation of vanadium (IV) is not fully understood. This must necessarily complicate the electrochemical studies. There are considerable pH effects to be associated with the redox chemistry of Vanadium (IV) and (V) in the process liquor. The influence of pH levels on, and the extent of, vanadium (IV) electro-oxidation remains unresolved.

2.2 Sulphur Chemistry

2.2.1 General Chemistry

Sulphur, element 32, has the electron configuration $3s^2$ $3p^4$, and is expected to exhibit the oxidation states: -2, 0, 2, 4, and 6. The higher oxidation states are stabilized by divalent oxygen, hydroxide, and/or sulphur in various oxidation states.

Elemental sulphur exists in a number of allotropic forms. The most common allotropes are rhombus (yellow, density 2.07g cm^{-3}), monoclinic (pale yellow, 1.96 g cm^{-3}), and amorphous (pale yellow, 1.92 g cm^{-3}). The rhombic and monoclinic allotropes are composed of S_8 rings, whereas the amorphous 'plastic sulphur' allotrope has a helical structure.

The stable oxidation states and speciation of sulphur in an alkaline sulphide solution were originally described by Fetzer [20]. These include elemental sulphur, sulphide, polysulphide, sulphate, thiosulphate, and dithionate ions. Although their formation is theoretically possible, the tri, tetra, pentathionates and persulphates ions do not accumulate as they are decomposed by alkaline sulphides. Sulphite cannot be observed in solutions containing elemental sulphur or polysulphide ion since it reacts to form thiosulphate ion.

The natural disproportionation of elemental sulphur in alkaline solutions, as shown in equation 2.54, has been reported [21]. The reaction is not important to the present study, however, since it only occurs in highly alkaline solutions [22].

$$12S + 6OH^- = S_2O_3^{2-} + 2S_5^{2-} + 3H_2O \qquad (2.54)$$

The chemistry of the vapour phase and liquid claus processes is summarized [3] in Table 2.2.1.

2.2.2 Anodic Discharge of Sulphide

The earliest studies of the electro-oxidation of sulphide ion include the work of Fetzer [20], in 1928, who advanced the turn of the century work of Kuester. Fetzer used the approach of electrode product analysis to show that the electro-oxidation of approximately 2 M sulphide in 4 M NaOH at platinum proceeded in three distinct stages that are distinguished by the potential applied to the electrode.

Stage 1: Sulphide is oxidized solely to polysulphide.

Stage 2: Polysulphide continues to form with elemental sulphur depositing on the electrode.

Stage 3: Polysulphide, elemental sulphur, sulphate and, towards the end of this stage, oxygen may be liberated. Thiosulphate is never observed to form.

Table 2.2.1

Gas and liquid phase Claus reactions [3]

__Gas Phase Claus__: $H_2S + 1/2O_2 = S^o + H_2O$

$H_2S + 3/2O_2 = SO_2 + H_2O$	$H_R^o = -77.5$ kcal mole^{-1}
$2H_2S + SO_2 = 3S^o + 2H_2O$	$H_R^o = -112$ kcal mole^{-1}
$3H_2S + 3/2O_2 = 3S^o + 3H_2O$	$H_R^o = -189.5$ kcal mole^{-1}

__Liquid Phase Claus__: $2H_2S + SO_2 = 3S^o + 2H_2O$

i) Reactions:

$SO_{2(aq)} + H_2O = H_2SO_{3(aq)} = HSO_3^- + H^+$

$2H_2S + 4SO_2 + H_2O = 3H_2S_2O_3$

$S_2S_xO_6^{2-} + S_2O_3^{2-} = S_2S_{x+1}O_6^{2-} + SO_3^{2-}$

b) Side reactions:

$S_2S_xO_6^{2-} + CN^- = S_2S_{x-1}O_6^{2-} + SCN^-$

$S_2O_3^{2-} + CN^- = SO_3^{2-} + SCN^-$

c) Sulphur elimination:

$S_2S_xO_6^{2-} = S_2S_{x-8}O_6^{2-} + S_8$

It is amusing to mention Fetzer's curious distinction between sodium sulphide (Na_2S) and sodium hydrogen sulphide (NaSH) in experiments conducted in 4 M NaOH, the latter forming hydrogen sulphide as an oxidation product. It is historically interesting to examine the equation given by Fetzer to represent the stage 3 oxidation of sulphide ion in 4 M sodium hydroxide.

$$4NaSH = Na_2S.S + 2H_2S \text{ (formed at anode)} + 2Na \text{ (liberated at cathode)}$$

The liberation of sodium at the cathode is an obvious reference to cathodic hydrogen evolution. The evolution of hydrogen sulphide gas from a 4 M sodium hydroxide solution is a chemical contradiction.

In 1933, Bohnholtzer and Heinrich [Bard [23]: reference 109] concluded that the electro-oxidation of 2 M sodium sulphide, disulphide, or trisulphide results in the deposition of elemental sulphur, which disolves, yielding polysulphides. The authors report that sulphur dissolution occurs more readily in solutions containing short chain polysulphide ions than sulphide ions.

In 1950, Gerischer [24] re-defined Fetzer's stages as regions. In region a, 0 to 0.9v, polysulphides are the sole product. In region b, 0.9 to 2.1v, Gerischer observed the formation of polysulphide, thiosulphate, and sulphate ions. In region c, 1.6 to 2.5v, only sulphate and dithionate ion are formed. The dithionate ion was a minor (insignificant ?) reaction product. Gerischer also observed that the electrode could be freed of electrodeposited sulphur at high anodic potentials, but, the electrode remained in a passive condition.

Gerischer interpreted this data in the following manner. In region a, sulphide and polysulphide ions are electro-oxidized to elemental sulphur (equation 2.55)

$$S_x^{2-} = xS^o + 2e^- \qquad (2.55)$$

The deposited sulphur subsequently disolves to form longer chain polysulphide ions (equation 2.56).

$$S_x^{2-} + S = S_{x+1}^{2-} \qquad (2.56)$$

In region b, sulphide and polysulphide are electrolysed to sulphite and thiosulphate ions as shown in equations 2.57 and 2.58.

$$S^{2-} + 6OH^- = SO_3^{2-} + 6e^- + 3H_2O \qquad (2.57)$$

$$S_x^{2-} + 6OH^- = S_2O_3^{2-} + 6e^- + 3H_2O + (x-2)S^o \qquad (2.58)$$

The sulphite and thiosulphate ions formed in region b, are oxidized to dithionate and tetrathionate (equations 2.59 and 2.60). Alternatively sulphite may react with elemental sulphur to form thiosulphate ion (equation 2.61). Tetrathionate reacts to form dithionate and trithionate ions (equation 2.62, which does not balance). The trithionate ion does not accumulate since it reacts to produce thiosulphate and sulphate ions (equation 2.63).

$$2SO_3^{2-} = S_2O_6^{2-} + 2e^- \qquad (2.59)$$

$$2S_2O_3^{2-} = S_4O_6^{2-} + 2e^- \qquad (2.60)$$

$$SO_3^{2-} + S^o = S_2O_3^{2-} \qquad (2.61)$$

$$4S_4O_6^{2-} + 6OH^- = 5S_2O_6^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad (2.62)$$

$$S_3O_6^{2-} + 2OH^- = S_2O_3^{2-} + SO_4^{2-} + H_2O \qquad (2.63)$$

In region c, Gerischer attributed sulphate formation to the electro-oxidation of sulphite and thiosulphate by equations 2.64 and 2.65.

$$SO_3^{2-} + 2OH^- = SO_4^{2-} + 2e^- + H_2O \qquad (2.64)$$

$$S_2O_3^{2-} + 2OH^- = SO_4^{2-} + 2e^- + H_2O + S^o \qquad (2.65)$$

It is a tribute to the work of these early researchers that the overall picture of sulphide electro-oxidation remains essentially unchanged to this day. A considerable number of investigators have contributed many details to refine our understanding of the subject.

A number of standard reduction potentials for the sulphide / polysulphide couple have been tabulated [23]. A selection of these is reproduced in Table 2.2.2. The majority of the E^o values lie in the range of -0.4 to -0.5 volts. In a 1 M sodium hydroxide solution containing approximately 1 M sulphide and dissolved sulphur, a platinum electrode assumes a stationary potential [25] (except at high sulphur concentrations), in accordance with the following expression:

$$E = E^o + (RT/nF) \ln ([S] / [Na_2S]^2)$$

where [S] is the total dissolved elemental sulphur and $[Na_2S]$ is the total sulphur (-II) in solution. The value for E^o was graphically estimated as -0.522v.

The current efficiency of continous hydrogen sulphide oxidation to

Table 2.2.2

Standard potentials of the sulphide / polysulphide couple [23].

Half-reaction	Standard Potential
$S_2^{2-} + 2e^- = 2S^{2-}$	−0.48 or −.524
$S_2^{2-} + 2e^- + 2H^+ = 2HS^-$	+0.298
$S_3^{2-} + 2e^- = 2S^{2-} + S_2^{2-}$	−0.49
$S_3^{2-} + 4e^- + 3H^+ = 3HS^-$	+0.097
$2S_3^{2-} + 2e^- = 3S_2^{2-}$	−0.506
$S_4^{2-} + 6e^- + 4H^+ = 4HS^-$	+0.033
$S_4^{2-} + 2e^- = 2S^{2-} + S_3^{2-}$	−0.52
$3S_4^{2-} + 2e^- = 4S_3^{2-}$	−0.478
$S_5^{2-} + 8e^- + 5H^+ = 5HS^-$	+0.003
$4S_5^{2-} + 2e^- = 5S_4^{2-}$	−0.441

Table 2.2.2 continued.

Half-reaction	Standard Potential
$S(s) + 2e^- + H^+ = HS^-$	-0.065
$S(s) + 2e^- + H_2O = HS^- + OH^-$	-0.52 (-.478)
$S(s) + 2e^- = S^{2-}$	-0.48 (-.508)
$4S(s) + 2e^- = S_4{}^{2-}$	-0.33
$5S(s) + 2e^- = S_5{}^{2-}$	-0.340 or -0.315

( ) denote Standard Reduction Potentials reported in CRC Handbook 57th Edition 1976-1977.

sulphur at a renewing platinum electrode surface with an applied potential of 1.21 v (NHE) in 0.1 M sulphuric acid was calculated to be 93 percent [26]. The controlled potential oxidation of 1 M sulphide to polysulphide, at platinum electrodes in 1 M sodium hydroxide, was observed [25] to proceed with a current efficiency of greater than 96 percent.

The deposition and accumulation of sulphur at platinum anodes is generally understood to inhibit sulphide discharge. Potentiostatic electrolysis [27] of hydrogen sulphide (saturated) in 0.1 M sulphuric acid at 1.45 v (SHE) covered a platinum gauze electrode (area 125 cm^2) with sulphur and produced a colloidal sulphur solution. Current-potential sweeps [28] of 1.5 v sec^{-1} on bright platinum in 0.2 M sodium sulphide (pH 12.8) produced a bluish white film that was observed to thicken and change colours through orange brown to greyish white. The x-ray energy spectrum (XES) of the film showed a characteristic emission of sulphur. The sulphur in the film was soluable in organic solvents (acetone, benzene, or toluene) and could be sublimed off the electrode. The authors concluded from the XES and solubility data that the sulphur in the film is the cyclohexa allotrope. Kapusta et al. [29] studied the electro-oxidation of 0.03 M sulphide in 0.1 M sodium hydroxide. They presented impedance and resistivity data to confirm sulphur deposition as a porous 'three dimensional phase formation.' Scanning electron microscopy of the sulphur deposits [28,30], while not conclusive, suggests the presence of 'discrete sulphur particles' on the electrode surface [30].

Kapusta et al. calculated the diffusion coefficient for the species involved in the oxidation rate determining step (transfer of the first electron) as $1x10^{-8}$ and $1x10^{-6}$ cm^2 sec^{-1} for hydrosulphide ion and sulphide ion respectively. The low values were attributed to the diffusion through sulphur films on the anode. The diffusion coefficient [22] for sulphide ion in an equimolar NaOH-H_2O melt at 100 °C was calculated to be $4.3x10^{-6}$ cm^2sec^{-1}. The low value was attributed to the high viscosity of the melt.

The formation of polysulphide ion within region a, as observed by Fetzer [20], Gerischer [24](0.8 and 1 M sulphide), and Bohnholtzer and Heinrich [23:109], was confirmed by Allen and Hickling [25]. These authors generally agree that polysulphide arizes from the sulphide or polysulphide assisted dissolution of elemental sulphur from the anode. The extent of dissolution varies the anodic overpotential [25] and the efficiency [29] of the anodic process. In the words of Allen and Hickling:

> 'If the discharge rate exceeded the speed of dissolution, then the anode underwent a process analogous to passivation.'

The dissolution of elemental sulphur into alkaline sulphide and polysulphide solutions, and the enhanced dissolution by short chain polysulphide ions (Bohnholtzer and Heinrich), are observations which are consistent with the chemistry of the polysulphides. Teder et al. [7] have reported that sulphur dissolution varies with the surface area of the sulphur particles and is fastest in short chain polysulphide ions solutions.

Teder [8] and Giggenbach [31] have investigated the distribution of different polysulphide species in alkaline solutions and studied the number of elemental sulphur atoms per polysulphide ion. In solutions where the ratio of elemental sulphur to sulphide ion never exceeded 0.1, Giggenbach presented visible observations and UV data to show that, as the pH was increased from 7 through 17.5, the polysulphide speciation progressed from the pentasulphide to the disulphide. The opposite was found to be true for solutions in equilibrium (saturated) with elemental sulphur. In these solutions Teder observed an average polysulphide chain length of 3 at pH 9 which increases to 5 at pH 10. The existance of the hexasulphide and longer chain polysulphides was indicated.

Allen and Hickling [25], reported overpotential-current density studies of the oxidation of 1 M sulphide in 1 M sodium hydroxide at several electrode materials. In this study the authors report an abrupt increase in overpotential, at current desities above 10mA cm^{-2}, at which point the electrodes became passivated. At 1mA, the overpotentials were smallest on platinized platinum, followed by carbon, and nickel. Gold, tungstun, and platinum electrodes showed the highest overpotentials to passivation. Tungstun was reported to darken and nickel became coated with nickel sulphide. Increases in temperature and polysulphide content were shown to retard the onset of the overpotential increase. Selected values of the anode overpotentials which were interpolated from Allen and Hickling [25] Fig. 2 are given in Table 2.2.3.

The passivation of the anode has not been unequivocally attributed to sulphur deposition. Gerischer attributed the passivation of a platinum electrode anodically freed of sulphur deposits to a thin oxide layer which inhibited the discharge of sulphide ion. In 1971, Loucka [32]

Table 2.2.3

Sulphide Oxidation Overpotentials [25].

Current Density $mAcm^{-2}$	Pt	Au	W	Ni	C	PtPt
0.1	0.090	0.095	0.105	0.040	0.060	0.005
0.31	0.120	0.120	0.125	0.075	0.075	0.010
1	0.158	0.154	0.156	0.115	0.100	0.024
3.16	0.195	0.158	0.185	0.155	0.125	0.055
10	0.280	0.245	0.245	0.225	0.195	0.105

$E^o = -0.522$ (determined graphically). The current densities interpolated from Allen and Hickling Figure 2 with the exception of the 1 mA cm^{-2} entries which were given by the authors.

observed platinum passivation associated with adsorbed sulphur or sulphide dioxide in 0.5 M sulphuric acid. Since the passivation was only removed by periodic polarization to positive potentials, Loucka proposed the formation of easily and poorly reducible surface oxides. On the contrary, Najdeker and Bishop [27] proposed the formation of platinum sulphides (equations 2.66 and 2.67).

$$Pt + S^{2-} = PtS + 2e^- \qquad (2.66)$$

$$Pt + 2S^{2-} = PtS_2 + 4e^- \qquad (2.67)$$

Platinum sulphide deposition was supported by three observations. First, a platinum electrode anodically and cathodically cycled in acidic $5x10^{-4}$ M hydrogen sulphide, then dipped into hot potasssium pentasulphide (known to dissolve platinum (IV) sulphides), sustained a measured weight loss. Second, a platinum electrode manually coated with platinum (IV) sulphide paste exhibited cyclic voltammetric behaviours similar to an anodically passivated electrode. Third, Najdeker and Bishop find evidence to support the view that platinum oxides can be converted to platinum (IV) sulphide either electrochemically, as expressed in equations 2.68 and 2.69,

$$PtO + 2S^{o} + 2H^{+} + 2e^- = PtS_2 + H_2O \qquad (2.68)$$

$$PtO_2 + 2S^{o} + 4H^{+} + 4e^- = PtS_2 + 2H_2O \qquad (2.69)$$

or chemically, via equations 2.70 through 2.72.

$$PtO + S^{o} = PtOS \qquad (2.70)$$

$$PtO_2 + 2S^o = PtS_2 + O_2 \tag{2.71}$$

$$PtO_2 + 3S^o = PtS_2 + SO_2 \tag{2.72}$$

Ramasubramanian [28] observed thin films exhibiting 'interference colours' on platinum electrodes made anodic in 0.1 molar sulphuric, hydrochloric, or nitric acids saturated with hydrogen sulphide. Similar films were formed from 0.1 M potassium nitrate or sulphate solutions (pH 4.5) saturated with H_2S. These films are formed at 1.3 +/- 0.1v (SHE), and were accompanied by bulk sulphur deposition. The films were insoluable in organic solvents and acids, but soluable in aqua regia or sodium sulphide solutions. Electron diffraction of the thin films deposited on platinum foil confirmed platinum (II) sulphide.

Ramasubramanian did not observe interference colours on platinum during the electrolysis of alkaline 0.2 M sodium sulphide solutions (pH 12.8). Cyclic voltammetry scans on bright platinum resulted in sulphur deposition and showed two anodic peaks- the first at 0.38 and the second at 0.8 v which gradually decreased with sucessive sweeps. The second peak had a clearly distorted shape. The cathodic scans were not extended sufficiently to characterize the cathodic current response evident in the author's Figure 5. It should be noted that a third anodic peak, at 1.25v, appeared on the first cathodic scan and increased in height with successive sweeps. Ramasubramanian did not identify this peak.

Kapusta et al. [29] investigated the passivation of platinum anodes during the oxidation of 0.03 M sulphide in 0.1 M sodium hydroxide. They observed two anodic peaks in the cyclic voltammograms, one at -0.05 and a second at 0.8 v (SCE), which they attributed to the deposition of films composed of platinum and sulphur. The tail of the first peak is marked by a double inflection near 0.2v. No specific oxidation reaction was assigned to either anodic peak, although the oxidation to sulphate was ruled out since it was considered only marginal below 1.5v. The current flow for the single cathodic peak at -0.8v did not entirely match that for the anodic peaks. The magnitude of the cathodic peak was found to decrease with increasing sulphide concentration.

Kapusta et al. noted that the oxidation products could be removed from the electrodes by oxidation at potentials greater than 0.9v (just prior to oxygen evolution), in agreement with Ramasubramanian and Gerischer, or by reduction at -0.8v. Oxidative cleaning of the electrode was complicated by bulk sulphide oxidation.

Kapusta et al. measured the cathodic charge required for film removal, at E = -0.8v, as a function of the anode (film deposition) potential. The study showed that the film deposition occured in two steps at potentials which approximately coincided with the anodic peak potentials. The cathodic charges for the removal of the film at each of these two steps were approximately equal. Assuming a monolayer deposition in each step, the authors attributed the cathodic charges to an n value of 4. The two mechanisms proposed to account for the stepwise phenomenon were (in their own words), either:

i) two monolayers of platinum (II) sulphide are deposited in the first step and oxidized to platinum (IV) sulphide in the second step, or

ii) one monolayer of platinum (IV) sulphide is deposited in each step. We consider this second mechanism to be more probable.

Kapusta et al. were apparently eager to be in agreement with Loucka, Najdeker and Bishop, Ramasubramanian, and others who have observed platinum sulphide deposition. It must be re-emphasized that platinum sulphide deposition was observed previously ONLY in acidic media and, according to Ramasubramanian, not in alkaline solutions. One source of misinterpretation may lie in the fact that Kapusta et al. confirmed sulphur deposition in the potential range -0.3 to 1.2v, but overlooked its reduction (or that of polysulphide) when interpreting the cathodic charge data. Furthermore the dependence of the cathodic current on sulphide concentration was not considered in the interpretation. For these reasons, the deposition of platinum sulphides in alkaline solutions is unlikely.

Kapusta et al. confirmed the existance of Ramasubramanian's third (unknown) peak, at 1.25v, in solutions with sulphide concentrations in excess of 0.2 M. In a cyclic voltammetry experiment they show, in their Figure 10, that the peak current decreases while the peak potential shifts negatively with increasing scan rate. At high scan rates, the potential of the third anodic peak coincided with that of the second anodic peak at 0.7v. This strongly suggests that a similar product is formed at both potentials. The authors attribute the mysterious appearance of the unknown peak to sulphide discharge following the removal of a platinum oxide film (which inhibits the sulphide discharge). The platinum oxide film is assumed to deposit simultaneously with platinum sulphide and elemental sulphur deposition during the second anodic peak. Alternatively the platinum oxide could be formed by oxidation of platinum sulphide (equations 2.73 and 2.74).

$$PtS_2 + 4OH^- = PtO_2 + S_2 + 2H_2O + 4e^- \qquad (2.73)$$

$$PtS_2 + 16OH^- = PtO_2 + 2SO_4^{2-} + 8H_2O + 16e^- \qquad (2.74)$$

The removal of the platinum oxide film was rationalized in terms of a chemical dissolution reaction (equation 2.75), or as considered previously (equations 2.68 through 2.72) [27].

$$PtO + S^{2-} + H_2O = PtS + 2OH^- \qquad (2.75)$$

The oxidation reaction in equation 2.74 is attractive in that it proposes a synthetic route to account for the formation of trace sulphate during Gerischer's region 'a' oxidation. Although the deposition and dissolution of platinum oxides is a plausible explaination for the restricted sulphide oxidation associated with the third anodic peak, it is not clear how platinum oxide dissolution can proceed in the presence of electrodeposited sulphur. Furthermore, the oxidative removal of sulphur or adsorbed polysulphides at potentials greater than 0.9v was not explained by Kapusta et al., nor considered in the study of the platinum sulphide deposits or the study of Ramasubramanian's unknown peak.

Moscardo-Levelut and Plichon [33] have employed voltammetric, potential step chronoamperometry, cyclic voltammetry, and controlled potential analysis techniques to study the oxidation of sulphide and small chain polysulphides. The experiments were conducted with gold electrodes in an equilmolar NaOH-H_2O melt (100 °C). The high alkalinity and temperature typically enhances sulphur dissolution and restricts polysulphide chain lengths. Sulphide concentrations employed in the study ranged from 0.2 to 0.0092 M.

The authors observed sulphide to be oxidized, at a rotating electrode, in two distinct anodic steps (-0.62 and -0.27v vs Ag / Ag(I) electrode). The first anodic step was diffusion controlled. It was assigned to the oxidation reaction:

$$2S^{2-} = S_2^{2-} + 2e^- \qquad (2.76)$$

although some sulphur deposition was implicated in the voltammetric experiments. The disulphide ion, but NOT the trisulphide ion, was reported to be electroactive at potentials corresponding to the first anodic step.

With particular reference to equation 2.76, the diffusion of an electroaactive species away from the electrode is not characteristic of a classical, diffusion limited, electrochemical response. For this reason it may be inappropriate to infer an n value to the second anodic wave by comparison to the height of the first wave. Under these circumstances, the second anodic step may not correspond to the irreversible formation of sulphite ion (equation 2.77).

$$S^{2-} + 6OH^- = SO_3^{2-} + 3H_2O + 6e^- \qquad (2.77)$$

The controlled potential oxidation of sulphide was investigated by Moscardo-Levelut and Plichon at potentials corresponding to the plateau of the first anodic step. In the initial stages of the electrolysis, the disulphide ion and later the trisulphide ion accumulated. With prolonged electrolysis there is a slow and simultaneous disappearance of the polysulphide colour, UV bands, and voltammetric curves. The authors conclude from the initial rate of oxidation that the largest stable polysulphide species to be found in the melt is the trisulphide ion. The trisulphide ion was thought to slowly disproportionate into an oxyanion (S_xO_y) and an electroactive species (sulphide or disulphide ion).

It should be pointed out that the initial rate of oxidation proceeds with complete dissolution of elemental sulphur yielding polysulphides. Towards the latter stages of electrolysis, when the trisulphide ion predominates in solution it is reasonable to assume that the anode may be passivated by elemental sulphur.

The hypothesised disproportionation of trisulphide ion into a sulphur oxyanion and sulphide after prolonged electrolysis is questionable. Their own UV data suggests that the trisulphide ion may be stable in solutions with a high sulphur content. The authors do not substantiate their hypothesis with the necessary analysis for the oxyanion. If the rate of elemental sulphur disproportionation (equation 2.54 or 2.78) in the melt is slow, and elemental sulphur is not electroactive, then the experimental observations during the latter stages of electrolysis are entirely consistent with the accumulation of elemental sulphur or large chain polysulphides.

$$S_8 + 6OH^- = 2S_3^{2-} + S_2O_3^{2-} + 3H_2O \qquad (2.78)$$

The formation of elemental sulphur or large chain polysulphides in the melts is consistent with other reported observations. In the cyclic voltammetry experiments the authors report the appearances of a prewave to the first anodic step at slow sweep rates and a prewave to the second anodic step at high melt temperatures. These observations appear similar to the suppressed responses, also diffusion limited, which were obtained in sulphide polarography (see Appendix A3). As pointed out by Osteryoung [34] the diffusion (mass transport) limiting kinetics may be expected when porous films are formed at electrodes. The involvement of porous films and their implication to the suppression of the first anodic step is that the suppression may be overcome, at the second anodic step, without necessarily changing the anode product. The deposition of elemental sulphur at both anodic steps is consistent with the observation that only one cathodic step is seen for the two anodic steps.

Further examination of the Moscardo-Levelut and Plichon study reveals a gross inconsistency associated with observations made at a rotating gold electrode. In Part II, the authors observe that successive additions of sulphur to a sulphide containing melt has no effect on the first anodic step, but sucessively increased the second anodic step. Irrespective of the electrode reaction, the limiting current is proportional to the quantity of added sulphur. If the sulphur is completely dissolved it will be present as polysulphide. This implies that the second anodic step responds to the total sulphur in the melt.

The problem lies with the voltammetric scans recorded for a sulphide containing melt which was subjected to controlled potential electrolysis. In the initial stages of the electrolysis, when disulphide and trisulphide predominate, the total sulphur in the melt remains constant, yet the second anodic step decreases with the conversion of sulphide to the di- and trisulphide. Since trisulphide disproportionation -the accumulation of an oxysulphur anion- is not expected until the latter stages of the electrolysis, there is an unexplained decrease in the total electroactive sulphur.

A decrease in electroactive sulphur would be consistent with the deposition of elemental sulphur accumulation in the melt or deposition at the cylindrical gauze electrode. A more detailed sulphur balance is needed to resolve the nature of the anodic response in the NaOH-H_2O melts.

The controversy surrounding the identity of the sulphide electro-oxidation products in the NaOH-H_2O melt has important ramifications in the aqueous studies. If sulphur is the major anode product in the melt, under conditions which can be considered more favourable to the electrosynthesis of sulphite and sulphate, then it may also be the major anode product in alkaline aqueous solutions. Indeed, the abnormal peak shapes associated with the cyclic voltammetry studies of aqueous alkaline sulphides by Ramasubramanian and Kapusta et al. may, in fact, be diagnostic of the type of suppressed responses observed in the melts and in sulphide polarography.

For these reasons the electrolytic formation of oxysulphur anions, at potentials defined within Gerischer's region 'a', in alkaline solutions is unlikely. Sulphur deposition may give rise to all observed electrode phenomenon, with the exception of the cathodic peak (which may be polysulphide reduction) and the electro-oxidative cleaning of heavily passivated electrodes.

Platinum electrode passivation has been reported to give rise to a noteworthy phenomenon. Platinum electrodes, passivated in 0.1 M sulphuric acid containing hydrogen sulphide, have been shown to exhibit electrocatalytic activity towards the oxidation of formic acid, methanol, or carbon monoxide [35,29]. It has been suggested that the activity may arize from the inhibition of platinum oxide formation. Kapusta et al. have shown that, in the presence of sulphide, the potential range at the platinum electrode is extended at the expense of the 'onset' potentials for hydrogen and oxygen evolution. The anodic and cathodic shifts were reported to amount to about 250mV.

The oxidation of alkaline sulphide solutions has been studied by cyclic voltametry at iron electrodes [30]. In the absence of sulphide, there is oxide deposition and a considerable electrode activation effect (towards oxide deposition) in 0.05 M sodium hydroxide, with repetative sweeps. In the presence of 0.01 M sulphide, oxide deposition and the activation effect are partially inhibited. It was suggested that the inhibition was caused by the competative adsorption of the SH^- ion relative to OH^-.

The cyclic voltamograms show a single, diffusion limited, anodic peak for sulphide which shifts to less anodic potentials with increasing sulphide concentration. Distortions in the peak, reminiscent of a supressed response, are observed in 0.5 M sulphide/0.1 M sodium hydroxide solution. The peak was attributed, in part, to the reaction:

$$8SH^- = S_8 + 8H^+ + 16e^- \qquad (2.79)$$

A cathodic peak, observed in the cyclic voltamograms, was attributed to the reduction of sulphur. Comparisons of the cathodic charge with the anodic charges associated with iron oxide and sulphur deposition showed that greater than 90 percent of the cathodic charge is due to the reduction of the deposited sulphur.

During the sulphide electro-oxidation, streams of fine particles leaving the electrode and the green colour of colloidal $NaFeS_2$ were observed in the solution. The electrodes were pitted as the result of the electrolysis. According to the authors, the sulphide-induced corrosion of the electrodes may be linked to iron oxide deposition.

Sulphide discharge at silver electrodes resulted in the formation of a porous silver sulphide film with weak mechanical properties [34].

2.2.3 Sulphur Electro-reduction

Tomilov, Kaabak, and Varshavcki [Bard [23] reference 116], were reported to have reduced sulphur suspensions, in neutral or alkaline solution to hydrogen sulphide on graphite electrodes. Current efficiencies of 55 to 75% were observed. No reduction was observed on lead or zinc cathodes.

The reduction of electrodeposited sulphur at iron electrodes [30] was mentioned in the previous section.

2.2.4 Fixed Salts Electrochemistry

Bard [23] has tabulated reduction potentials for many electrochemical reactions of sulphite, thiosulphate, and sulphate, with the warning that many are the result of theoretical calculations. A selection of these reactions is given in Table 2.2.4. One particular reference involving thiosulphate electrochemistry is of interest. Konopik and

Table 2.2.4

Standard potentials of selected oxysulphur anions [23]

Half-reaction	Standard Potential
$S_2O_6^{2-} + 2e^- = 2SO_3^{2-}$	+0.026
$S_2O_6^{2-} + 2e^- + 4H^+ = 2H_2SO_3$	+0.564
$S_2O_6^{2-} + 2e^- + 2H^+ = 2HSO_3^-$	+0.564
$2SO_4^{2-} + 2e^- + 4H^+ = S_2O_6^{2-} + 2H_2O$	-0.22
$SO_4^{2-} + 2e^- + H_2O = SO_3^{2-} + 2OH^-$	-0.93
$SO_4^{2-} + 6e^- + 8H^+ = S^o + 4H_2O$	+0.357
$SO_4^{2-} + 8e^- + 10H^+ = H_2S(aq) + 4H_2O$	+0.303
$SO_4^{2-} + 8e^- + 9H^+ = HS^- + 4H_2O$	+0.252
$SO_4^{2-} + 8e^- + 8H^+ = S^{2-} + 4H_2O$	+0.149
$2SO_3^{2-} + 4e^- + 3H_2O = S_2O_3^{2-} + 6OH^-$	-0.58
$2SO_3^{2-} + 4e^- + 6H^+ = S_2O_3^{2-} + 3H_2O$	+0.705
$SO_3^{2-} + 4e^- + 3H_2O = S(s) + 6OH^-$	-0.66
$SO_3^{2-} + 6e^- + 6H^+ = S^{2-} + 3H_2O$	+0.231

Table 2.2.4 continued

Half-reaction	Standard Potential
$S_2O_3^{2-} + 4e^- + 6H^+ = 2S(s) + 3H_2O$	+0.465
$S_2O_3^{2-} + 8e^- + 8H^+ = 2SH^- + 3H_2O$	+0.200
$_2O_3^{2-} + 8e^- + 6H^+ = 2S^{2-} + 3H_2O$	-0.006

Holzinger [Bard references 48, 49] studied the reduction of thiosulphate ion to sulphite ion by equation:

$$S_2O_3^{2-} + 2e^- = S^{2-} + SO_3^{2-} \qquad (2.80)$$

It should be noted that sulphite produced in this manner could react with sulphur to regenerate thiosulphate. The catalytic reduction of sulphur described below was not addressed in the study.

$$S_2O_3^{2-} + 2e^- = S^{2-} + SO_3^{2-} \qquad (2.80)$$

$$S^o + SO_3^{2-} = S_2O_3^{2-} \qquad (2.61)$$

$$S^o + 2e^- = S^{2-} \qquad (2.81)$$

Glasstone and Hickling [36] studied the oxidation of thiosulphate to tetrathionate and sulphate at pH 7 (equations 2.82 and 2.83).

$$2S_2O_3^{2-} = S_4O_6^{2-} + 2e^- \qquad (2.82)$$

$$S_2O_3^{2-} + 5H_2O = 2SO_4^{2-} + 8\ e^- + 10\ H^+ \qquad (2.83)$$

At pH 9 and a thiosulphate concentration of 0.025 M, of the 74 percent of the thiosulphate oxidized, 60 % of the thiosulphate appeared as tetrathionate and 14 % (presumably) appeared as sulphate. The authors suggest that in highly alkaline solutions, where tetrathionate is unstable, that sulphate should be the predominate product.

Sulphate reduction on platinum has been observed [32] only from concentrated sulphuric acid.

2.2.5 Summary

The electro-oxidation of sulphide in aqueous alkaline solutions results in the formation of different products depending on the applied potential. At applied potentials of 0 to 1.2 volts, elemental sulphur is the major product. The elemental sulphur accumulates in solution or is electrodeposited at the electrode (possibly as discrete particles). The elemental sulphur can be dissolved by the action of excess sulphide ion forming long chain polysulphides. The electro-oxidation of sulphide or polysulphide ion is associated with anode passivation. There is much controversy concerning the role of platinum sulphides and oxides with elemental sulphur in causing this passivation. Many of the experimental findings used to support the existance of platinum sulphides in alkaline solutions could be attributed to the deposition of elemental sulphur at the electrode surface.

The electro-oxidation of sulphide at potentials beyond 1.2v leads to an increasing formation of thiosulphate and sulphate. No electrochemical studies have seriously addressed the kinetics of thiosulphate and sulphate electrosynthesis, although in one study the oxidation of thiosulphate ion to sulphate ion at platinum electrodes with low current densities was investigated.

There are several reports of the electo-reduction of elemental sulphur in the literature. A possible electrocatalytic mechanism, involving thiosulphate ion, for the reduction of sulphur was deduced from the scientific literature.

The most suitable anode materials for use in sulphide oxidations are platinum, graphite, and nickel. Platinum is apparently the most resistent of the three to passivation at low current densities and low sulphide concentrations.

2.3 Electrocatalysis

Electrochemical reactions can be differentiated [37] in terms of direct or indirect electron transfer processes. In direct processes, electron transfer occurs directly between the electrode and the 'electrophore.' In an indirect process, the electron transfer occurs first with an electron transfer reagent which then reacts with the electrophore. Such a reagent may be chemically bonded to an electrode, adsorbed on the electrode surface, or dissolved in solution.

Many direct and indirect electron transfer reactions have been characterized using methods developed by Nicholson and Shain in 1964. One indirect electron transfer mechanism identified by them may be relevant to the operation of the modified Stretford process. The mechanism [38] considers the case of Catalytic Reaction with Irreversible Charge Transfer:

$$R = O + ne$$

$$O + Z = R + \text{Product}$$

The redox couple R/O is considered to be electrocatalytic towards reactant Z if the chemical reaction consuming Z is very fast. A fast reaction regenerating R at the electrode surface effectively inhibits polarization effects at the electrode since R is rarely depleated in the vicintiy of the electrode. This electro-catalytic effect is said to allow unparalleled electrode control due to a buffering of the electrode potential by the relatively constant concentration of the intermediate species at the electrode. Electrocatalytic mechanisms allow for high current densities and an associated decrease in electrolyser size.

2.4 Miscellaneous Industrial Processes

There are several industrial processes and patents which exist that are based on interesting catalytic or electrocatalytic phenomenon. These are noted in this section.

2.4.1 U.S. Patent 3,401,101

Removal of hydrogen sulphide and mercaptains from carbon dioxide-containing hydrocarbon streams. H.F. Keller Jr. (September 10, 1968). The HS radical in liquid and gaseous streams containing carbon dioxide is oxidized to elemental sulphur by the trihalide, peroxydecarbonate, peroxydiphosphate, peroxydiborate, vanadate, or ferricyanide of an alkali metal, which is capable of being raised again to the higher oxidation state after the reaction by hydrolysis. A typical reaction is

$$KI_3 + 2KOH + H_2S = 3KI + S + 2H_2O \qquad (2.84)$$

or the reaction

$$KI_3 + 2KOH + RSH = 3KI + S + ROH + H_2O \qquad (2.85)$$

followed by the electrolytic regeneration

$$3KI + 2H_2O = KI_3 + 2KOH + H_2 \qquad (2.86)$$

The process is not affected by the presence of carbon dioxide, and the solution should be maintained at pH 7.5 to 8.2 before mixture with the hydrocarbon stream.

2.4.2 U.S. Patent 2,438,871

Vanadium-catalytic hydrogen evolution. B.P. Sutherland, J.P. Thompson, C.H. Simpinkson, and D.D. Morris. (January 6, 1948). The addition of a vanadium compound to an alkaline aqueous electrolyte decreases the voltage necessary to maintain a given current density in the electrolytic production of hydrogen and oxygen.

2.4.3 Catalytic Hydrogen Evolution

A study [39] of hydrogen evolution in 1 M sodium hydroxide on nickel cathodes coated with nickel sulphide has been published. It was reported therein that the hydrogen overpotential on nickel is lowered by the presence of nickel sulphide. At 100 mA cm^{-2}, the overpotentials on nickel, nickel sulphide coated, and smooth platinum electrodes are 1.084v, 0.060 to 0.110v, and 0.288v respectively. The noble behaviour of nickel sulphide electrodes is subject to cathodic deterioration. This deterioration has been attributed to hydrogen penetration into the coating which induces blistering and embrittlement phenomenon.

A Belgian patent #864275 and a Nederlands patent #7801955 (1978) have made use of the phenomenon.

2.5 Research Definition

The review of the literature revealed:

i) that the electrochemistry of vanadium in alkaline solutions has not been well characterized;

ii) that the speciation of vanadium (IV) and (V) is diverse and not completely understood;

iii) that the electro-oxidation of sulphide solutions can be controlled to prevent thiosulphate and sulphate ion formation;

iv) platinum, graphite, and nickel as the most compatable electrode materials for use with sulphide ion electro-oxidation;

v) that vanadium (IV/V) may catalyse the hydrogen evolution reaction at the cathode;

vi) that the process may have been previously characterized and patented.

There are many aspects of the vanadium mediated electrolysis of hydrogen sulphide that are not addressed in the scientific literature. The evaluation of the proposed desulphurization process presented in this study will concentrate on:

i) an extended demonstration of the modified process;

ii) an estimation of the rate of by-products formation in the process liquors;

iii) the selection of analytical techniques for use in the current efficiency determinations.

iv) an estimation of the current efficiencies for vanadium (IV) oxidation under process-like conditions;

v) the investigation of sulphide and vanadium electrochemistry at platinum electrodes alkaline carbonate solutions containing citrate;

vi) the identification of those factors with the greatest influence on the vanadium (IV) oxidation potential.

The study will conclude with an economic assessment of the process and suggestions for its future development.

CHAPTER 3

EXPERIMENTAL

CHAPTER 3

EXPERIMENTAL

3.1 Solution Preparations

The carbonate citrate buffer employed in the study was prepared by dissolving 10g tri-sodium citrate dihydrate, and 20g sodium hydrogen carbonate in one litre of distilled water. The resulting buffer solution was 0.236 M in carbonate and 0.034 M in citrate. The buffer pH was adjusted with sodium hydroxide pellets, which were added as required. The carbonate buffers used in the voltametry experiments were prepared from sodium hydrogen carbonate and sodium hydroxide. The molarity of the carbonate buffers refers to the total carbonate in solution.

The solutions of Vanadium (IV) were prepared by the cautious addition of vanadyl sulphate into the requisite volume of deoxygenated carbonate citrate buffer. The slow addition of vanadyl sulphate salt to the well stirred buffer minimizes the loss of reagents through the intense effervescence that results. Upon complete dissolution of the vanadyl salt, the pH was adjusted with sodium hydroxide pellets. (The solid sodium hydroxide was not allowed to contact the solid vanadyl salt in solution since this produces a light brown precipitate. This precipitate is slow to dissolve at pH 9.)

Vanadium (V) solutions contained 3.5 grams of sodium meta-vanadate per litre. The solutions were prepared by first dissolving 5 grams trisodium citrate and the sodium meta-vanadate in approximately 200 ml of distilled water. The solution was heated to speed dissolution. The resulting solution was transfered to a larger vessel containing sufficient sodium hydrogen carbonate, sodium hydroxide, trisodium citrate, and distilled water to give 1 litre of 0.03 M vanadate in a buffered solution.

Sulphide solutions were prepared by dissolving the requisite mass of sodium sulphide in deoxygenated buffer, pH 8. The pH was adjusted with sodium hydroxide pellets. Polysulphide solutions were prepared by dissolution of 'flowers of sulphur' in a sulphide solution.

Solutions were de-oxygenated and blanketed with laboratory grade nitrogen, which was scavenged for oxygen in a gas cleaning apparatus.

The pH measurements in Sections 3.2 and 3.4 were made using a Fisher Microprobe Combination pH electrode and a Leeds β Northrup meter. A Corning 130 pH meter equipped with a Fisher combination polymer body, gel filled pH electrode was used in all other Sections. Ph meters were calibrated with Colorkey 7 and 10 buffer solutions.

The chemicals used are listed below:

NaOH (reagent grade)	BDH Chem. Ltd.
$NaHCO_3$ (analytical grade)	Toronto, Ont., Canada
Trisodium Citrate Dihydrate	BDH (Poole, England)
$Na_3C_6H_5O_7.2H_2O$, (Anala R^R),	
flowers of sulphur,	
Sodium metavanadate, $NaVO_3$, and	
Vanadyl sulphate, VO_{SO4} xH_2O	
(voltametry and current efficiency study)	

Vanadyl sulphate, $VO_{SO4}\ xH_2O$ (current efficiency study only)	A.D. MacKay (New York, N.Y.)
Commercial grade ADA	courtesy of DOFASCO (Hamilton, Ont., Canada)
Colorkey Buffer solutions	BDH Chem. Ltd (Toronto, Ont., Canada)
Sodium sulphide, 9-hydrate 'Baker Analysed' reagent	J.T. Baker Chemical Co. Phillipsburg, N.J.

3.2 Electrolysis Studies

The electro-oxidation of vanadium (IV) ion was studied in a simple electrochemical cell. The anode compartment was a 250 ml beaker containing 200 ml of a buffered vanadyl sulphate solution. The cathode compartment was a 250 ml beaker containing 200 ml dilute hydrochloric acid. A cotton stoppered, 1 M KCl salt bridge provided the electrical contact between the compartments. The electrode compartments were magnetically stirred and covered with parafilm. Oxygen was not excluded from the anode compartment.

The electrodes used in this cell were made of platinum. The anode was a 3 cm square planar electrode. The cathode was a cylindrical gauze basket 5 cm long x 1.2 cm in diameter. Constant currents of 0.005, 0.01, 0.02, 0.05, 0.1, or 0.2 amps were supplied by a Sargent Model IV Coulometric Current Source. The highest current settings below excessive gas evolution from the anodes were used.

3.3 Pilot Plant

The Stretford process bench-top pilot plant used in this study is shown in Figure A1.1.1 and is described in Appendix 1. It was assembled prior to the present study. Several modifications were made to the apparatus to permit the electrolytic regeneration of vanadium (IV) ion. These are described in Section 3.3.2. The modifications were made so as to not interfere with the normal operation of the apparatus.

3.3.1 Normal Stretford Operations

The normal pilot plant liquor was prepared by the dissolution of 6 grams of purified ADA into 2 litres of buffered vanadate solution (Section 3.1). The liquor was prepared immediately before use.

Laboratory grade nitrogen was introduced through the absorber during filling and start-up of the pilot plant. The hydrogen sulphide/nitrogen mixture was introduced into the absorber only when the pH of the re-circulating liquor had stabilized.

The general operating conditions of the pilot plant are given below:

CO_2 output gauge pressure	5 lb/in^2
H_2S/N_2 output guage pressure	15 lb/in^2
Absorber exit (soap bubble meter)	~ 70 ml/min
air supply/oxidizers	~ 150 ml/min
Liquor flow rate	~ 10 ml/min
Plant volume	1400 ml
Liquor recirculation rate	~ 10 cycles/day

The hydrogen sulphide/nitrogen mixture used in the pilot plant was prepared 'in house.' The following gases were used in the pilot plant.

C.P. Grade H_2S (99.5% min.)	Matheson of Canada Ltd. (Whitby, Ont., Canada)
Technical Grade N_2 and Dry CO_2	Canada Liquid Air Ltd. (Hamilton, Ont., Canada)

3.3.2 Modified Process Operations

ADA was excluded from all modified process runs. The bench-top pilot plant was modified to accomodate the electrolytic regeneration of the liquor with the addition of magnetically stirred electrolysis cell(s). The reduced liquor was gravity fed into this cell from the second 'froth' tank. The oxidized liquor was pumped from the electrolysis cell to the absorber. To prevent air oxidation in the froth tanks, laboratory grade nitrogen was substituted for the air supply (to maintain sulphur froth flotation). The final modification of the pilot plant operations involved reducing the hydrogen sulphide/ nitrogen supply to the absorber to give an exit flow rate of 50 ml min^{-1}.

The modified process was operated with constant current and with controlled anode potential supplies to the electrolysis cells. These pilot plant experiments are described in Sections 3.3.2.1 and 3.3.2.2.

3.3.2.1 Constant Current

A 600 ml beaker, with a working volume of 500 ml, was used as the electrolysis vessel in the constant current experiments. Three cylindrical platinum gauze electrodes, 4.5 cm high x 2.5 cm in diameter were used as anodes. Two pairs of platinum stirring loops and the cylindrical platinum gauze electrode (Section 3.2) were used as cathodes.

The current requirement of the pilot plant, necessary for the continuous vanadium assisted electrolysis of hydrogen sulphide, was calculated to be between 0.5 and 0.6 amps. A current efficiency of 70 % was assumed in this calculation. Three Sargent Coulometric Current sources capable of supplying a total of 0.6 amps constant current were connected, one to each of three anode-cathode pairs. These sources were activated individually and set to provide a total current which maintained a faint yellow to pale blue colour in the electrolysis cell.

3.3.2.2 Constant Potential

A 'polisher' cell consisting of a 350 ml plastic bottle (inverted with the bottom cut out) with a working volume of 300 ml volume was substituted for the large beaker used in Section 3.3.2.1. A large cylindrical platinum gauze anode and the small cylindrical platinum gauze cathode (Section 3.2) were used in the polisher. Two cylindrical platinum gauze electrodes and four platinum paddles served as a primary anode-cathode pair. The primary anode-cathode pair were put in the second froth tank.

Individual constant potential supply to each cell was afforded from the twinned stations of a Fischer Controlled Potential Analyser. Starting potentials were chosen to allow a total current flow of 0.6 amps, and refined by trial and error to maintain a faint yellow to pale blue liquor colour in the exit stream from the polishing cell. The current flow to the polisher was 25 to 30 percent of the total electrolysis current. The anode potentials were held constant relative to a reference electrode placed in the primary electrolysis cell. The reference electrode was connected in parallel to the two stations on the controlled potential source.

The percentage oxygen saturation was measured in the electrolysis cell effluent following seven days of continuous, vanadium assisted, hydrogen sulphide electrolysis. O.E. Hileman used a YSI model 54A oxygen meter to make this measurement. This was calibrated in a carbonate/ bicarbonate buffer. The presence of sulphate ion in the pilot plant liquor at the conclusion of the experiment was determined using the tlc technique described in the next Section.

3.4 Qualitative Sulphate Analysis

The presence of sulphate in pilot plant liquors was determined using the techniques reported by Handa and Johri [40]. The proceedures were followed directly except for the use of filter paper instead of microcrystaline cellulose plates. Drawn capillary tubes were used to apply reagents and test solutions to filter paper rectangles 10.5 x 12 cm. A 1 percent aqueous zinc acetate solution was spotted at 2 cm intervals along the baseline. Standard solutions containing individual oxysulphur anions, buffered vanadate, or buffered vanadate with sulphate and the test solutions were applied randomly to each zinc acetate spot.

The filter paper was developed by the ascending technique in a 600 ml jar using an n-propanol-1 M ammonmia-acetone (30:20:2 v/v) mobile phase for 10 to 15 minutes at 20 ^{o}. The filter paper was dried in the draught of the fume hood.

The sulphide and thiosulphate ions were developed with the reagents listed in Table 3.4.1. The rhodizonate solution was prepared within hours of use and kept refrigerated to prolong its shelf life. A freshly prepared solution of potassium rhodizonate was deep orange. The expired solution was a deep yellow colour.

The reagents used in the tlc analysis are listed below:

Sodium azide, Rhodizonic acid (dipotassium salt), n-pronanol.	Fisher Scientific
Cobaltous nitrate (AnalaR)	BDH (Poole, England)
Barium chloride, reagent grade	Shawinigan
Acetone and ammonium hydroxide	Caledon Laboratories Ltd. Georgetown, Ontario.
Silver nitrate (Assured)	BDH Chemicals Ltd.

3.5 Current Efficiency Measurements

This Section describes the experimental aspects of the coulometric current efficiency measurements for sulphide and vanadium and vanadium ions. The apparatus designed for use in these studies is described in Appendix 2. The proceedures for solution preparation are given in Section 3.5.1. The analytical methods used for liquor analysis are described in Sections 3.7 to 3.10.

Table 3.4.1

Detection of Anions after tlc Separation

Ion	Spray Reagent	Colour
S^{2-}	Aqueous 1 % $AgNO_3$	Brown black
$SO_4{}^{2-}$	Aqueous 0.1 % BaCl and 0.1 % aqueous potassium rhodizonate	Yellow on red background
$S_2O_3{}^{2-}$	Aqueous 1 % $AgNO_3$	Brown black
$SO_3{}^{2-}$	Mixture of equal volumes of aqueous 1 % cobaltous nitrate and saturated sodium azide.	Yellow

The apparatus employed in the coulometry studies offers some flexibility. The electrolysis cell can be operated with a fritted or an open compartment format and can accomodate either a batch or continuous flow steady-state electrolysis.

The current efficiency calculations for the flow experiments were made according to the equation given in Section A2.5. The current efficiencies for the batch electrolysis were determined from Faraday's law. The calculations were made using 5 programs written in Basic for the Osborne 1.

3.5.1 Preparation of Solutions and Electrodes

Liquors were prepared in two litre quantities and were deoxygenated during preparation and use.

Carbonate citrate buffer: prepared as per Section 3.1. In the sulphide oxidation experiments, 0.5 M potassium nitrate is added to increase the conductivity of the electrolyte.

Vanadyl liquor: The stated amount of vanadyl sulphate salt is dissolved in de-oxygenated carbonate citrate buffer as per Section 3.1.

Sulphide and Polysulphide liquors: Sulphide liqours were prepared as described in Section 3.1. Polysulphide liquors were prepared by dissolving enough sulphur to give stoichiometric $S.S^{2-}$. The rate of sulphur dissolution can be significantly enhanced in an ultrasonic bath.

Vanadyl and sulphide liquor: In virtually all studies, 13.5 grams of vanadyl sulphate were dissolved into the buffer prior to dissolution of the stated amount of disodium sulphide salt.

Preparation of electrodes: Electrodes were washed clean of visible deposits then soaked overnight in 1 M nitric acid. Prior to use, the electrodes were anodically and cathodically cycled in 1 M sulphuric acid using an Electro Model D-612T Filtered DC power supply operating at 6 to 8 amps, for 2 minutes each cycle. Unless otherwise specified the cycling order was A (anode), C(cathode), A, C. Electrodes used twice in one day were rinsed in nitric acid then cycled as above.

3.5.2 Continuous Flow Coulometry

The experimental conditions used in the continuous flow cell coulometry electrolysis are given in Table 3.5.1. A constant current of 0.2 amps was supplied to the electrolysis cell. The vanadium (V) was determined by coulometric titration or polarographically. The sulphide and polysulphide were determined polarographically.

The pump flow rate was measured to +/- 0.1 ml/min. The coulometric titration times were measured to +/- 4 sec/100 sec. The polarographic wave height measurements were associated with a reading error of 1 mm/100 mm. The sulphide titrations were reproducible to 3 ppt. These uncertainties give rize to uncertainties in the current measurements of 8-10 percent.

3.5.3 Batch Coulometry

The batch coulometry method was used to estimate the reduction current efficiencies for 0.03 M vanadate and for 0.013 M polysulphide. A constant current of 0.2 amps was applied across four platinum basket electrodes and the cylindrical gauze electrode (in the fritted compartment). The electrolyses were stopped after one hour (or after a noticeable colour change had occured in the vanadate solution). The concentration of vanadate ion was determined by coulometric titration. The concentration of polysulphide ion was determined polarographically.

3.6 Voltammetry

Voltammetric studies of vanadium (IV), vanadate, sulphide and polysulphide were conducted at Rotating Platinum Wire and Carbon Paste electrodes. Voltammograms were recorded with a Metrohm E 506 Polarecord

Table 3.5.1

The Experimental Conditions used in the Continuous Flow Cell.

Species	[species]	Flow Rate (ml/min)	Time to 95% steady-state	Cell	Anal. Method
v(IV)	0.03 M	7.5	1:59	F	C,P
S^{2-}	0.015 M	3.5	3:13	F	P
v(IV)+S^{2-}	*0.032 M	5.5	2:32	F,O	P

* 0.028 M +2(0.002 M)

F = Frit separated anode and cathode

O = Open cell with no anode-cathode separator

C = Coulometric Titration

P = Polarography

equipped with Ag/ AgCl, saturated KCl (Metrohm EA 427) counter and auxilliary electrodes. DC voltammograms were recorded in the potential range 0 to 1.2 volts (Ag/AgCl).

The current output from the polarograph was digitized using channel 2 of a Smartface analogue to digital converter. The data points were 'aquired' at 0.5 Hz into a random access file using an aquisition program (sfa) written, in Fortran, by Michael Malott for the Osborne I computer. The data files were transfered to IBM PC compatable format using the 'Uniform' utility program and the Osborne I. All subsequent work with the data files was performed with a Columbia (PC compatable) computer.

The random access files were scaled and the factorial design experiment analysed using the spreadsheet capabilities of Symphony (Lotus Corporation). The data was 'imported' and structured into the spreadsheets using a 'macro' program written in the Symphony Command Language. The composite voltammograms shown in Figures 4.4.1 to 4.4.13 were ploted using Symphony's graphing functions. The figures were drawn with a serially driven Hewlett Packard 7470A.

Each curve in Figure 4.4.1 was defined by 25 points entered manually from measurements taken from a Metrohm polarecord tracing. The curves in Figures 4.4.2 to 4.4.6 and 4.4.10 were defined by 125 data points. The factorial design voltammograms and results were defined and calculated using 118 data points. The voltammetric curves recorded from sulphide containing solutions (Figures 4.4.11 to 4.4.13) were defined by 250 data points. The voltage axes used to plot the voltammograms from Symphony were generated within the spreadsheet.

The electrolytic cell was a 400 ml Berzelius beaker containing 200 ml of de-oxygenated buffer, which was blanketed with purified nitrogen during the experiment. The concentration increments in the solutions of the species of interest were prepared by successive additions of 1 molar stock solutions using a Eppendorf 250 and 500 microlitre pipette. The 0.25 mM sulphide addition in Figure 4.4.13. was made using an Eppendorf 1-100 microlitre continuously adjustable pipette (4710).

The Rotating Platinum Wire Electrodes were supplied by Sargent. They consisted of a 19.5 cm length of glass tubing sealed and blown into a small bulb at one end. A 5.4 mm length of platinum wire, 0.9 mm in diameter (geometric area = 0.16 cm^2), extends from the bulb at a right angle to the axis of the tube. When in use the tube was filled with mercury and secured in the chuck of a Sargent Synchronous rotator. Electrical contact to the platinum wire was established through the mercury from a copper wire in contact with the mercury. The platinum wire was stored in 6 M HNO_3 and rinsed with distilled water before use.

The Carbon Paste electrode (Metrohm EA 267) was used in unstirred solutions. The active electrode surface was planar and circular with a diameter of 0.8 mm. The electrode surface was prepared using the following proceedure. Small quantities of paste (Metrohm EA 267c) were pressed out of the electrode and shaved off using a razor blade. A thin layer of paste 0.5 mm is pressed out past the electrode housing. The electrode is pressed vertically onto a teflon surface, and polished with light pressure and circular motions. A second thin layer is pressed out, polished, and brought flush with the glass housing by releasing the pressure on the paste during the final polishing. Surfaces prepared in this manner were flat and free from pitting. The electrode was made ready for use with a single voltammetric sweep in the buffer.

The solutions used in the voltammetry experiment were prepared as follows:

1 M sulphide: 36 g $Na_2S.9H_2O$ in 150 ml deoxygenated distilled water.

1 M polysulphide: 3.2 g 'flowers of sulphur' in 100 ml 1 M sulphide solution.

1 M vanadium (IV): 36 g $VOSO_4.xH_2O$ + 44.1 g trisodium citrate dihydrate in 150 ml deoxygenated 1.2 M carbonate buffer.

1 M vanadium (V): 18.3 g $NaVO_3$ + 3 g $NaHCO_3$ in 150 ml distilled water. The solution was boiled to speed dissolution. After cooling, 44.1 g trisodium citrate dihydrate was dissolved in the solution.

1.2 M carbonate buffer: 201.6 g $NaHCO_3$ in 2 litres distilled water.

The stock solutions were kept stoppered in glass bottles to minimize air oxidation and were prepared for use over three days. The buffer solutions of varying concentrations used in the factorial design experiments were prepared by dilution of 1.2 M carbonate buffer, pH 8.8. The pH was adjusted with sodium hydroxide pellets.

The design settings for the 2^3 factorial experiment [43] are given in Table 4.4.2. The design matrix (Table 3.6.1) and the Table of Contrast Coefficients (Table 3.6.2) were used in the execution and interpretation of the experiment. The observable in the experiment was the current flow at each of 118 discrete anode potentials in the 8 factorial

Table 3.6.1

Factorial Design Matrix

Run Order	[Carbonate]	pH	[Vanadium (IV)]
11	+	+	+
3	+	+	−
7	+	−	+
9	+	−	−
12	−	+	+
6	−	+	−
2	−	−	+
8	−	−	−
10	0	0	0
4	0	0	0
5	0	0	0
1	0	0	0

Table 3.6.2

Table of Contrast Coefficients

Mean	C	P	V	CP	CV	PV	CPV	Voltammogram Run number
+	−	−	−	+	+	+	−	8
+	+	−	−	−	−	+	+	9
+	−	+	−	−	+	−	+	6
+	+	+	−	+	−	−	−	3
+	−	−	+	+	−	−	+	2
+	+	−	+	−	+	−	−	7
+	−	+	+	−	−	+	−	12
+	+	+	+	+	+	+	+	11

C = Carbonate concentration

P = pH

V = Vanadate concentration

and 4 zero point voltammograms. The four zero point replicate curves were used to determine the error associated with curve reproducibility.

3.7 Titrimetric Analysis

The sulphide content of sulphide and polysulphide solutions and the analysis of thiosulphate ion were determined by iodimetric titration [41]. The iodine titrant was prepared and standardized as outlined in Section 3.7.1. The iodine solution was standardized against Arsenic (III) which was prepared by dissolution of arsenious oxide. The equations for the standardization and analysis are summarized below:

$$As_2O_3(s) + 4OH^- = 2HAsO_3^{2-} + H_2O \qquad (3.87)$$

$$H_3AsO_3^{2-} + I_2 + H_2O = H_3AsO_4^{2-} + 2I^- + 2H^+ \qquad (3.88)$$

$$SH^- + 2I = S^o + 2I^- \qquad (3.89)$$

$$S_x^{2-} + 2I = xS^o + 2I^- \qquad (3.90)$$

$$2S_2O_3^{2-} + 2I = S_4O_6^{2-} + 2I^- \qquad (3.91)$$

3.7.1 Preparation and Standardization of Iodine

A 0.1 N iodine solution was used as a titrant. This was prepared by the following proceedure:

40 grams of potassium iodide and 12.7 grams iodine were dissolved with 10 ml distilled water in a 100 ml beaker. The solution was filtered through a fritted glass crucible then diluted to approximately 1 litre. This was stored in a brown bottle in the dark.

The iodine was standardized as follows:

Accurately weigh 0.15-0.2g samples of primary standard grade (previously dried at 110 C for 1 hour) into 250 ml flasks.

Disolve in approximately 10 ml 1 M NaOH.

Dilute with approximately 70 ml.

Add two drops of phenolpthalein indicator.

Neutralize with 6 M HCl adding 1 ml in excess.

Carefully add 3-4g $NaHCO_3$ avoiding sample losses through effervescence.

Titrate in triplicate to the starch endpoint.

The iodine concentration was calculated using the following equation:

$$[I] = (\text{mass } As_2O_3)\ (4)\ (1000) / [197.85\ (\text{ml Iodine})]$$

$$= 20.2174\ (\text{mass } As_2O_3) / (\text{ml Iodine})$$

3.7.2 Sulphide and Thiosulphate Analysis

Sulphide and thiosulphate solutions were titrated according to the proceedure described below. The spiking solutions for the polarographic analysis were 0.33 molar. The sample aliquot sizes used in the titrations were 2 ml for the sulphide and 4 ml for the thiosulphate solutions.

Transfer the unknown solution to a 125 ml flask.

Dilute with approximately 20 ml slightly alkaline water.

Add 3-4g $NaHCO_3$ avoiding sample losses through effervescence.

Titrate in triplicate to the starch endpoint.

The sulphide and thiosulphate concentrations were calculated using the following expressions:

$$[S^{2-}] = (\text{ml Iodine})\ (\text{normality Iodine}) /\ [(2)\ (\text{ml sulphide})]$$

$$[S_2O_3{}^{2-}] = (\text{ml Iodine})(\text{normality Iodine}/(\text{ml sulphide})$$

The reagents used in this section are listed below:

Primary Standard grade Arsenic trioxide	Fisher Scientific Co.
Reagent grade Potassium iodide	Shawinigan (McArthur Chemical Co., Montreal)
A.C.S. sublimed Iodine	A and K Petrochem Ind. Toronto, Ontario.

3.8 Coulometric Titration of Vanadate

Vanadate ion concentrations were determinationed by coulometric titration. The computer controlled apparatus used in the analysis is described in Appendix A4. The electrolysis cell was modified to allow degasing of the cell contents with laboratory grade nitrogen. The analytical procedure is described below:

An electrolyte stock solution containing 0.2 M Cu^{2+} ion in 12 M HCl was prepared by dissolution of 53.3 grams copper sulphate, $CuSO_4 \cdot 5H_2O$, in 1 litre concentrated HCl.

A 15 ml aliquot of the electrolyte stock solution was transfered to the electrolyticcell

The cell volume is made up 75 ml with distilled water, and the cell contents are de-oxygenated for 5 minutes.

100 microlitres of a sample solution was transfered to the cell with an Eppendorf 4710 micropipette. A small volume of distilled water was used to wash the sample through the delivery funnel on the apparatus. The total amount of vanadium (V) in the cell was in the range of 2 to 10 x 10^{-6} moles.

Samples were taken from before and after an electrolysis and were determined in triplicate. The vanadium (V) concentration affected by the electrolysis was determined by Faraday's law as:

$$[V^{5+}] = i \, |t_{after} - t_{before}| \, / \, nFV$$

where V is the sample volume (in litres), i was 0.005 amps, and $|t_{after} - t_{before}|$ is the absolute value of the difference in coulometric titration times.

3.9 Sulphide and Thiosulphate Polarography

It has been shown in Appendix A3 that sulphide, in the presence of small amounts of thiosulphate (1-2mM), gives rise to an enhanced thiosulphate wave which assists the determination of sulphide and polysulphide ions.

The proceedure used in the analysis was derived from the method of Standard Addition and is described in Section A3.2.5. The response for sulphide ion was determined by measuring its combined response with thiosulphate ion, then subtracting the response of thiosulphate ion alone.

The standard additions were made with an Eppendorf 4710 pipette. The stock solution concentrations were determined titrimetrically.

3.9.1 Procedure

The diffusion wave height for the thiosulphate wave was measured at a potential of -0.14 volts (Ag/AgCl, sat. KCl). This value was chosen as one closest to the half-wave potential of most of the enhanced thiosulphate waves. An arbitrary potential was chosen because of the irregular wave shape, even though it was recognized that the half-wave potential for thiosulphate is not a constant [42]. The current at this potential was taken as the difference between the extrapolated linear plateau of the enhanced wave and the current extrapolated from before the sulphide wave. The current flow extrapolated from this region was identical with that from a carbonate citrate buffer in the absence of depolarizers.

A stepwise procedure for obtaining sulphide concentrations from polarographic data is described below.

Record the polarogram of an unknown sulphide solution. An enhanced wave verifies the presence of thiosulphate in the sample. (sensitive to approx 1 mM thiosulphate).

Record the diffusion wave, id 1, for the unknown sulphide solution with a measurable quantity of thiosulphate ion.

Record the diffusion wave, id 2, for the unknown sulphide solution with twice the measurable quantity of thiosulphate ion.

Record the diffusion wave, id 3, for the unknown sulphide solution with a measurable quantity of thiosulphate ion and a known quantity of sulphide ion (spike).

The difference in wave heights between id 1 and id 2 corresponds to the response of the measurable quantity of thiosulphide.

Subtracting the measurable quantity of thiosulphate from id 1 and id3 gives the response for sulphide present in the unknown and the spiked unknown respectively.

The sulphide concentration can be calculated using the equation below:

$$[S^{2-}] = \frac{[id1s - (id2s - id1s)]\ C_s\ V_s}{(id3s - id1s)\ V_{cell} + V_s(id3s)}$$

$$= \frac{[2id1s - id2s]\ C_s\ V_s}{[id3s - id1s]\ V_{cell} + id3s\ V_s}$$

$$= \frac{[2id1s - id2s]\ C_s\ V_s}{[id3s - id1s]\ V_{cell}}$$

where:

C_s = the concentration of the spiking solution

V_{cell} = volume in polarographic cell

V_s = volume of spiking solution

id1s = diffusion current for unknown with thiosulphate spike

id2s = diffusion current for unknown with two thiosulphate spikes.

id3s = diffusion current for unknown with sulphide and thiosulphate spikes.

3.10 Vanadate Polarography

The polarographic analysis of vanadium (V) was accomplished using the reduction wave at a half wave potential of −1.08 v. There is some controversy (see Appendix 3) regarding the cathode product, however, a linear response between wave height and concentration was observed in the range of 0–15 mM. Since the response is marginally affected in the presence of thiocyanate, thiosulphate, and trace sulphide ions (although not affected by vanadium (IV) ion), the analysis by standard addition is prefered. The use of a surfactant (Triton X-100) is recomended to suppress a polarographic maxima. The vanadate standards were determined by coulometric titration.

$$[V^{5+}] = \frac{C_s\,V_s\,(id_1)}{[(V_{cell}+V_s)id_2 - V_{cell}\,(id_1)]}$$

When V_s is small then,

$$[V^{5+}] = C_sV_s\ id_1\ /\ [V_{cell}\,(id_2-id_1)]$$

where,

V_s = the volume of spiking solution

C_s = the concentration of the spiking solution

V_{cell} = the volume of unknown solution in cell

id_1 = diffusion current for unknown solution

id_2 = diffusion current for unknown solution + spike

3.11 Computer Use

This thesis was written with the aid of Wordstar (MicroPro Corp.). Roughly one quarter was written with the Osborne I, one third on an IBM PC (made available during the summer of 1984 by the McMaster School of Adult Education), and the remainder on a Columbia Data Products MPC 1600-1 (IBM PC compatible) computer.

The figures hand drawn for the thesis were done with the 'AutoCad' computer aided drawing program and an optical mouse. The completed figures were drawn by a Hewlett-Packard, serially driven HP 7470A plotter.

Figure 4.3.1 was plotted using Plot 80 (a program run on the Osborne I), and a parallel driven Hewlett-Packard 7470A plotter.

CHAPTER 4

RESULTS AND DISCUSSION

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Electro-oxidation of Vanadium (IV) ion

4.1.1 Introduction

The electro-oxidation of vanadium (IV) ion at platinum in a carbonate citrate buffer, pH 9, has not been reported in the literature. This was attempted at the onset of experimentation. Constant current methods were selected on the basis of simplicity and instrument availability.

4.1.2 Results

The electrolysis of buffered vanadyl sulphate solutions was investigated using the cell configuration shown below:

$$\mathrm{Pt} \mid V^{4+},\ V^{5+},\ \text{c.c. buffer pH 9} \parallel \mathrm{HCl}\ \text{pH 1},\ H^+,\ H_2 \mid \mathrm{Pt}$$

The gradual disappearance of the characteristic blue colour of vanadium (IV) ion during the electrolysis indicated that it is oxidized to vanadium (V) at the platinum anode. Given sufficient time, it was clear that a solution of any concentration of vanadium (IV) ion could be completely decolourized to the pale yellow colour characteristic of a vanadate solution. That the vanadate ion is produced during the electrolysis was confirmed by its reaction with an alkaline sulphide solution. The reaction produces a suspension of elemental sulphur in a blue (vanadium (IV) ion) solution.

The electrochemical irreversibility of the vanadium (IV/V) redox couple was demonstrated in a cell which allows the simultaneous oxidation and reduction of a well stirred solution. The configuration of this cell is depicted below:

$$\mathrm{Pt} \mid V^{4+},\ V^{5+},\ \text{c.c. buffer pH 9},\ H^{+},\ H_2 \mid \mathrm{Pt}$$

The vanadium (IV) solutions electrolysed in this manner were readily decolourized. The net synthesis of vanadate ion under such conditions reveals an interesting tendency of vanadium (V) to resist reduction at platinum cathodes. This is a significant observation as it may be an expoitable phenomenon in the design of the electrolysis cells.

The discharge of vanadium (IV) ion was accompanied by the evolution of a colourless gas at the anode. The gas evolution was barely noticeable at low applied currents, but was especially pronounced at higher applied currents. It was assumed that the gas was oxygen, but a glowing splint failed to ignite (and was often immediately extinguished) when thrust into a sample of this gas. The gas was probably carbon dioxide.

There was a substantial decrease in buffer pH observed during vanadium (IV) electro-oxidation. The acidification is consistent with the redox behaviour of the couple as illustrated in equation 1.32.

$$2VO^{2+} + 4H_2O = 2VO_3^{-} + 8H^{+} + 2e^{-} \qquad (1.32)$$

It must be emphasized that this acidification effect originates in the vicinity of the anode surface. If this gives rise to a strong localization of acid there may be carbon dioxide liberated near the anode. This would be consistent with the negative oxygen test and would provide an argument to question gas evolution at the anode as an indication of oxygen formation and a loss of anode current efficiency.

The acidification may also be involved in the formation of yellow-grey deposits which were sometimes observed on the platinum anodes. These deposits were observed with high vanadium (IV) ion concentrations, high applied currents, and low citrate concentrations and were easily rinsed off the anodes. The deposits may be a vanadium (IV) salt, described by Britton and Welford [12], which was observed in the absence of citrate and in solutions of neutral pH. The deposition of this salt at the anode would be consistent with a solution envelope of neutral or acidic pH surrounding the anode.

The product of the cathodic reaction, in either cell configuration, was a colourless gas. The platinum cathodes remained clean and bright throughout an electrolysis run.

4.2 Pilot Plant

4.2.1 Introduction

The investigations undertaken with the pilot plant were concerned with:

i) accumulating data from Stretford and the electrolytic processes as the basis for qualitative comparisons between the two processes;

ii) verifying that a sustained vanadium mediated electrolysis of hydrogen sulphide was possible;

iii) detecting sulphate as a byproduct in a sustained electrolysis.

A description of the changes of liquor colour in Stretford and modified process runs is presented in Section 4.2.2 and Section 4.2.5.

The cell configuration employed in the modified pilot plant is summarized below:

$$\mathrm{Pt} \mid V^{4+}, V^{5+}, \text{ADA-free process liquor pH} = 9, H^{+}, H_2 \mid \mathrm{Pt}$$

The lack of a cell divider reflects the decision to take advantage of the irreversibility of the vanadium (IV/V) redox couple.

4.2.2 Normal Operations

The changes of liquor colour and elemental sulphur quality in the Stretford process, during startup and continuous operation, have been characterized by Pitts [6]. Prior to startup, the light orange ADA colour is observed in the liquor. The orange colour of the liquor leaving the absorber in the first reductive cycle is observed to darken, gradually becoming reddish brown after the first day of operation. Initially the oxidized liquor leaving the absorber is light orange, but this darkens to a blood red colour within 24 hours. The blood red colour has been attributed to the presence of ADA and, to a lesser extent, the presence of polysulphides in solution.

The product sulphur appears as suspended solids in the liquor and in the froth. In time, the suspended sulphur particles darken in colour, increase in size, and accumulate throughout the pilot plant tubing.

was discontinued to prevent corrosion of the anodes.

4.2.4 Controlled Potential

The re-improvisation of the open cell design in the pilot plant and the use of the twinned stations of a controlled potential power source made sustained electrolysis of the process possible. The controlled potential source made it easier to balance the current flow to the hydrogen sulphide feed. The controlled anode potentials were selected to maintain a faint blue-grey colour in the polisher electrolysis cell. Potentials were adjusted 10 to 12 times during the first 12 hours of operation and approximately every 12 hours thereafter.

The vanadium (IV) ion was continuously electro-oxidized in the recirculated liquor in the pilot plant for 7 days. The liquor pH was maintained at 9.00 +/- 0.01 with few interuptions for the duration of the run. The colour changes in the liquor were the same as described in Section 4.2.5 but with one exception. By the beginning of the sixth day, the reduced liquor had acquired a black/green colouration. The addition of trisodium citrate dihydrate to the froth tanks lead to a re-establishment of the blue colour.

The elemental sulphur formed during controlled potential electrolysis in the pilot plant did not froth effectively. It could be seen as a thin coating on the anodes and a thin film at the air-solution interfaces, but the majority circulated with the process liquor. (As the sulphur accumulated in the pilot plant, it tended to do so at low turbulence locations throughout.) At the end of the sixth day, the accumulation of elemental sulphur in the plant was so great that it lead to a pump failure. This failure caused an extreme hydrogen sulphide over-loading in the absorber (see Section 4.2.5) and excessive electrolysis of the liquor in the cells. After the liquor circulation was resumed and the liquor entirely electro-oxidized, the process operated as before with no visible side effects.

The anode potential selected during start-up and applied during the electrolysis was approximately 1.2 volts. The current efficiency calculated in the first hours of operation at this potential was found to be in excess of 120 %. This was calculated from the exit gas flow rate from the absorber and the cell current.

The measurement of dissolved oxygen in the electrolytically re-oxidized liquor entering the absorber showed that oxygen was present at 60 percent saturation for air above carbonate/ bicarbonate buffer, pH 9. The qualitative analysis for sulphate, by paper chromatography, showed that sulphate was not formed in detectable amounts (less than 1 g/litre) after 12 hours. The concentration of sulphate in the liquor after 7 days was of the order of 1 g/litre.

On Dr. Hileman's recomendation, an attempt was made to re-oxidize vanadium (IV) ion with oxygen introduced through the absorber and the oxidizer tanks in the absence of ADA and without any electrolytic current. This made the operation of the process impossible, even at a reduced sulphide loading; the rate of the air re-oxidation reactions were extremely slow. This confirms that vanadium (IV) is being electro-oxidized and not chemically oxidized by electrolytically generated oxygen.

4.2.5 Liquor Colour Changes in Modified Operations

The liquor prepared for use in the modified process is the faint yellow characteristic of the vanadate ion. On startup, the liquor contacting hydrogen sulphide undergoes a progression of colour changes. Within 5 minutes of initial contact, the liquor in the absorber turns deep yellow. At 7 minutes the yellow liquor entering the plug-flow section of the absorber undergoes a sudden transition to a cloudy grey colour, characterized by a distinct boundry which sweeps yellow liquor through the remainder of the absorber. At 12 to 15 minutes, the cloudy grey liquor entering the plug-flow section of the absorber turns blue two minutes beyond the entrance to the plug-flow section. A diffuse cloudy grey/blue boundry sweeps the cloudy-grey liquor out of the absorber. Thereafter liquor on its first reductive cycle contacts hydrogen sulphide, turns cloudy-grey, enters and proceeds through the plug-flow section of the absorber where it turns blue two minutes into the plug flow section.

The blue reduced liquor leaving the absorber is electro-oxidized to the pale yellow colour characteristic of vanadate ion. This re-oxidized liquor, containing sulphur as suspended solids, turns the absorber a uniform blue colour on the second and subsequent cycles. The incomplete re-oxidation of the liquor between two and seven hours into a run produced a green liquor with no suspended sulphur particles. The green liquor later changed colour to cloudy blue and was accompanied by a sudden formation of sulphur.

On one occasion a small quantity of the ADA-free liquor assumed a blood red colour. This occured as the result of a pump failure during the 7 day controlled potential pilot plant run. The small quantity of liquor in question was confined to the absorber where it was saturated in the hydrogen sulphide/nitrogen gas stream for 4 to 6 hours. When the pump failure was discovered, nitrogen was substituted for the hydrogen sulphide feed to the absorber while the liquor recirculation was resumed. This distributed the red liquor throughout the pilot plant as a uniform purple colour. This purple liquor was electro-oxidized to a pale yellow liquor which was capable of continued use in the pilot plant.

4.2.6 Discussion

The oxidation of sulphide to elemental sulphur with the constant current and with the controlled potential electro-oxidation of vanadium (IV) ion, in a recirculated ADA-free liquor, has been confirmed in the pilot plant. The process was operated at pH 9 and pH 10.14, but there was some difficulty in operating at the extreme pH of 6.9 in the absence of carbonate. The absence of a cell divider in the well stirred electrolysis cell(s) confirms earlier observations of the irreversibility of the vanadium (IV/V) redox couple.

Certain features of the pilot plant runs can be explained. The deep yellow colour in the absorber at the onset of sulphide loading could signal the formation of polysulphide in the solution, however it could also indicate the reaction between vanadate ion and evolved base. This can be illustrated independently by adding base to a buffered vanadate solution. The pale yellow colour deepens in transition to a brown colour.

The set-point pH levels in the pilot plant runs were measured and reported with respect to the pH in the first froth tank. This means that only the exit pH from the absorber was controlled to 9 +/- 0.01 pH units. The pH in the electrolysis cells was 0.5 to 1 pH unit lower since considerable acid is released there.

The quality of the elemental sulphur produced in the electrolytic process was noticeably different from that produced in a normal Stretford operation. It was more dense, appeared almost crystalline, and settled readily. This may be due, in part, to the absence of a frothing agent in the new process. This suggests an opportunity to remove sulphur from the liquor by sedimentation or centrifugation as alternatives to froth flotation.

The controlled potential levels chosen for the electrolysis in Section 4.2.3 were selected iteratively on the basis of the oxidized liquor colour in the pilot plant. Because the same electrodes were used in the constant current runs, the constant potential approach differed only in preventing some excess oxidation of the liquor. No other attempt was made to optimize the electrolysis in the pilot plant.

The applied anode potential of 1.2 volts was required to supply the requisite current to the pilot plant. This potential is in considerable excess of 0.45 volts which was indicated as the oxidation potential for vanadium (IV) in preliminary voltametric investigations. For this reason, the pilot plant potentials were considered to be an unreliable measure of the vanadium (IV) oxidation potential. The high potential was thought to be necessary to overcome electrode polarization effects. The high value increases the probability of byproduct formation in the pilot plant.

The detection of oxygen at 60 percent of saturation in the electrolytically regenerated liquor is suprising since the nitrogen flow through the froth tanks and the evolved hydrogen in the electrolyser should provide an efficient blanket of protection from aerial oxygen. Furthermore the sour gas flow through the absorber should prevent any accumulation and recirculation of oxygen in the liquor. The presence of oxygen in the oxidized liquor then suggests that it may generated at the anode. Since oxygen evolution represents lost current efficiency, the extent of its formation must be examined.

The concentration of oxygen in water is approximately 0.012 M. At 60 percent saturation this corresponds to 0.0077 M or 0.0289 N (where n is taken as 4). Given an applied electrolytic current of 0.5 amps and a liquor flow rate of 10 ml/min, the number of electrochemical equivalents available per litre of liquor is:

$$\frac{(0.5 \text{ coulomb sec}^{-1})\ (60 \text{ sec min}^{-1})\ (1000 \text{ ml l}^{-1})}{(96487 \text{ coulomb equiv}^{-1})\ (10 \text{ ml min}^{-1})}$$

$$= 0.0311 \text{ equivalents l}^{-1}$$

The oxygen is present in an amount which is approximately 93 percent of the available electrochemical equivalents. This is clearly impossible since hydrogen sulphide was electrolysed with a high current efficiency in the pilot plant. The presence of oxygen in the pilot plant must be attributed aerial oxygen and points to the need to isolate the process solutions from air during dissolved oxygen measurements.

The initial high current efficiency of the process may be explained by a small fraction of sulphide ion not reacting in the process liquor. This may involve an incomplete vanadate-sulphide reaction, the formation of large chain polysulphides, or the adsorption of sulphide or polysulphide onto elemental sulphur particles. Alternatively, the dissolved aerial oxygen may give rise to direct sulphide oxidation.

There are two long term side reactions which became evident in the 7 day controlled potential run. The first of these is the 8 electron oxidation of sulphide ion to sulphate ion. This is likely to be a direct electrochemical process. The second side reaction is the depletion of citrate. This loss may arize from an adsorption onto elemental sulphur, a direct electrochemical process, or an indirect electrochemical process mediated by vanadium. The latter is more likely the case since Habayeb [17] has observed a reaction between vanadium (V) and citrate at pH less than 5. This would be in agreement with the previous suggestion that acid is generated and localized at the anode.

The rates of accumulation of sulphate and the depletion of citrate in the liquor should be compared in terms of current efficiency. The number of equivalents available from a current flow of 0.5 amps for 7 days is 3.13. The formation of 1 gram per litre sulphate ion, from sulphide ion with n equal to 8, in 1400 millilitres liquor may account for 0.079 equivalents or 2.5% of the applied current. The depleation of ca. 90% of the 0.034 M citrate ion, assuming a two electron oxidation, may account for 0.086 equivalents or 2.7% of the applied current. The formation of sulphate and the disappearance of citrate at these rates is an inconvenience. The true current efficiency losses are probably lower by a factor of ten.

4.3 Current Efficiency Measurements

4.3.1 Introduction

The successful operation of the modified process in the pilot plant was quickly overshadowed by the need to estimate the anodic current efficiencies for vanadium (IV) and the extent of electrolytic by-products formation. The anodic current efficiency for vanadium (IV) was expected to be affected by trace polysulphide and the lack of an anode-cathode divider. The extent of by-products formation is a complicated measurement since there are difficulties in measuring the expected low concentrations of sulphate, thiosulphate and oxygen in the process liquor and since sulphate and thiosulphate may be formed by sulphur disproportionation reactions. For these reasons the rates of by-products formation may be calculated from the lost current efficiency for vanadium (IV) oxidation and/or the oxidation of (poly)sulphide.

The current efficiencies were estimated directly using the coulometric [electron counting' method and the chemical analysis of the electroactive species. It was asssumed that the percentage of current flow not accounted for by the two electron oxidation of sulphide and the one electron oxidation of vanadium (IV) ion represented current flow to by-product formation. Current losses due to Ohmic resistance or 'open' cell inefficiencies were not considered. For the purposes of comparison, the anodic current efficiencies for sulphide oxidation and the cathodic current efficiencies for polysulphide and for vanadium (V) reduction were determined using suitable analytical techniques.

To infer a reasonably precise estimation of by-products formation during vanadium (IV) with trace polysulphide electro-oxidation, it is necessary to ensure electrode surface conditions which are representative of a functioning electrolytic cell. This is difficult because electrode surface conditions are expected to vary with the sulphide slippage into the electrolyser, and the rates of sulphur deposition and dissolution at the anode. Electrode surface conditions are expected to be further complicated by the pH changes associated with the anodic oxidation of vanadium (IV).

In an attempt to simulate reproducable electrode surface conditions, experiments were performed using the flow coulometry cell described in Appendix A2. A mathematical model was used to interpret the data generated from this apparatus. Where electrochemical reactions were expected to proceed with low efficiencies, batch electrolysis was employed. The current efficiencies for the batch reductions were determined from Faraday's law comparison of the chemical equivalents reacted with the total electrochemical equivalents passed. Admittedly this method is not as accurate as the evaluation of current efficiencies from the initial slope of the concentration vs it/nF curve. The limitations possed by the analytical sample size and the number of concentration measurements required influenced the selection.

Three assumptions are made in employing the flow coulometric method for the evaluation of current efficiencies. The first assumption is that sufficient time is allotted for the development of the steady state. Under steady state conditions the solution pH and electrode surface conditions are constant and assumed to permit the establishment of a constant and selective electrode potential under a constant applied current. Finally it is assumed that no sulphide could escape oxidation when vanadium (V) was present in the cell.

4.3.2 Coulometry Model Description

The mathematical equations used to interpret the changes in concentration of vanadium (IV) or sulphide ions during continuous solution inflow and outflow and electrochemical discharge are given below and derived in Appendix 2. They represent the concentration in the cell at time t, the steady state concentration (from which the current efficiency, E, was calculated), and the time to 95 % steady state concentrations.

$$C_t = C^o - iE/nFR + iE\,[\exp(-tR/V)]/nFR$$

$$C_{ss} = C^o - iE/nFR$$

$$t_{ss} = -(V/R)\ \ln(\ 5\% C_{ss} nFR/iE)$$

The flow rates, R, were selected using the second equation to give measurable concentration changes. The flow rates were used to calculate the times to 95 % steady state. These times were exceeded by 25 to 50 percent in every run. With 10 minutes of batch electrolysis in the cell prior to the flow, the starting concentrations could be altered by 0.004 N and the steady state approached sooner.

4.3.3 Results

4.3.3.1 Vanadium (IV) Oxidation

The oxidation of the vanadium (IV) ion was studied using the flow coulometry apparatus described in Section A2.2. The cathode was placed in the fritted compartment to permit a [closed' cell anodic oxidation. The pH of the vanadium (IV) solutions was adjusted to give cell effluent pH values of either 7.6 +- 0.1 or 8.7 +- 0.1. The concentrations of electrogenerated vanadium (V) were determined coulometrically or polarographically.

The electrolytic oxidation of vanadium (IV) ion proceeded with the noticable discharge of its characteristic blue colour and a substantial decrease in pH. For instance, a typical flow experiment had a solution pH which changed 1.2 pH units in a time interval of less than one hour (Table 4.3.1). The evolution of a colourless gas at the anode was barely observable in the pH 8.7 solutions, but was considerably more pronounced in the pH 7.6 solutions in which it was estimated at between 20 and 35 ml/hour.

The total vanadium (IV) concentration in the inflow for the results listed in Table 4.3.1 was determined to be 0.0295 M. This shows that 50 percent of the available vanadium (IV) ion is being oxidized. From this it is clear that there is an sufficient vanadium (IV) concentration present to consume the electrochemical input to the cell.

The anodic current efficiencies for vanadium (IV), calculated from the coulometric titration of vanadate, were found to lie in the range of 89 to 99 % (Table 4.3.2). The current efficiencies calculated from polarographic data varied from 98 to 127 percent. (These impossible

Table 4.3.1

The Variation of pH and Vanadium (V) Concentration in the Flow Cell.

Clock Time	pH	$[V^{5+}]$
12:45	8.8	
13:30	8.2	
13:10	7.9	
13:30	7.6	
14:00	7.6	14.3 mM
14:30	7.5	13.9
15:30	7.5	15.5
16:00	7.5	15.5

Table 4.3.2

Current Efficiencies for Vanadium (IV) Oxidation

Date	pH	Analytical Method	dC (moles)	R (ml/min)	Current Efficiency
June 15a	~9	C	.0113	7.2	65 #
15b	7.7	C	.0152	7.8	95.6
16a	7.5	C	.0155	7.6	95.0
16b	8.75	C	.0163	7.0	91.9
17a	7.4	C	.0167	7.1	95.3
17b	7.6	C	.0169	5.5	74.9 #
18a	8.7	C	.0157	7.1	89.6
18b	8.8	C	.0156	7.9	99.1
20	8.6	C	.0149	7.9	94.8
21	7.6	C	.0141	6.5	73.9 #
Nov 22	9.17	P			127
24	7.2	P			98 + 107
27b	9.75	P			110.5

difficulties in maintaining constant flow
C Coulometric analysis of vanadium (V)
P Polarographic analysis of vanadium (V)

current efficiencies are since known to be the result of a high polarographic standard which gave vanadium (V) concentrations 15 to 18 % too high). The current efficiencies were not dependent upon the number of platinum basket anodes (electrode area), the variation in electrode preparation procedure, or the steady state solution pH.

4.3.3.2 Vanadium (V) Reduction

The batch reduction of vanadium (V) ion was investigated with the anode isolated in the fritted comparment. The cathodic current efficiencies were calculated from decreases in vanadate concentration after the electro-reduction. The analysis for vanadium (V) was accomplished by coulometric titration. The results of the vanadium (V) reductions are shown in Table 4.3.3.

Two batch reductions of vanadium (V) solutions with pH values of pH 8.8 and 8.9 proceeded with nearly identical current efficiencies of 12.8 and 12.3 percent. There was considerable gas evolution observed at the cathode during these reductions.

Two batch reductions of vanadate at lower pH were also performed. The first of these, the pH = 5.25 run, was performed with the absence of carbonate and twice the normal citrate concentration. This solution was a dark orange colour characteristic of pyrovandate. Upon reduction this solution assumed an olive-brown/black colour which indicates vanadyl vanadate formation. The current efficiency for this reduction was calculated to be 92.3 percent. The second low pH reduction was performed in a carbonate citrate buffer acidified to pH 5.4 with concentrated sulphuric acid. This solution retained the pale yellow colouration

Table 4.3.3

Current Efficiencies for Batch Vanadium (V) Reduction

Date	pH	Analytical Method	Electrolysis Duration	Efficiency
June 23	8.9	C	3600 sec	12.8 %
28a	8.8	C	3600	12.3
28b	5.25	C	1555.5	92.3
29	5.4	C	1555	70.7

characteristic of metavanadate. Upon reduction this solution changed from pale yellow to dark green with a calculated current efficiency of 70.7 percent.

It should be noted that since the current efficiency for vanadate reduction is determined by the disappearance of vanadate in the electrolytic cell, the calculation is sensitive to losses of vanadium (V) through the deposition of vanadyl vanadate on the anode (not seen) or in solution. The former would cause an over estimation of the current efficiency, since vanadate is not available for analysis. Vanadyl vanadates suspended in solution are presumably decomposed in the hydrochloric acid used in the coulometric titration and are not expected to affect the calculated current efficiencies.

4.3.3.3 Sulphide Oxidation

Sulphide solutions of 0.017 to 0.037 M were electro-oxidized in the flow coulometry apparatus to consume 0.005 to 0.013 M sulphide. The current efficiencies were calculated from the feed and exit sulphide concentrations which were determined polarographically (Table 4.3.4). Thiosulphate was not detected in the electro-oxidized solutions. At the onset of current flow, a patchy white coating was observed to form on the anodes. In time the sulphide solution acquired the yellow colour characteristic of polysulphide. There was some gas evolution from the anodes, but this was localized in the regions closest to the fritted cathode compartment. Elemental sulphur was observed to accumulate on the liquor surface, the electrodes, and also on the surface of the gas bubbles forming at the anode.

Table 4.3.4

The anodic oxidation of sulphide and polysulphide

Date	Species	pH	Feed sulphide	delta C	R (ml/min)	Efficiency
Dec 5	S^{2-}	8.7	.0376	.0089	2.9	41.7%
7a		9.7	.0253	.0131	2.35	49.7
9		9.9	.0199	.0067	3.6	38.7
12a	S_x^{2-}	9.95	.0172	.0064	4.0	41
12b	S^{2-} +.01 M v(IV)	9.18	.0173	.0051	3.4	27.9

The electro-oxidation of polysulphide ion proceeds with the formation of a white coating and some localized gas evolution. With time there is substantial sulphur buildup on the anodes in the region previously defined by the localized gas evolution.

The localization of the electrochemical reactions on the anode suggests poor utilization of electrode surface areas. The addition of 0.25 M potassium nitrate to the sulphide solutions used in the current efficiency determinations increased the solution conductivities and improved electrode area utilization.

The current efficiencies of sulphide oxidation were found to range from 38 to 49 percent. This implies considerably lower current efficiencies than reported in the literature by Allen and Hickling. The disparity must be attributed to the different extents of elemental sulphur deposition and dissolution at the anode caused by the lower sulphide concentrations employed in these experiments. The oxidation of polysulphide at the electrodes proceeds with an enhanced deposition of sulphur.

4.3.3.4 Polysulphide Reduction

A single batch reduction of polysulphide ion to sulphide and smaller chain polysulphides was performed with a solution pH of 9.7. The total polysulphide content in the batch reactor was observed to increase from 0.016 M to 0.026 M (0.0048 moles to 0.0078 moles) with the passage of 0.0056 moles of electrons. The corresponding cathodic current efficiency of 54 percent is consistent with the current efficiencies for sulphur reduction, at graphite, reported by Tomilov et al. in Section 2.3.3.

4.3.3.5 Sulphide and Vanadium (IV) Oxidation

The electro-oxidation of sulphide (polysulphide) and vanadium (IV) ion was investigated in the flowing coulometry apparatus at different pH, sulphide concentrations and cell configurations. Solutions were electro-oxidized (with one exception) to consume all sulphide present and to generate a measureable concentration of vanadate. Potassium nitrate was not added to improve electrode surface utilization, as in Section 4.3.5, since vanadium (IV) has been reported to be oxidized by nitrate [9].

The electro-oxidation of vanadium (IV) and sulphide was accompanied by the fading of the characteristic blue colour of vanadium (IV) ion. The blue colour was never totally discharged. Elemental sulphur was observed to form and to accumulate in the cell, tinting the blue vanadium (IV) solution with finely divided pale yellow particles. Gas evolution was evident, but not pronounced at the anode. Thiosulphate was not detected in the solutions. Considerable gas evolution was observed at the cathode during each electrolysis. The gas evolution in the 'open' cell design averaged 74 ml/hour over 2.5 hours.

In the first electro-oxidation experiment, the high concentration of sulphide ion made impossible to completely discharge the sulphide and allow vanadium (V) to accumulate in the solution. In this experiment, a solution of 0.0173 M sulphide and 0.01 M vanadium (IV) ion was electro-oxidized to consume 0.0051 M sulphide. Under these conditions, there is sufficient vanadium (IV) ion available throughout the electro-oxidation to function as an electrocatalyst. Apparently vanadium (IV) ion does not increase the efficiency of sulphide electro-oxidation at the platinum electrode.

The current efficiencies for the oxidation of sulphide to elemental sulphur, under conditions where vanadate was formed in excess, were found vary between 63 and 78 percent (Table 4.3.5). The last four runs (March 1a, 1b, 2, 3) employed the open cell design in the flowing coulometry apparatus.

The electro-oxidation performed with an exit pH of 9.53, is thought to be subject to some error. This run was distinguished by the presence of a blue-black exit solution indicative of some vanadyl vanadate formation. The polarographic feed sulphide analysis was complicated in this solution but was accomplished with the use of cyanide ion instead of thiosulphate ion.

4.3.4 Discussion

The electro-oxidation of vanadium (IV) ions in 0.24 M carbonate buffer and 0.034 M citrate proceeded with greater than 90 percent current efficiency. The current efficiencies were independent of solution pH and independent of the rate of gas evolution at the anode. This last point is a strong indication that the gas is carbon dioxide. This conclusion can be substantiated by a comparison of the rate of gas formation with the electrochemical input to the cell. Neglecting the vapour pressure of water, the number of moles of gas given by the ideal gas law for 30 ml/hour is 0.001. The number of electrochemical equivalents supplied from 0.2 amps for 1 hour is 0.00746 equivalents. If the gas is oxygen the rate of gas formation in the cell corresponds to 0.004 equivalents. This gives an apparent anodic current efficiency for

Table 4.3.5

The anodic current efficiencies for vanadium (IV)
and trace sulphide

Date		pH	Input Sulphide	Exit v(V)	Flow Rate	Current Efficiency	
						total	v(V) alone
Feb	28	8.2	.0026 M	.0104 M	5.9	74.2	49.3
	29a	8.6	.0015	.0105	6.2	66.8	52
	29b	9.53	.0014	.0103	6.0	63.2	49.7
Mar	1a	7.71	.0017	.0124	5.13	65.3	51.1
	1b	9.16	.0029	.0108	5.75	76.7	49.9
	2	9.09	.0031	.0101	6.0	78.6	48.7
	3	8.8	.0029	.0091	5.5	66.1	40.2

oxygen formation of 54 percent. The gas can not be pure oxygen.

If the gas is carbon dioxide, it must be evolved through the release of H^+ at the anode according to equations 1.1 and 1.32. Assuming 100 percent current efficiency of vanadium (IV) to Vanadium (V), the number of equivalents of H^+ released in one hour is 0.0298. Therefore as little as 0.002/0.0298 = 7 percent of the evolved acid is consumed in the carbon dioxide evolution reaction.

$$HCO_3^- + H^+ = H_2CO_3 = H_2O + CO_2 \qquad (1.1)$$

$$2VO^{2+} + 4H_2O = 2VO_3^- + 8H^+ + 2e^- \qquad (1.32)$$

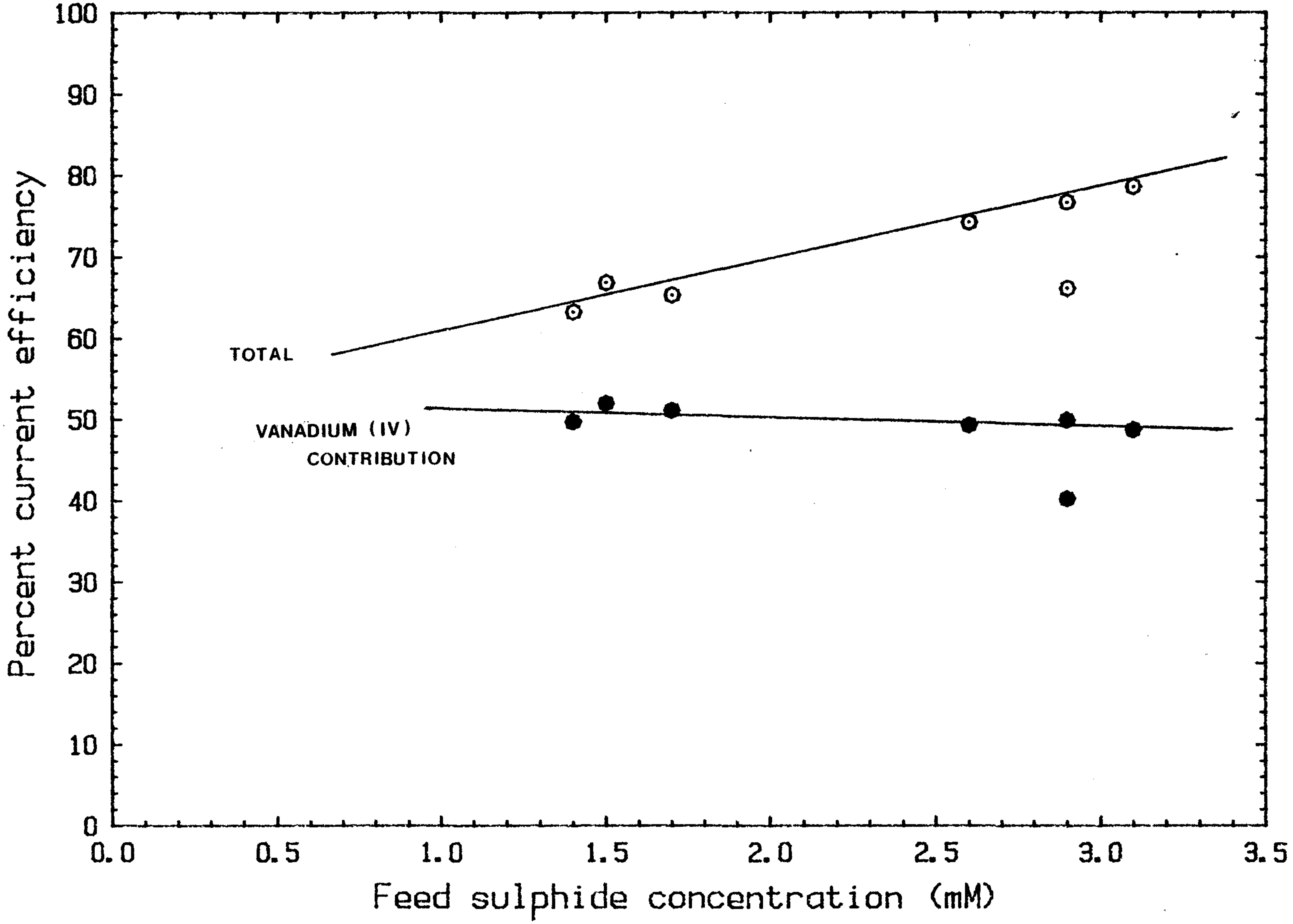
The low current efficiencies of vanadate reduction near pH 9 are in agreement with previous observations of the irreversibility of the vanadium (IV/V) couple at this pH. The enhanced reducibility at pH 5.25 is the result of speciation changes. (The orange pyrovanadate ion is apparently easier to reduce.) The increase in reducibility is in agreement with the ease of reduction of vanadium (V) in acidic solutions. A speciation change may be infered from the inadequecy of increased citrate concentrations to prevent the formation of vanadyl vanadates at pH 5.25. The slightly lower cathodic current efficiency, the different solution colours, and the less evident formation of vanadyl vanadates observed with the acidified buffer, pH 5.4, may be attributed to the presence of saturated carbonic acid in the solution. The enhanced current efficiency for vanadate reduction with decreasing pH is significant since acidification effects are suspected at the anode surface.

The anodic current efficiencies for sulphide and polysulphide oxidation are approximately 40 percent. This factor, and the poor electrode area utilization, reveals that the applied currents demanded anode potentials which allowed oxygen (and sulphate ion ?) formation. Since the presence of 10 mM vanadium (IV) in solution did not improve the current efficiency, the vanadium (IV/V) redox couple cannot function as an electrocatalyst.

The electro-oxidation of vanadium (IV) in the presence of 1 to 3 mM sulphide proceded with current efficiencies of 65 to 75 percent. The current efficiencies were not affected by an 'open' or 'closed' cell design. The predominant anode products were elemental sulphur and vanadium (V). No thiosulphate ion was detectable. These results reflect the behaviour of partially passivated platinum electrodes at which the applied current demanded some byproduct formation. It is clear that vanadium (IV) oxidation still proceeds fairly efficiently under these conditions however. The 'open' cell design reflects the lack of vanadium (V) and elemental sulphur reducibility at the cathode and the lack of oxidation of evolved hydrogen at the anode.

The extent and reproducibiliy of anode passivation is thought to be constant due to the steady state assumption. One test of the steady state assumption would be a plot current efficiency vs sulphide concentration as shown in Figure 4.3.1. The apparent linear increase in the total current efficiency with increasing sulphide concentration suggests that increasing sulphide concentrations decreases anode passivation. Actually the outlying current efficiency value at high sulphide concentrations suggest a different interpretation. This value was obtained by extending the duration of the flow experiment from 3 to 7 hours. The

Figure 4.3.1 Percent current efficiency versus Feed sulphide concentration.



decreased current efficiency measured in this run may indicate an swing in the adsorption/ desorption equilibrium for sulphide on elemental sulphur. This suggests an equilibration process which extends beyond the time-frame of the flow experiment.

4.4 Voltametry

4.4.1 Introduction

Prior to electrolysis in the pilot plant (Section 4.2), a preliminary voltametric survey of the electrochemistry of vanadate, vanadium (IV), sulphide, and polysulphide ions in carbonate citrate buffers was conducted. The electrochemistry was investigated using Carbon Paste (CPE) and Rotating Platinum Wire Electrodes (RPWE). The survey showed a well defined wave for vanadium (IV) ion which was anodically shifted but otherwise unaffected by the presence of vanadium (V). The voltametric response of sulphide ion at carbon paste was a double wave, whereas that for polysulphide appeared as a single wave similar to the second of the two sulphide waves.

The voltametric investigations undertaken after the current efficiency study were directed towards:

(i) reproducing earlier observations;

(ii) investigating the linearity of vanadium (IV) at the RPW electrode;

(iii) investigating the influence of carbonate and citrate concentrations and pH on the electrochemistry of vanadium (IV) ion;

(iv) investigating the influence of xanthate anion on the sulphide and polysulphide suppresion of the vanadium (IV) wave.

The redox potentials corresponding to the electroactive species of interest were determined from the voltammograms and are listed in Table 4.4.1.

4.4.2 Results

4.4.2.1 Vanadium (IV/V) Voltametry

The anodic current-potential curves for vanadium (IV) ion were studied in the concentration range of 0 to 25 mM. The voltametric wave shape was dependent on the total carbonate concentration, the vanadium (IV) concentration, and the solution pH. The vanadate ion was not reduced at either electrode in the potential range of 0 to 1.0 volts (Ag/AgCl).

The voltametric response of vanadium (IV) in an ADA-free Stretford-like liquor was ill defined. The anodic current increased linearly with applied potential with no obvious development of a mass transport polarization plateau (Figure 4.4.1). As the buffer concentration was increased the anodic current flow in the voltametric waves increased substantially and the polarization effects became evident. This is illustrated in Figure 4.4.2 or by comparison of Figures 4.4.3 to 4.4.5. The effect of increasing the vanadium (IV) concentration was to anodically shift the voltametric halfwave potential. This is seen most clearly in Figure 4.4.5. The halfwave potential of 0.375 volts for 5 mM vanadium (IV) shifts to 0.405 volts for 10 mM vanadium (IV), 0.43 for 15 mM, and 0.445 for 25 mM vanadium (IV) in 1.2 M carbonate buffer, pH 9.

At carbonate concentrations in excess of 0.4 M, the vanadium (IV) wave is well developed at either electrode, but the plateau current at

Table 4.4.1

Half-wave Potentials at Carbon Paste and Rotating Platinum Electrodes

Species	E(1/2)	comments
		<u>Carbon Paste</u>
V(IV)	0.6	0.04 M vanadyl sulphate, 1.2 M carbonate buffer, 0.04 M citrate, pH 8.9
S^{2-}	0.32, 0.95	0.01 M sulphide, 1.2 M CO_3^{2-} pH 9. Waves decrease and shift anodically with 15 time. (Electrode passivation).
S_x^{2-}	0.32, 0.95	0.01 M polysulphide. Electrode quickly passivated.
		<u>Rotating Platinum Wire electrode</u>
V(IV)		0.01 M V^{4+}, 0.01 M V^{5+} 1.2 M carbonate, pH 9, and
	0.4	0.02 M citrate
	0.34	0.025 M citrate.
S_x^{2-}		Rapidly passivated.
S_x^{2-}+ V(IV)	(0.35) (0.75) (0.5)	0.01 M V^{4+}, 0.01 M V^{5+} 1.2 M carbonate, pH 9, 0.045 M citrate, and 0.00025 M polysulphide (5 minute intervals).

Carbon Paste electrode is not constant, and dips with increasing potential (Figure 4.4.6).

The effects of vanadium (IV), total carbonate concentrations, and pH on the variation of current flow and voltametric wave shape, with electrode potential were investigated using a 2^3 factorial design. The design settings are listed in Table 4.4.2. The citrate concentration was stoichiometrically equivalent to the total vanadium concentration while the vanadate concentration was kept constant. The voltammograms were recorded at the RPW electrode.

The observable for the experiment was the current flow at a given applied potential. The factorial was evaluated at each of 118 discrete electrode potentials in the range of 0 to 0.9 volts (Ag/AgCl). The average currents and the main, two factor, and three factor effects on current at each potential are plotted as a function of potential in Figures 4.4.7, 4.4.8, and 4.4.9. A measure of the random error, associated with the reproducibility of the current flow at each potential obtained from the four 'center point' curves, is included in the figures.

The effect of citrate ion on the wave shape is illustrated in Figure 4.4.10. Subsequent increases in the citrate concentration had little effect on the wave shape.

In some solutions, a small anodic wave was observed at -0.1 volts (Ag/AgCl, saturated KCl).

Table 4.4.2

Factorial Design Settings

	–	0	+
$[CO_3^{2-}]$	1.0	1.1	1.2 M
pH	8.8	9	9.2
$[V^{4+}]$	15	20	25 mM
$[V^{5+}]$	10	10	10 mM

Figure 4.4.1
Vanadium (IV) at RPWE in 0.24 M carbonate buffer pH 9

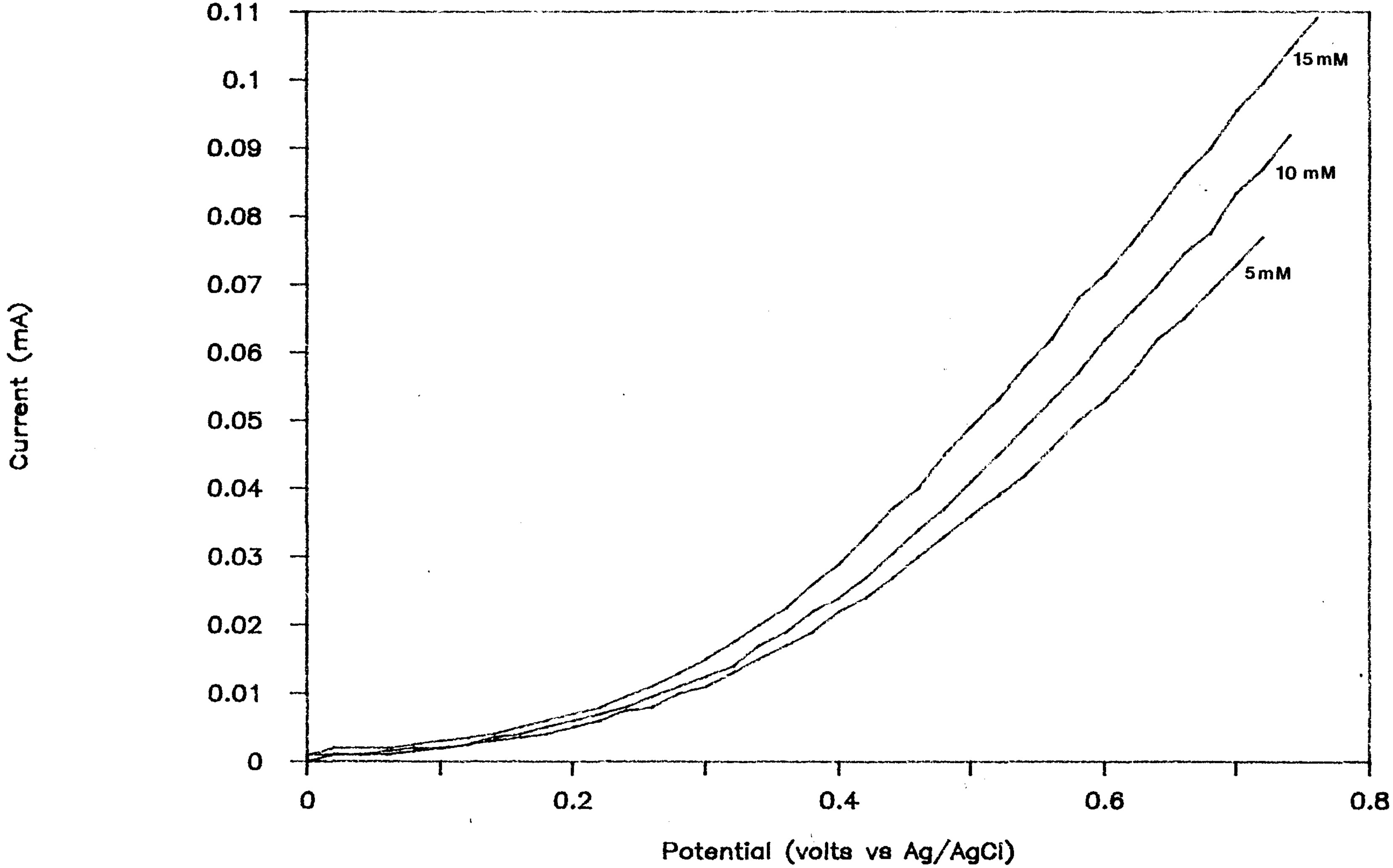


Figure 4.4.2

15 mM Vanadium (IV) at RPWE in carbonate buffers pH 9

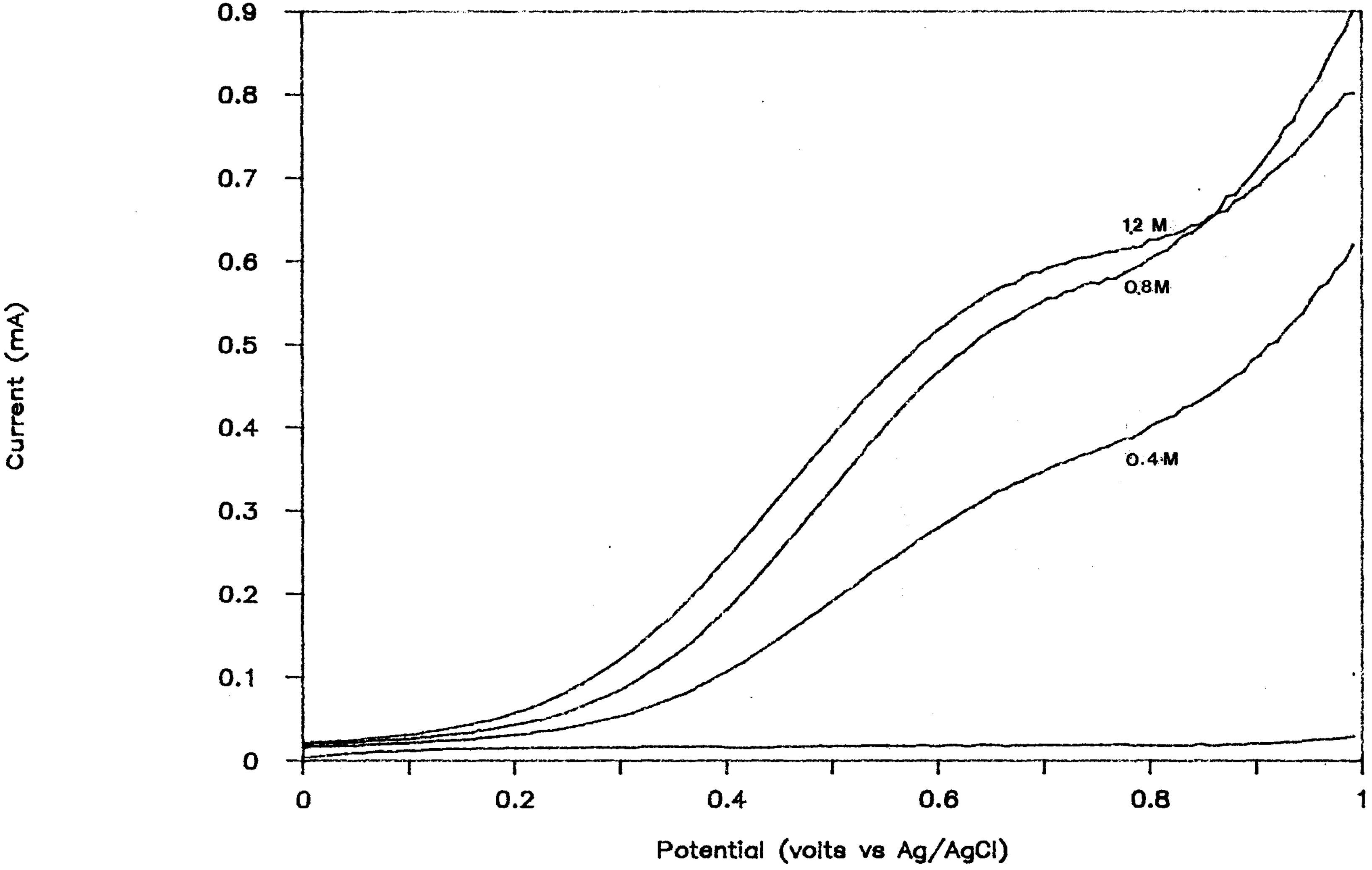


Figure 4.4.3

Vanadium (IV) at RPWE in 0.4 M carbonate buffer pH 9

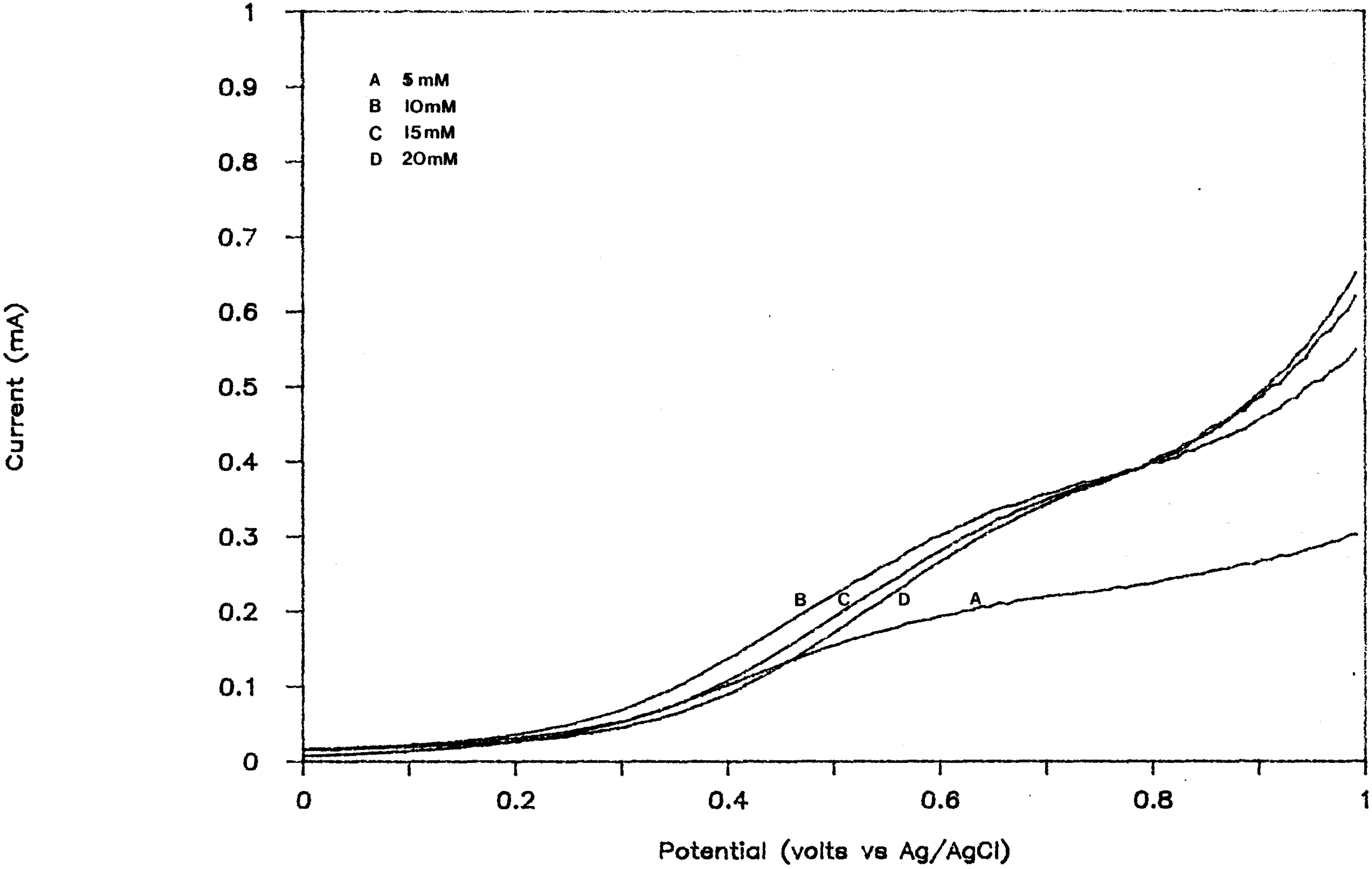


Figure 4.4.4

Vanadium (IV) at RPWE in 0.8 M carbonate buffer pH 9

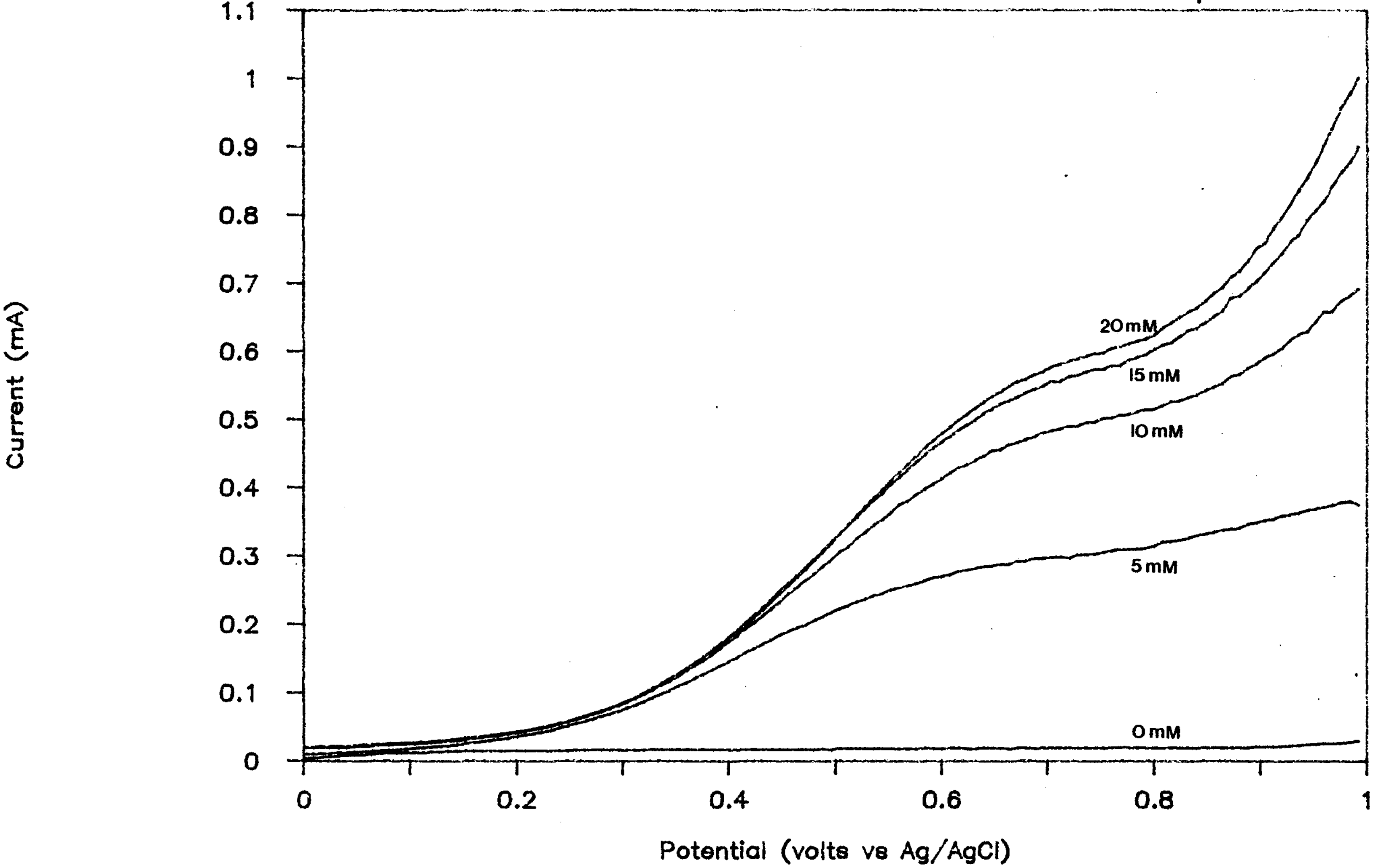


Figure 4.4.5

Vanadium (IV) at RPWE in 1.2 M carbonate buffer pH 9

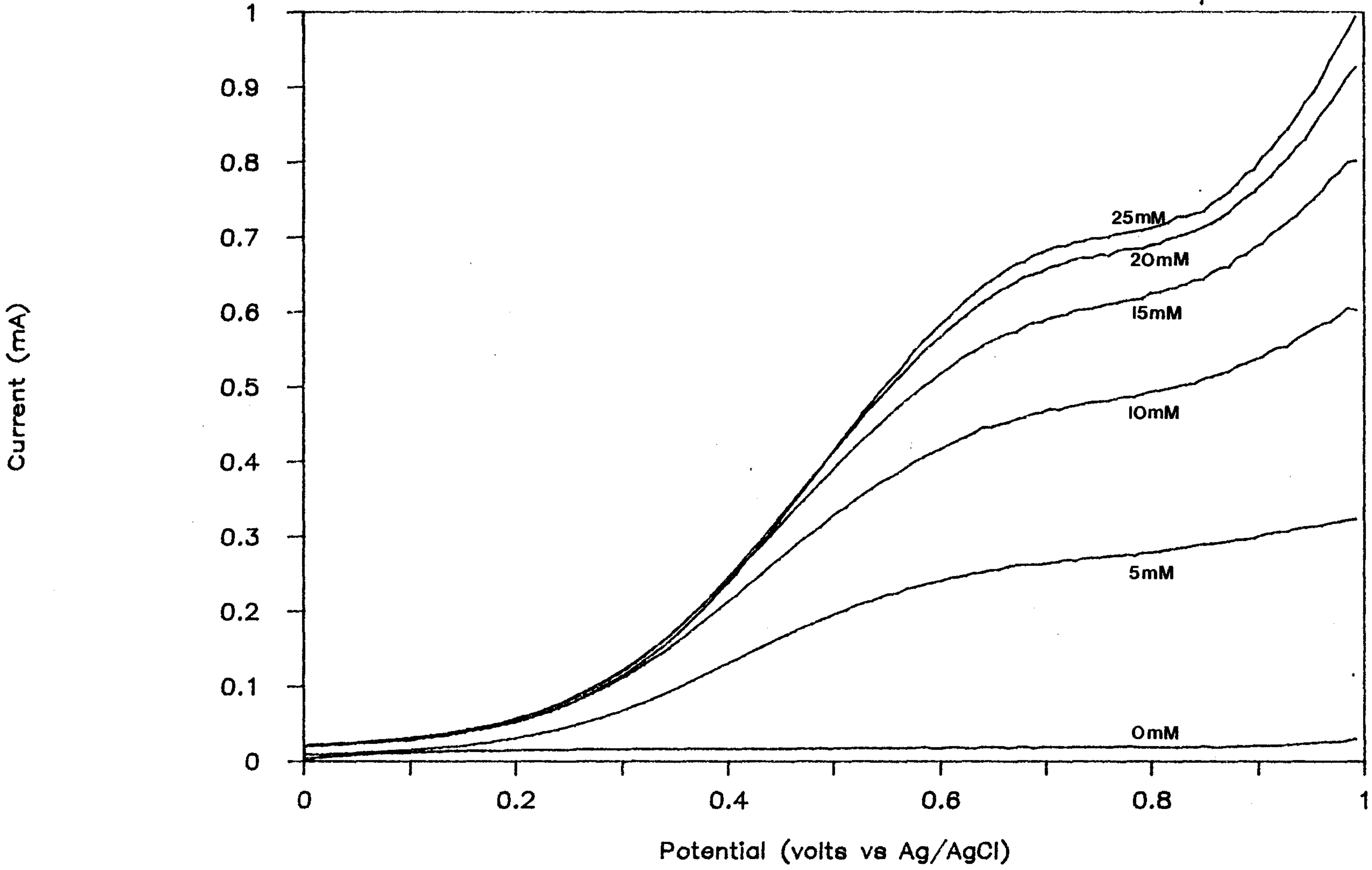


Figure 4.4.6

40 mM Vanadium (IV) at CP in 1.2 M carbonate buffer pH 9

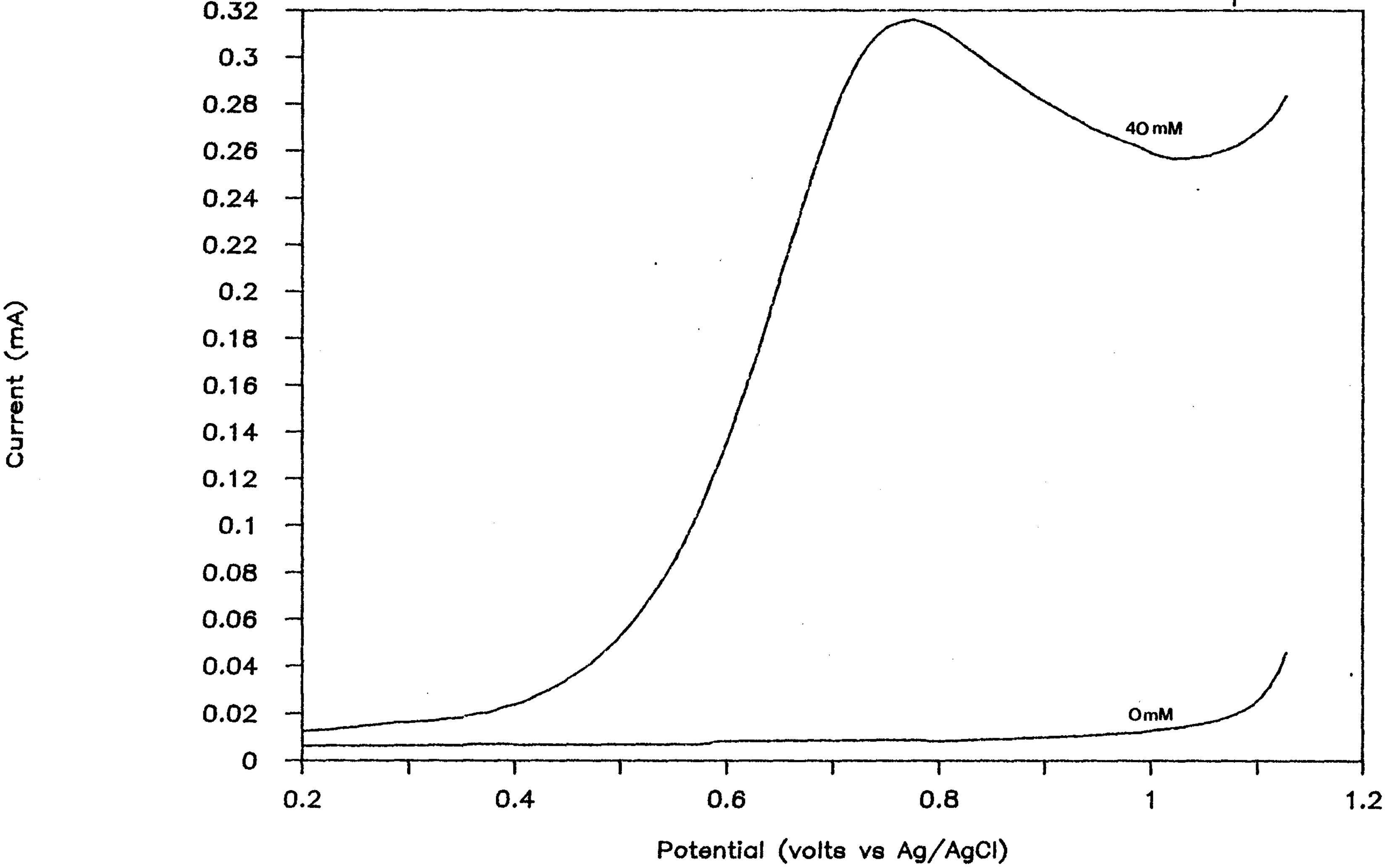


Figure 4.4.7

The Average and Main effects in the factorial design experiment

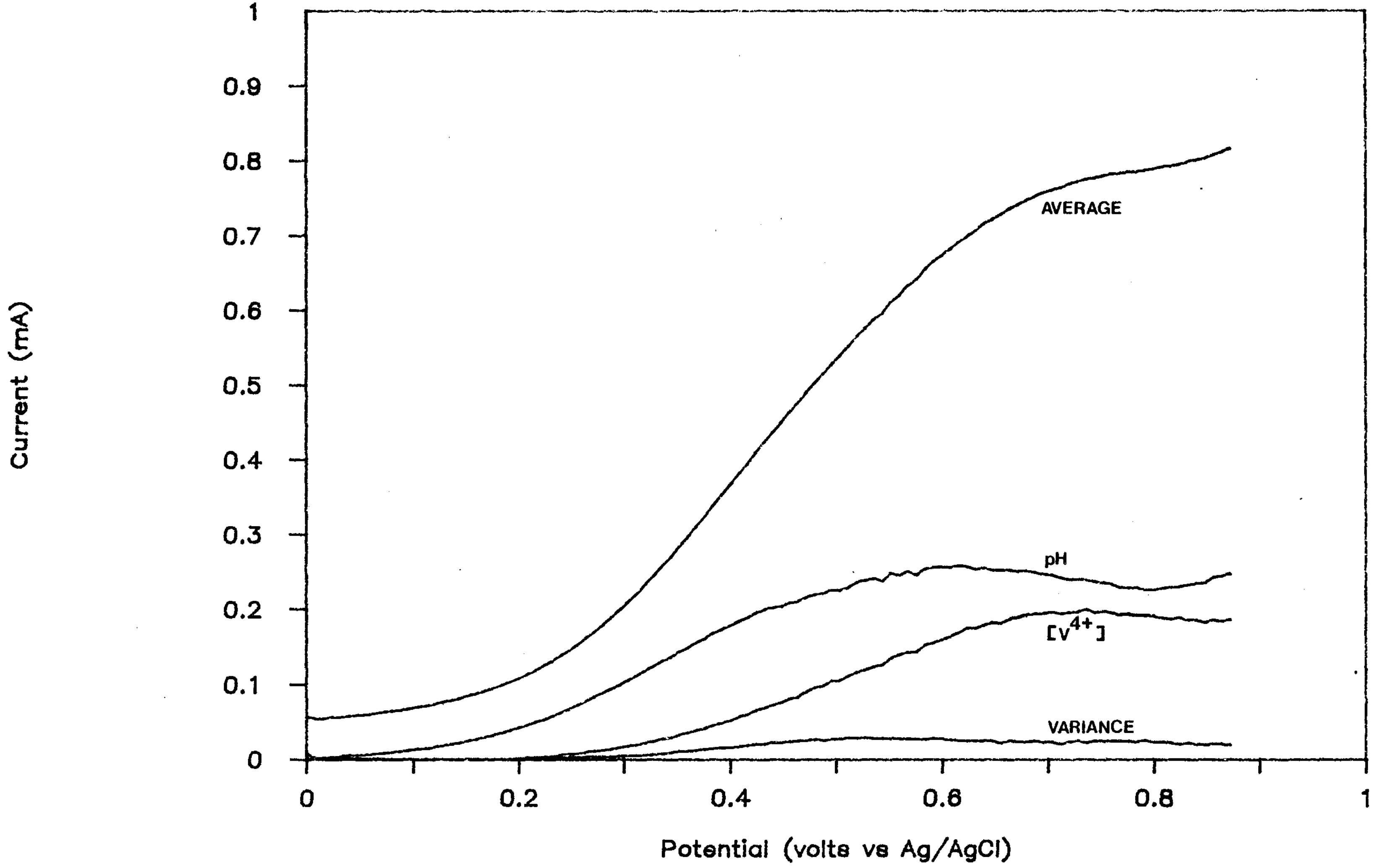


Figure 4.4.8

The Main and a Two-factor effect in the factorial design experiment

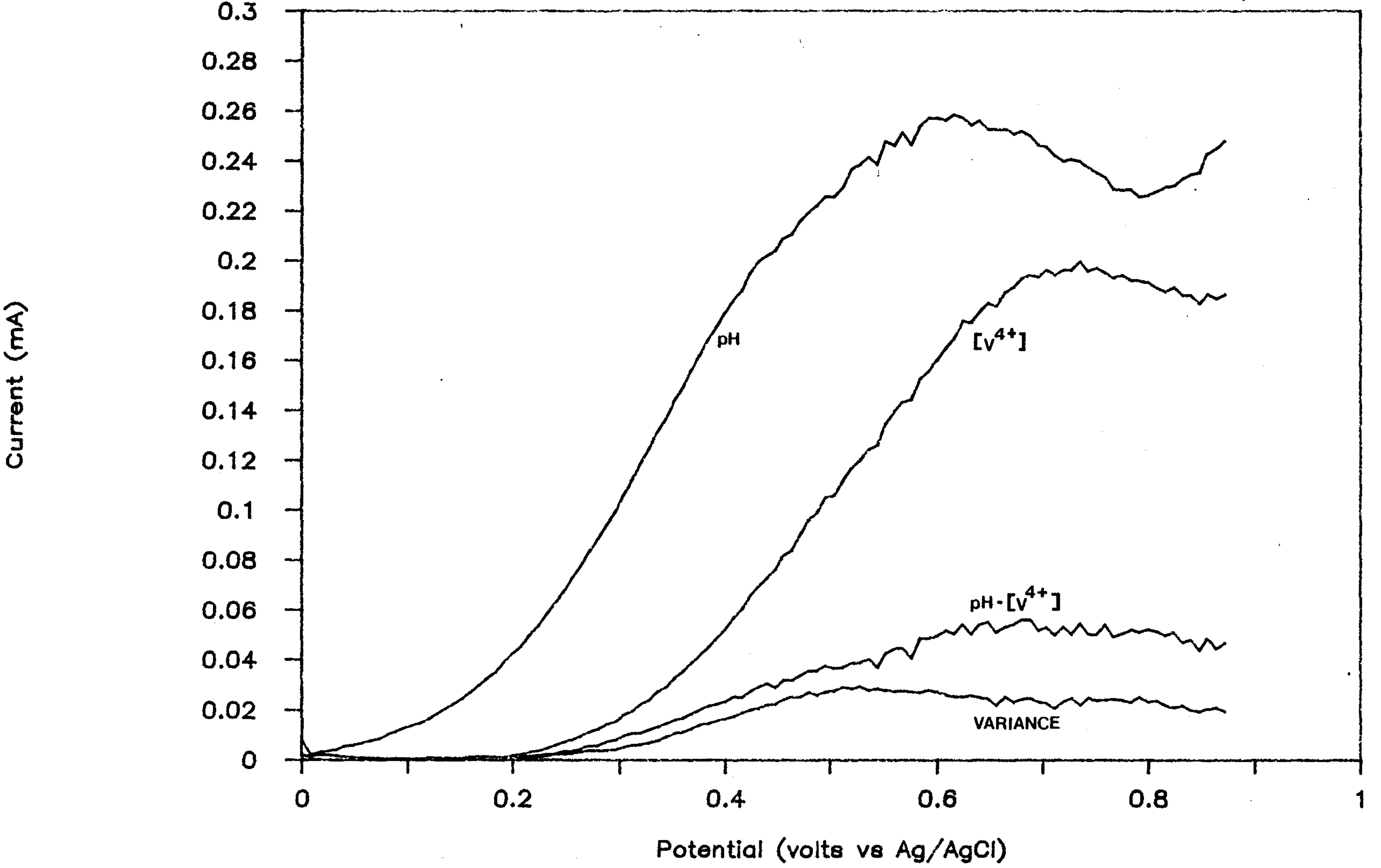


Figure 4.4.9

Small effects on current in the factorial design experiment

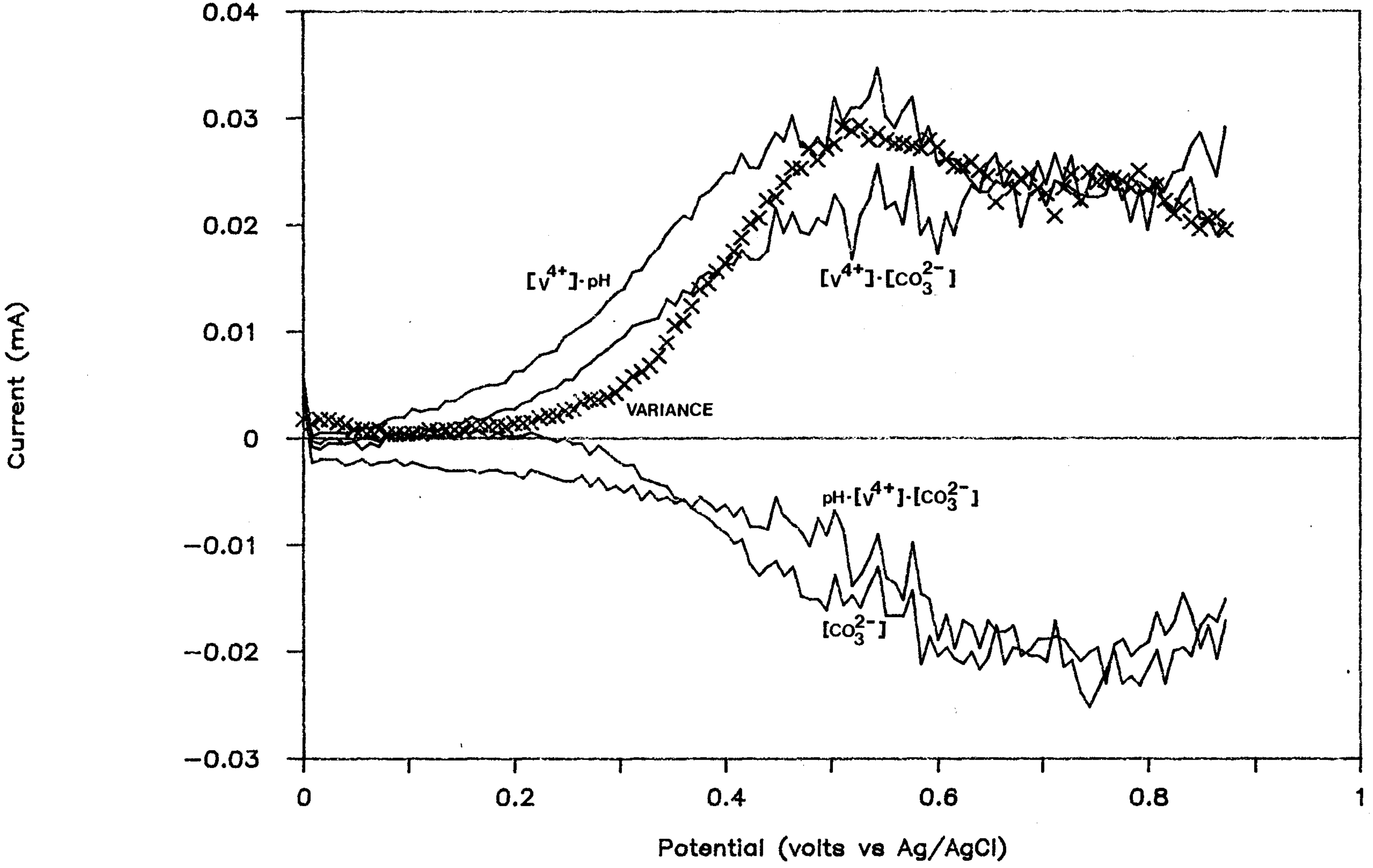
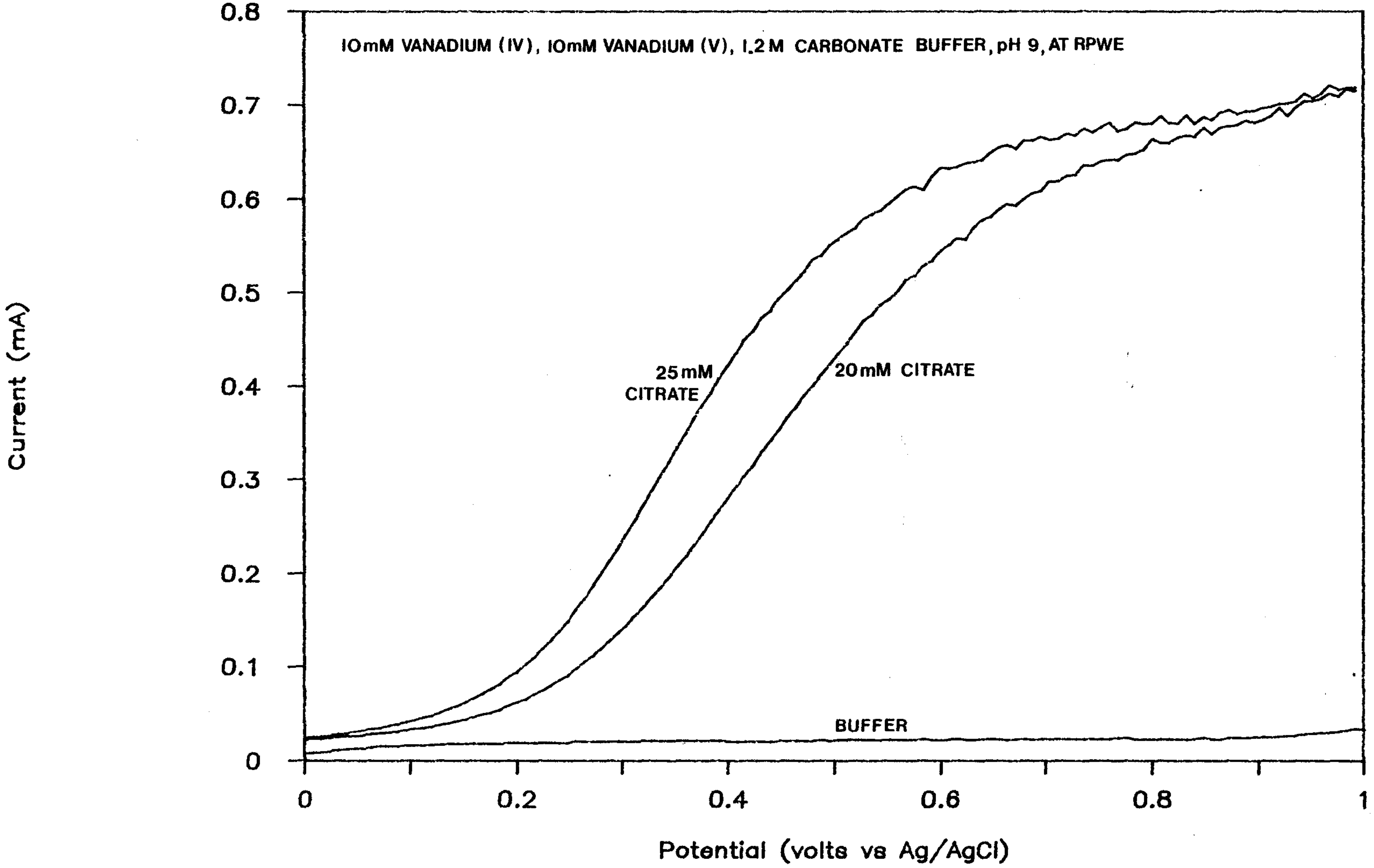


Figure 4.4.10

The effect of citrate ion



4.4.2.2 Sulphide and Polysulphide Voltametry

The voltametric responses of sulphide and polysulphide at CP and RPW electrodes are qualitatively similar. As shown in Figure 4.4.11, the wave shape for sulphide ion at carbon paste was not reproducible since the current decreased and the wave shifted anodically with time. This effect was especially pronounced at the RPWE and with polysulphide anions at the CP electrode (Figure 4.4.12). The sulphur deposited at the RPWE, the appearance of the carbon paste surface (interference patterns), and the lack of current flow from 0.4 to 1.2 volts indicates electrode passivation. The elemental sulphur deposit on the RPWE could be wiped off to reveal the bright platinum surface (without complete recovery of current flow). The addition of Triton X-100 or sodium ethyl xanthate had no effect on the electrode passivation.

The zero current flow up to 1.2 volts (1.4 volts S.H.E.) is in agreement with the observation [20, 24, 25, 23:109] that sulphide will not be oxidized beyond elemental sulphur at potentials below 1.5 volts (S.H.E.). The nature of the second anodic wave at carbon paste is unknown.

4.4.2.3 Sulphide and Vanadium (IV) Voltametry

The decreases in current flow and the anodic shift of the vanadium (IV) wave at the RPWE in the presence of as little as 0.25 mM polysulphide with time is shown in Figure 4.4.13. The overall inhibition of current flow is in agreement with the previous observations of sulphur induced electrode passivation. The addition of ethyl xanthate did not remove deposited sulphur from the RPWE nor prevent its further

.pa

Figure 4.4.11

10 mM sulphide at CP in 1.2 M carbonate buffer pH 9

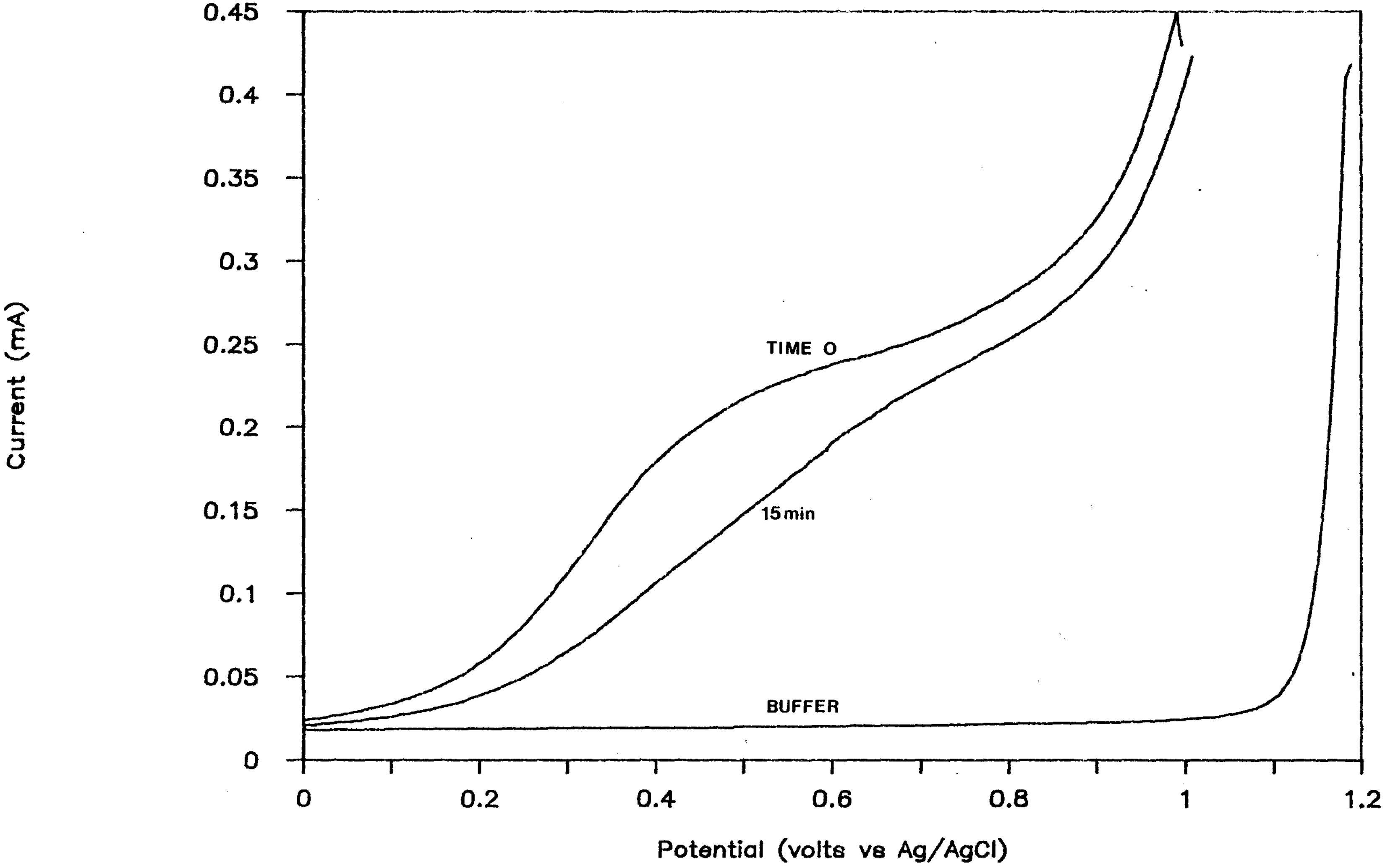


Figure 4.4.12

Sulphide and polysulphide at CP in 1.2 M carbonate buffer pH 9

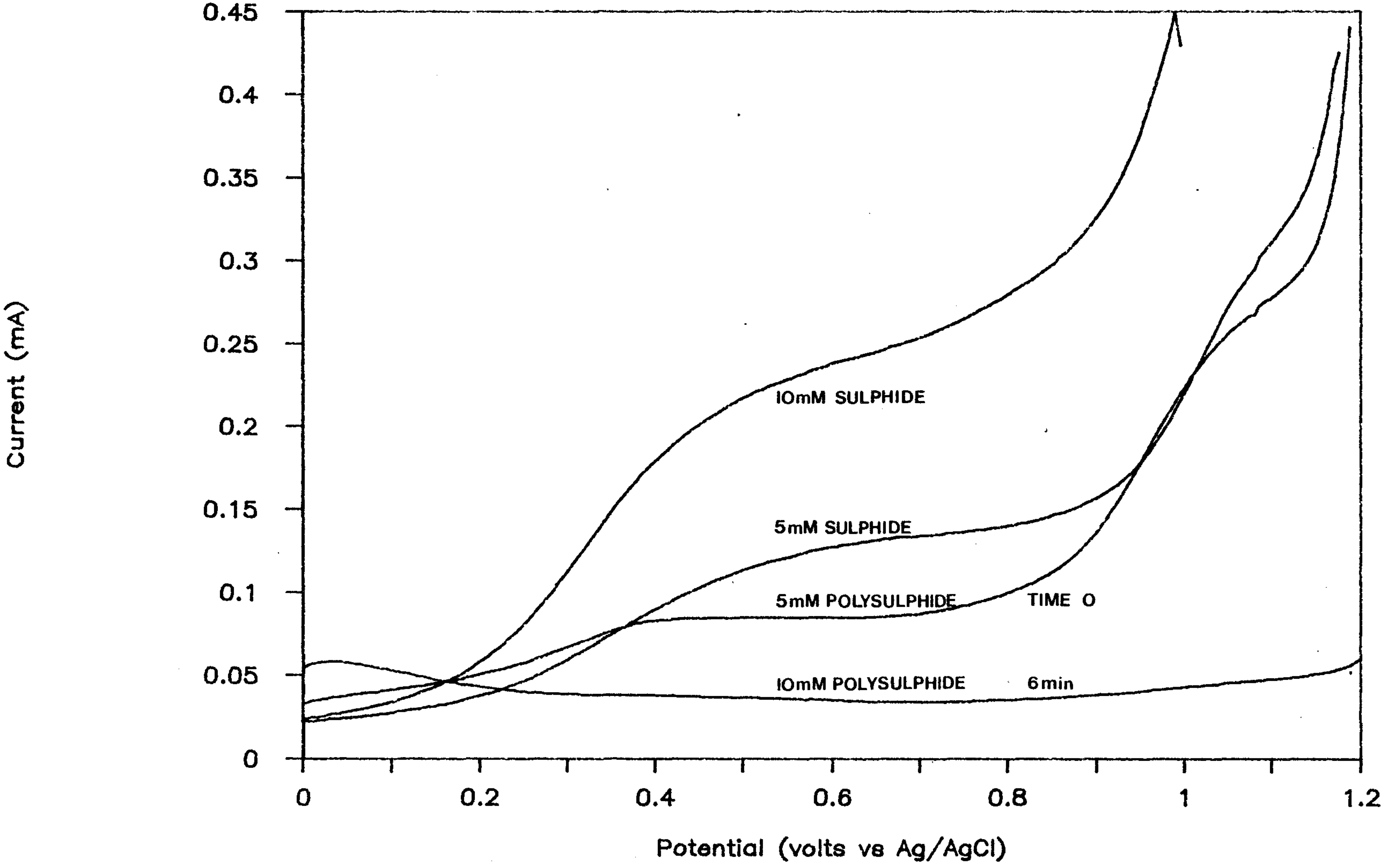
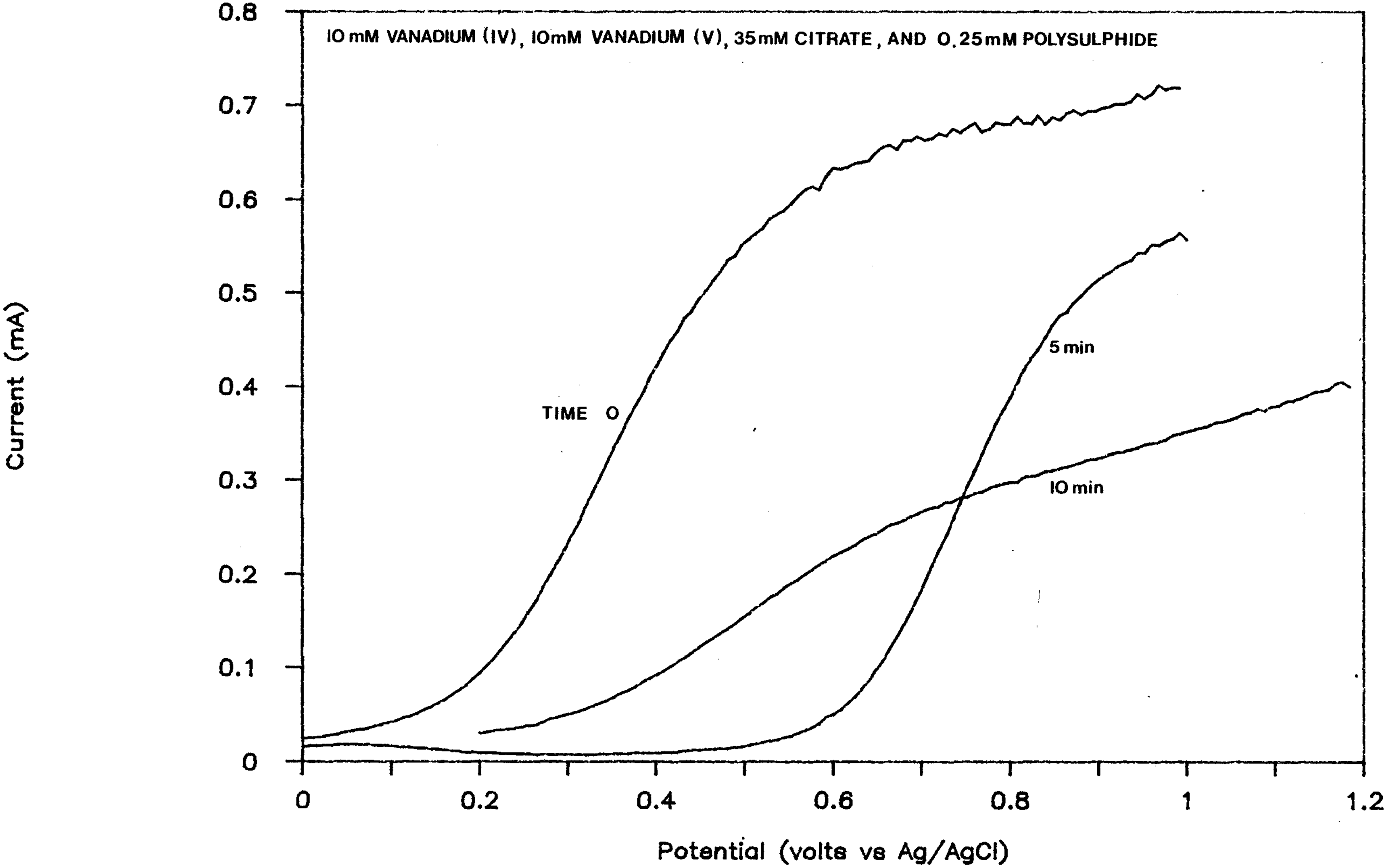


Figure 4.4.13

The effect of trace sulphide on the vanadium (IV) wave in 1.2 M carbonate buffer pH 9



deposition.

4.4.3 Discussion

The anodic discharge of vanadium (IV) ion was observed to proceed readily at carbon paste and rotating platinum wire electrodes. The lack of reduction of vanadium (V) at either electrode confirms the earlier observation of the irreversibility of the redox couple at platinum. The small anodic wave at the voltametric halfwave potential of -0.1 volts may be in agreement with the standard potentials calculated from Table 2.2.1 for the VO^{++}/VO_2^{+} or the $HV_2O_4^{-}/H_2VO_4^{-}$ couples at pH 9. This response was not investigated.

The low current flow and the linear response observed in the voltammograms for vanadium (IV), in Figure 4.4.1, suggests that the electrode reaction is being suppressed. The straight line behaviour is so reminiscent of a classical ohmic response that the temptation to draw the analogy is irresistable. An ohmic resistances could result from insufficient ionic strength in the bulk solution (unlikely) or the decreased conductivity of the solution adjacent to the anode surface. The latter effect could result from the acidification of the anode surface if carbonate and bicarbonate ions consume acid to form non-conducting carbonic acid or adsorbed carbon dioxide.

Alternatively, the release of proton near the anode surface may decrease the stability of the incoming vanadium (IV) species or complex. This would imply that the straight line response is an example of activation polarization with the kinetically hindered step being an acid /base dissociation or an acid/base dependent complexation reaction. The similarity between the first dissociation constant of carbonic acid (6.37) and the third dissociation constant of citric acid (6.39) suggests that both conductivity and complexation effects may be involved.

In 0.4 M carbonate buffer (Figure 4.4.3) the vanadium (IV) voltametric curves have assumed a classical shape, however, this degenerates towards lower currents and less classical wave shapes with increasing vanadium (IV) concentrations. At vanadium (IV) concentrations in excess of 10 mM, the response is clearly suppressed.

In the more concentrated carbonate buffer solutions, where conductivity and buffering capacity are greater, the vanadium (IV) wave shapes are more recognizable and show reasonable variation with vanadium (IV) concentration. Under these circumstances, the electrochemistry of the vanadium (IV) was considered to be predictable enough to perform a factorial design experiment. The main contributions to the current flow in the vanadium (IV) wave come from increasing the solution pH from 8.8 to 9.2 and from increasing the vanadium (IV) concentration from 15 to 25 mM (Figure 4.4.8). The contribution to the vanadium (IV) wave from changing the carbonate concentration from 1.0 to 1.2 M (Figure 4.4.9) may be negative, but is really indistinguishable from experimental error. Also indistinguishable are the combined interactions arizing from vanadium (IV) concentration and/or pH with these chosen carbonate concentrations.

The contributions of pH and vanadium (IV) concentration to the current flow in the vanadium (IV) waves require further discussion. With reference to Figure 4.4.8, it is apparent that the effect of pH is localized towards the rising portion of the wave whereas that for the concentration of vanadium (IV) is localized towards the latter section of the plateau. This implies that the effect of increasing the pH is to enhance the oxidizability of vanadium (IV), whereas increasing the vanadium (IV) concentration inhibits the oxidizability of vanadium (IV) at potentials corresponding to the rising portion of the vanadium (IV) wave. If the results of Figure 4.4.10 are considered it is evident that citrate ion exhibits effects similar to increasing pH by enhancing vanadium (IV) oxidizability.

The added citrate ion may enhance the stability of a vanadium-citrate complex. Alternatively the added citrate may provide additional buffering at the electrode. In either case, the effects of citrate ion are of great practical importance in the optimization of the electro-oxidation of vanadium (IV).

The passivation of the rotating platinum electrode in a 10 mM vanadium (IV) solution containing a stoichiometric excess of 10 mM vanadium (V) over 0.25 mM polysulphide showed that the vanadium couple will not electro-catalyse the polysulphide ion oxidation. It also indicates that the slippage of sulphide or polysulphide ion, or a reacting mixture of polysulphide and vanadium (V) into the electrolysis cells should be avoided.

CHAPTER 5

ECONOMICS AND FUTURE DEVELOPMENT

CHAPTER 5

ECONOMICS AND FUTURE DEVELOPMENT

5.1 Cost Analysis

The implimentation of the electrolytic upgrading of hydrogen sulphide into hydrogen and elemental sulphur is dependent upon the use of a reasonable current density and cell voltage. If the diffusion limited responses observed at the rotating platinum wire electrode can be reproduced and improved upon at a planar electrode in a bipolar cell, the following cost analysis will be industrially actualized.

Given an anode potential for the oxidation of vanadium (IV) of 0.93 volts (vs Ag/AgCl, sat. KCl), a solution IR drop of 0.5 volts, and a cathode overvoltage of 0.2 volts, the energy expended in the cell for the vanadium mediated electrolysis of 1 mole of hydrogen sulphide can be calculated. A sample calculation is shown in Table 5.1.1.

Given 1 long ton of sulphur, the volume of hydrogen (STP) produced per ton (m^3 ton^{-1}), the energy consumed per ton sulphur (kwhr ton^{-1}), and the energy efficiency to hydrogen (m^3 kwhr) can be calculated using equations i), ii), and iii). Typical energy consumption and hydrogen production efficiency figures for the vanadium assisted electrolysis of hydrogen sulphide are shown in Table 5.1.2. The costs per ton sulphur were calculated from the energy consumption at 2 cents per kilowatt-hour.

i) Cubic meters hydrogen per ton sulphur:

$$1\ (2240)\ (0.45359)\ (1000)\ (22.414)\ (0.001)\ /32 = 711.67\ m^3$$

ii) Energy consumed per ton sulphur:

$1\ (2240)\ (0.45359)\ (1000)\ E_{cell}\ /(32x3600) = A\ \text{kwhr ton}^{-1}$

iii) Energy efficiency:

$22.414\ (0.001)\ (3600)/E_{cell} = B\ (m^3\ \text{hydrogen kwhr}^{-1})$

The first row of Table 5.1.2 characterizes the electrolysis at an anode potential near the voltametric half-wave potential. An electrolysis with this anode potential may be industrially impossible if immense electrode areas are required. The energy consumed by the cell under these conditions, however, is interesting since it is less than the energy made available from the combustion of hydrogen into water. If it were possible to oxidize hydrogen to water in a fuel cell with 100 percent efficiency, the energy produced in the fuel cell would be greater than the energy consumed in electrolysis cell. This excess energy would be entirely consistent with the First law of Thermodynamics since the electrode reactions are different in the two cells. The excess energy represents a fractional recovery of the energy evolved in the partial oxidation of hydrogen sulphide summarized below:

$$H_2S = H_2 + S^o \qquad G = 33\ \text{KJ mole}^{-1}$$

$$H_2 + 1/2O_2 = H_2O(g) \qquad G = -228.19\ \text{KJ mole}^{-1}$$

$$H_2S + 1/2O_2 = H_2O(g) + S^o \qquad G = -195.19\ \text{KJ mole}^{-1}$$

The remaining entries in Table 5.1.2 compare favourably with published data for water electrolysis and the market values of hydrogen and elemental sulphur. The energy efficiencies for conventional acidic

Table 5.1.1

Energy Consumption in the Electrolysis Cell

Cell Voltage	Energy (nFE) KJ mole^{-1}
0.93 v	90 KJ/mole vanadium (vs Ag/AgCl, sat.KCl)
+.198 v	+19 KJ (Ag/AgCl, sat. KCL vs S.H.E.)
1.13 v	109 KJ/mole vanadium
	x2 equivalents vanadium per equivalent sulphide
	218 KJ/mole sulphide
+0.5 v	+48 KJ solution IR drop
+0.2 v	+19 KJ cathode overpotential
1.93	285 kJ/mole sulphide

Table 5.1.2

Energy Consumption and Hydrogen Production Efficiencies

Anode Potential (Ag/AgCl, sat.KCl)	E_{cell} KJ mole^{-1}	Consumption kwhr ton^{-1}	Cost*	Efficiency m^3 kwhr^{-1}
0.3 v	201	1772.8	35.46	0.40
0.65 v	231	2037.4	40.75	0.35
0.93 v	285	2513.7	50.27	0.28
1.2 v	384	3386.9	67.74	0.21

* dollars per ton.

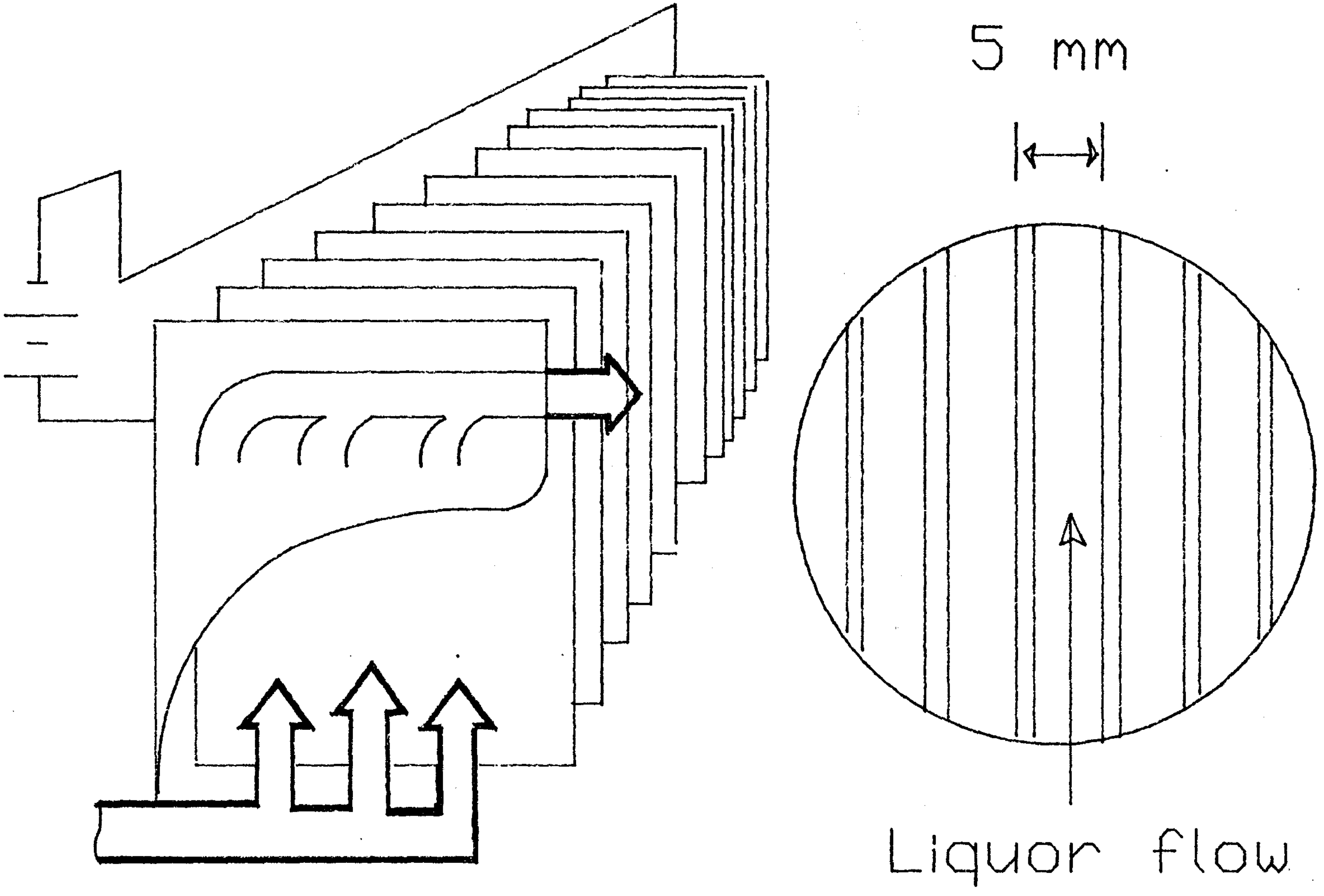
water electrolysis [44] are 0.14 m^3 hydrogen per kilowatt-hour and 0.19 to 0.23 m^3 per kilowatt-hour for high pressure alkaline water electrolysis [45]. Raymont's total product value [46] of 1 ton of sulphur and the 25 Mscf hydrogen produced from it was 37.50 + 25.00 = 62.50 dollars. These values suggest that the vanadium mediated electrolysis of hydrogen sulphide can be competative with water electrolysis for hydrogen production with the operating costs for the desulphurization comparable to the value of the hydrogen and sulphur produced.

5.2 Electrolyser Design

The demonstrated irreversibility of the vanadium mediated hydrogen sulphide electrolysis in cells which lack an anode/ cathode separator is a phenomenon which can be exploited in the design of an industrial sized cell. We envisage a bipolar cell constructed of parallel sheets of a metal (yet to be identified) 3 to 5 mm apart. The reduced liquor from a continuous solid sulphur separator will be distributed between the plates along the bottom of the cell by a distribution manifold. The liquor flows upwards between the plates where it is oxidized and stirred by the flow and the evolved hydrogen. The hydrogen gas and the oxidized liquor flow from between the plates through a collection manifold into a gas liquid separator.

A bipolar cell of the type illustrated in Figure 5.1.1 could contain 200 or more plates per meter. A cubic meter of bipolar cells would contain 200 square meters anode and 200 square meters cathode area. The lack of a cell divider would allow the distribution and collection manifolds to be simple and less expensive than a conventional water

Figure 5.1.1 A Bipolar cell design



electrolysis diaphragm cell (which must collect hydrogen and oxygen gases as distinct product streams). Furthermore, since oxygen will not be a contaminant in the hydrogen gas stream, there is a lower likelihood of forming explosive gas mixtures in the process plants.

5.3 Optimization and Implementation

The current densities arising at the RPWE for a 10 mM vanadium (IV) ion and 25 mM citrate ion in 1.2 M carbonate buffer pH 9 (Figure 4.4.10) were approximately 0.6 mA / 0.16 cm^2 = 3.75 mA/cm^2. It should be possible to optimize the electrochemistry with higher pH, vanadium (IV) and citrate concentrations so as to operate with higher current densities in a bipolar cell.

If a working current density of 5 mA/cm^2 (50 A/m^2) and a current efficiency of 70 percent are assummed, the volume occupied by the electrolysis cells (described in Section 5.2) can be estimated for some quantity of sulphur. The current required for 1 long ton of sulphur per day is given by:

$$\frac{1\ (2240)\ (0.45359)\ (1000)\ (2)\ (96487)}{(3600)\ (24)\ (32)\ (.7)} = 101{,}301 \text{ amps}$$

The corresponding electrolyser volume is given by:

$$\frac{(101{,}301 \text{ amps})}{(50\ \text{A m}^{-2})\ (200\ \text{m}^2 \text{ cubic meter}^{-1})} = 10.13 \text{ cubic meters}$$

This may be a reasonable cell size, unless the electrolyser cells are operated to give a very low vanadium (IV) concentration in the exit stream. Low exit concentrations demand small current densities towards the later stages of the electrolysis.

Due to the threat of sulphur passivation of the electrolyser anodes, the cells should be protected with a guard cell which, by virtue of its design, is easy to clean. Organic substances swept into the system by the sour gas feed may present complications at the electrode surfaces. In such an event, efficient organics scrubbing must be maintained upstream from (and possibly within) this process plant.

5.4 Suggestions for Future work

Although the open cell design functioned well, and offers potential savings in cell construction, this study did not address the relative merits of an open versus closed cell design. Of particular interest are the questions of catalytic hydrogen evolution by vanadium and the extent of chemical short circuiting of the open cell. A chemical short circuit could arize from:

i) the electro-reduction of electrosynthesized vanadium (V);

ii) the electro-oxidation of hydrogen;

iii) the electro-reduction of elemental sulphur either directly, as in equation 5.92, or indirectly as summarized by equation 5.81.

$$S_x^{2-} + 2e^- = S_{x-1}^{2-} + S^{2-} \tag{5.92}$$

$$S_2O_3^{2-} + 2e^- = SO_3^{2-} + S^{2-} \qquad (5.80)$$

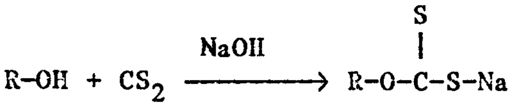
$$SO_3^{2-} + S^o = S_2O_3^{2-} \qquad (5.61)$$

$$S^o + 2e^- = S^{2-} \qquad (5.81)$$

The irreversibility of the vanadium (IV/V) couple is crucial to the operation of the open cell design. For this reason it should be investigated at a fundamental level. To be specific, a study should be undertaken using a ring-disc electrode to investigate the effects of high pH, high citrate concentration, the thiocyanate ion, and ammonia on vanadium (IV/V) irreversibility.

If the open cell retains a position of prominence, a bipolar cell should be constructed and the electrochemistry optimized. This study should concentrate on the selection of suitable electrode materials and the maximization of current densities.

The industrial success of this process depends on the efficient removal of sulphur particulates fron the liquor. This removal is complicated by the tendency of the sulphur particles to be wetted in the process liquor. This wetting may arize from the adsorption of citrate ion or the chemistry of polysulphide. It may be possible to alter this phenomenon with xanthate ions. The xanthate ion can be prepared [63] from an alcohol and carbon disulphide in alkaline solution (reaction 5.93).



$$R\text{-}OH + CS_2 \xrightarrow{NaOH} R\text{-}O\text{-}\overset{S}{\overset{|}{C}}\text{-}S\text{-}Na \qquad (5.93)$$

Xanthates have been employed in the selective flotation of sulphide ores [64], although the mechanism by which they interact with the metal sulphide surface is not understood. If the xanthate ion can be adsorbed onto elemental sulphur, changes in the R group may enhance sulphur separation from the liquor. Another possible effect might be the modification of polysulphide chemistries. This would arise if a xanthate reacts with elemental sulphur to form the polysulphide analogue shown in equation 5.94.

$$R\text{-}O\text{-}\overset{\overset{S}{|}}{C}\text{-}S\text{-}Na + xS \text{---------}\!\!> R\text{-}O\text{-}\overset{\overset{S}{|}}{C}\text{-}(S_x)\text{-}S\text{-}Na \qquad (5.94)$$

Such a polysulphide analogue might be engineered to mediate the formation of cyclo-octa sulphur in the process liquor. In this event, the polysulphide chemistry may be isolated and easier to control.

The wetting of elemental sulphur by citrate ion may result in significant reagent loss from the liquor. This reagent loss and the rate of byproduct formation should be evaluated in a full scale pilot plant and at the process plant level.

CHAPTER 6

SUMMARY

CHAPTER 6

SUMMARY

The vanadium mediated electrolysis of hydrogen sulphide has been investigated at platinum electrodes in carbonate buffers containing the citrate ion. The anode reaction consists of the oxidation of vanadium (IV) to vanadium (V). Hydrogen gas is evolved at the cathode. The vanadium (V) enriched solution can be reacted with aqueous hydrogen sulphide (preferably outside the electrolysis cell) which reduces the vanadium (V) to vanadium (IV) and forms yellow sulphur. The vanadium (IV) rich solution is returned to the electrolysis cells. The process chemistry is summarized below:

$$H_2S + OH^- = HS^- + H_2O \qquad (6.6)$$

$$HS^- + 2VO_3{}^- + 3H_2O = S^o + 2VO^{2+} + 7OH^- \qquad (6.21)$$

$$2VO^{2+} + 8OH^- = 2VO_3{}^- + 4H_2O + 2e^- \qquad (6.32)$$

$$2H^+ + 2e^- = H_{2(g)} \qquad (6.33)$$

$$H_2S = H_{2(g)} + S^o \qquad (6.34)$$

The process was operated continuously for 7 days, using an open cell design, in a bench top pilot plant. The predominant byproduct was sulphate ion, which accumulated in the liquor to a degree which could account for 3 percent of the electrochemical equivalents consumed in the process. The electrosynthesis of oxygen was suspected, but high background concentrations prevented the calculation of a current efficiency.

The oxidation of vanadium (IV) to vanadium (V) in the liquor is irreversible at platinum. The voltametric half-wave potential at a rotating platinum wire electrode was 0.34 v (vs Ag/AgCl, sat. KCl). The anodic current efficiency for vanadium (IV) oxidation exceeds 90 percent. Lower current efficiencies (approximately 70 percent) are associated with the slippage of sulphide or polysulphide ions into the electrolysis cell. Such slippage causes the deposition of elemental sulphur at the anodes which passivates them. Any attempt to maintain a given current flow at a passivated anode requires an increase in the anode potential. Anode potentials in excess of 1.2 volts (Ag/AgCl, sat. KCl) enhance the rate of sulphate and oxygen formation and increases the energy consumed by the cell.

The discharge of vanadium (IV) at the anode is associated with the release of 4 protons. This results in the acidification of the solution adjacent the electrode surface, which can induce carbon dioxide evolution and inhibit the discharge of vanadium (IV). The inhibition appears as a suppressed current and an anodic shift in the voltametric half-wave potential. This inhibition can be minimized at high pH, buffer capacity, and citrate concentrations.

The anode potential requirements for the oxidation of vanadium (IV) indicate that the electrolysis cells could be operated with high energy efficiencies to hydrogen production (measured in standard cubic meters per kilowatt-hour). Energy efficiencies of greater then 0.28 (versus

0.14 for conventional acid electrolysis) may be realized in the process. Higher energy efficiencies may be possible at the expense of increasing electrode areas.

The reduction of elemental sulphur and vanadium (V) is apparently restricted in the process liquor. This may preclude the need for an anode/cathode divider (such as a frit, diaphragm, or membrane) which points towards considerable savings in electrolysis cell construction. This factor may offset the expense of increasing electrode areas and allow high energy efficiencies to hydrogen production to be realized.

The study of this desulphurization process featured:

i) a critical review of the electro-oxidation of sulphide ion;

ii) the identification of a catalytic response for the polarographic determination of sulphide ion. A mechanism based upon the assisted anodic dissolution of mercury by sulphite, thiosulphate, or cyanide ions was proposed;

iv) the electro-oxidation of vanadium (IV) to vanadium (V) in alkaline carbonate buffers containing citrate ion. This has not been previously reported in the scientific literature;

v) a factorial design voltammetric experiment which indicated that the anodic discharge of vanadium (IV) was favoured and can be optimized at high carbonate buffer concentrations, at high pH (in the range of 8.8 to 9.2, and a greater than two times stoichiometric excess of citrate ions.

The possible re-invention of the desulphurization process described in U.S. Patent #3,401,101 (Section 2.4.1) is unlikely since:

i) the need for a complexing agent, such as citrate ion, was not emphasized in the patent abstract;

ii) carbon dioxide in the gas stream DOES affect the process chemistry by contributing a much needed buffering effect during vanadium (IV) electro-oxidation;

iii) the liquor pH leaving the electrolysis cell should be in the upper extreme of the pH range of 8.8 to 9.2 in order to maximize the anodic discharge and restrict the vanadium (V) reduction in an open cell;

iv) the electrochemical cell can be operated without a cell divider.

References

1. G.E. Likens, R.F. Wright, J.N. Galloway and T.J. Butler. 1979. Acid Rain. Scientific American 241:43.
2. G.W. Kutney and K. Turnbull. 1984. The Sulphur Chemist: The bearer of ill wind? J. Chem Ed. 61:272-376.
3. R.J. Falkiner and O.E. Hileman Jr. 1977. COG Desulphurization, A Summary of Current and Potential Processes with Emphasis on Basic Process Chemistry, McMaster Symposium on Iron and Steelmaking, No. 5, Treatment of Coke Oven Gas. McMaster University Press, Hamilton, Ontario.
4. Personal communication with O.E. Hileman Jr.
5. T. Nicklin and E. Brunner. 1961. How Stretford Process is Working. Hydrocarbon Processing and Petroleum Refiner 40:141-146.
6. S.J. Pitts. 1983. M.Sc. Thesis, Department of Chemistry, McMaster University. Hamilton, Ontario.
7. N. Hartler, J. Libert and A. Teder. 1967. Rate of Sulphur Dissolution in Aqueous Sodium Sulphide. I and E C Process Design and Development 6:398-406.
8. A. Teder. 1971. The Equilibrium Between Elementary Sulphur and Aqueous Polysulphide Solutions. Acta Chemica Scandinavica 25:1722-1728.
9. J. Selbin. 1965. The Chemistry of Oxovanadium (IV). Chemical Reviews 65:153-175.
10. A.J. Bard. 1976. Encyclopedia of Electrochemistry of the Elements -

Volume VII, Chapter 2, by Y. Israel and L. Meites. Marcell Dekker Inc. New York and Basel.

11. M. Pourbaix. 1966. Atlas of Electrochemical Equilibrium in Aqueous Solutions; Chapter IV, E. Deltombe, N. deZoubov and M. Pourbaix. Pergamon Press, LCCC# 65-11670.

12. H.T.S. Britton and G. Welford. 1940. Electrometric Studies of the precipitation of hydroxides, Part XV. The Amphoteric Nature of Vanadium Tetroxide. J. Chem Soc. 758.

13. G.A. Brydon and G.F. Atkinson. 1970. The Coulometric Generation of Lower Oxidation States of Vanadium. Analytica Chimica Acta 51:425-430.

14. E. Bishop and P.H. Hitchcock. 1973. Mass and Charge Transfer Kinetics and Coulometric Current Efficiencies Part VII. Analyst 98:553-562.

15. H.H. Willard and G.D. Manalo. 1947. Some Formal Oxidation-Reduction Potentials. Analytical Chemistry 19:462-463.

16. M.T. Pope and B.W. Dale. 1968. Isopolyvanadates, niobates and tantalates. Quarterly Reviews Chem. Soc. 22:527-539.

17. M.A. Habayeb. 1981. Ph.D. Thesis, Department of Chemistry, McMaster University, Hamilton, Ontario.

18. M.A. Habayeb and O.E. Hileman, Jr. 1980. ^{51}V FT-nmr Investigations of Metavanadate ions in Aqueous Solutions. Canadian Journal of Chemistry 58:2255-2261.

19. T.A. Walker. 1983. Senior Thesis, Department of Chemistry, McMaster University, Hamilton, Ontario. Spectroscopic Studies on Vanadium (IV) Speciation in Aqueous Solutions Containing Citrate Ligand

20. W.R. Fetzer. 1928. The Electrolysis of Sodium Sulphide Solutions. Journal of Physical Chemistry 32:1787-1807.

21. M. Pourbaix. 1966. Atlas of Electrochemical Equilibrium in Aqueous Solutions; Chapter III and IV. Pergamon Press, LCCC# 65-11670.

22. M.N. Moscardo-Levelut and V. Plichon. 1984. Sulphur Chemistry in Equimolar NaOH-H_2O Melt, Parts 1 and 2. Journal of the Electrochemistry Society 131:1538-1551.

23. A.J. Bard. 1976. Encyclopedia of Electrochemistry of the Elements - Volume IV, Chapter 6, by S.I. Zhdanov. Marcell Dekker Inc. New York and Basel.

24. Gerischer. 1950. Reaktionen und periodische Vorgaengen an einer Platinanode in Alkalisulfidloesungen. [Bard [23]: reference 109].

25. P.L. Allen and A. Hickling. 1957. Electrochemistry of Sulphur Part 1.- Overpotential in the Discharge of the Sulphide ion. Transactions of the Faraday Society 53:1626-1635.

26. M. Farooque and T.Z. Fahidy. 1978. The Electrochemical Oxidation of Hydrogen Sulphide in the Tafel Region and under Mass Transport Control. Journal of the Electrochemistry Society 125:544-546.

27. E. Najdeker and E. Bishop. 1973. The Formation and Behaviour of Platinum Sulphide on Platinum Electrodes. J.E.C.I.E. 41:79-87.

28. N. Ramasubramanian. 1975. Anodic Behaviour of Platinum Electrodes in Sulphide Solutions and the Formation of Platinum Sulphide. J.E.C.I.E. 64:21-37.

29. S. Kapusta, A. Viehbeck, S.M. Wilhelm and N. Hackerman. 1983. The Anodic Oxidation of Sulphide on Platinum Electrodes. J.E.C.I.E.

153:157-174.

30. D.W. Shoesmith, P. Taylor, M.G. Bailey and B. Ikeda. 1978. Electrochemical Behaviour of Iron in Alkaline Sulphide Solutions. Electrochimica Acta 23:903-916.

31. W. Giggenbach. 1972. Optical Spectra and Equilibrium Distribution of Polysulphide Ions in Aqueous Solutions. Inorganic Chemistry 11:1201-1207.

32. T. Loucka. 1971. Adsorption and Oxidation of Sulphur and of Sulphur Dioxide at the Platinum Electrode. J.E.C.I.E. 31:319-332.

33. M.N. Moscardo-Levelut and V. Plichon. 1984. Sulphur Chemistry in Equimolar NaOH-H_2O Melt, Parts 1 and 2, Journal of the Electrochemistry Society 131:1538-1551.

34. K. Shimizu, K. Aoki and R.A. Osteryoung. 1981. Electrochemical Behaviour of Sulphide at the Silver Rotating Disc Electrode. Part 1.- Polarization Behaviour of Silver Sulphide Films. J.E.C.I.E. 129:159-169.

35. N. Binder, A. Koehling and G. Sandstede. 1968. Adsorption und Anodische Oxydation von Ameisensaure und Kohlenmonoxid an Platinelektroden mit und Ohne Schwefeladsorbat. J.E.C.I.E. 17:111-127.

36. S. Glasstone and A. Hickling. 1934. Studies in Electrolytic Oxidation. Part 1.- The Electrolytic Oxidation of Sodium Thiosulphate at a Platinum Anode. J.A.C.S 2345-2356.

37. N.L. Weinberg. 1983. Electrosynthesis Technology; Journal of Chemical Education. 60:268.

38. A.J. Fry. 1972. Synthetic Organic Electrochemistry. Harper and Row, New York.

39. H. Vandenborre, Ph. Vermeiren and R. Leysen. 1984. Hydrogen Evolution at Nickel Sulphide Cathodes in Alkaline Medium. Electrochimica Acta 29:297-301.

40. A.C. Handra and K.N. Johri. 1973. Microanalysis of Sulphide, Sulphite, Sulphate, and Thiosulphate by Thin-layer Chromatography and Ring-colourimetry. Talanta 20:219-222.

41. D.A. Skoog and D.M. West. 1967. Fundamentals of Analytical Chemistry, Third Edition. Holt, Rinehart, and Winston.

42. I.M. Kolthoff and C.S. Miller. 1941. Anodic Waves Involving Electrooxidation of Mercury at the Dropping Mercury Electrode. J.A.C.S. 63:1405-1411.

43. G.E.P. Box, W.G. Hunter, and J.S. Hunter. 1978. Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building. John Wiley and Sons. New York.

44. Y-S. Shih and M-J. Jong. 1982. Coproduction of sulphuric acid and hydrogen by sulphur-assisted water electrolysis process. Journal of Applied Electrochemistry 12:23-26.

45. Lurgi. 1960. Pressure Lowers Electrolytic Hydrogen Cost. Chemical Engineering March 7:66-67.

46. M.E.D. Raymont. 1975. Make Hydrogen from hydrogen sulphide. Hydrocarbon Processing July:139-142.

47. R. Kennedy. 1980. Senior Thesis, Department of Chemistry, McMaster University, Hamilton, Ontario.

48. L. Szekeres. 1974. Talanta Review: Analytical Chemistry of the Sulphur Acids. Talanta 21:1-44.

49. R.J. Williams. 1983. Determination of Inorganic Anions by Ion Chromatography with Ultraviolet Absorbance Detection. Analytical Chemistry 55:851-854.

50. Wescan company brochure. 1982. The Wescan Ion Analyser.No. 4 (Fall).

51. R.D. Rocklin and E.L. Johnson. 1983. Determination of Cyanide, Sulphide, Iodide, and Bromide by Ion Chromatography with Electrochemical Detection. Analytical Chemistry 55:4-7.

52. A.W. Wolkoff and R.H. Larose. 1975. Separation and Detection of Low Concentrations of Polythionates by High Speed Anion Exchange Liquid Chromatography. Analytical Chemistry 47:1003-1007.

53. R.N. Reeve. 1979. Determination of Inorganic Main Group Anions by High-performance Liquid Chromatography. Journal of Chromatography 177:393-397.

54. Metrohm 506 Polarograph: Instrument manual.

55. I.M. Kolthoff and C. Lingane. 1941. Polarography. Interscience Publishers Inc. New York.

56. D.R. Canterford and A.S. Buchanan. 1973. Polarographic Behaviour of Sulphide Ion. J.E.C.I.E. 45:193-203.

57. D.R. Canterford. 1973. Direct Determination of Sulphide by Rapid Direct Current Polarography. Analytical Chemistry 45:2414-2417.

58. I. Fliipovic, Z. Hahl, Z. Gasparac, and V. Klemencic. 1954. Polarographic Characteristics of +5 Vanadium in Phosphate, Borate and Carbonate Buffers. J.A.C.S. 76:2074-2079.

59. E.J. Breda, L. Meites, T.B. Reddy and P. W. West. 1956. Half-wave Potentials of Metal ions in Organic Hydroxyacid Supporting Electro-

lytes. Analytica Chimica Acta 14:390-399.

60. H.A. Catherino and L. Meites. 1960. Polarographic Determination of Manganese. Analytica Chimica Acta 23:57-65.

61. J.J. Lingane. Polarographic Characteristics of Vanadium in its Various Oxidation States. J.A.C.S. 67:182-188.

62. J.J. Lingane and L. Meites Jr. 1947. Polarographic Oxidation of +4 Vanadium. J.A.C.S. 69:1882-1886.

63. R.T. Morrison and R.N. Boyd. 1973. Organic Chemistry. Allyn and Bacon, Inc. Boston. LCCC# 72-91904.

64. T. Rosenqvist. 1983. Principles of Extractive Metallurgy. McGraw-Hill, Inc. New York.

65. Analytical Chemistry 3A4/3K6/2M5/2N4 Lab Manual. McMaster University, Ontario, Canada.

APPENDIX 1

MINI-PILOT PLANT DESIGN FEATURES

This section describes the construction and operation of the bench top Stretford process pilot plant. Reproduced in its entirety from the Senior Thesis written by Roger Kenedy [47].

Appendix 1

A1 Mini-Pilot Plant Design Features

A1.1 Apparatus

The H_2S/N_2 mixture is contained in a gas cylinder and an ourlet line from this cylinder feeds into the bottom of the absorber. A glass frit is situated in the line between the cylinder and the absorber to create a pressure drop and give increased control of gas flow rates. A coarse glass frit penetrates the bottom of the absorber to allow gas to pass into the absorber withour loss of solution from the absorber. The gas rises up the absorber and contacts the falling liquor. The sweetened gas is exhausted through the top of the absorber. The reduced solution is carried in a plug-flow manner up through the delay chamber of the vessel into the electrode-port section and then into the primary oxidizer. Air is introduced into the primary and secondary oxidizers through separate glass frits and the rate of air flow is controlled by separate flow meters. The partially reoxidized solution flows from the primary oxidizer into the secondary oxidizer and the totally regenerated liquor is then pumped to a delay tank before entering the top of the absorber.

A glass pH electrode monitors the pH of the solution contained in the primary oxidizer. Set pH levels are maintained by a servo controlled needle valve in the CO_2 feed line to the primary oxidizer. The servo controller responds to the output of the pH meter. The setup maintains set point pH levels to +- 0.01 pH units. A more detailed discussion of this pH control unit is given in Section A1.2.

To obtain EMF values that represent the two extreme oxidation states of the solution the potential of the solution must be measured immediately prior to its contact with the H_2S and immediately after its exit from the absorber. Complete electrical contact must be maintained between these two sites. Figure A1.1.1 illustrates how these criteria are met in the laboratory unit. The oxidized solution enters the top of the absorber through a glass pipe that is closed at the bottom. Three holes approximately 2 mm in diameter, are equally spaced around the perimeter of the pipe. The pipe is inserted into the top of the absorber so that the solution quietly issues out of the holes and immediately contacts the existing solution in the absorber. The holes are sufficiently small so that the solution flowing out of the pipe blocks any reduced solution from reentering the pipe and it also provides a liquid seal against gas flow into the oxidized solution. This ensures that the platinum electrode (I) is measuring the EMF of a fully oxidized solution. The exit pipe from the delay section is U-shaped and the solution level within this exit pipe is established by the height of the arm that leads to the primary oxidizer. This arm sits above the arm exiting from the absorber and this ensures that there is complete solution contact between platinum electrode (I) and platinum electrode (II). The design of the apparatus allows for constant electrical contact between the two platinum electrodes and ensures that the EMF values represent the extreme oxidation states of the solution.

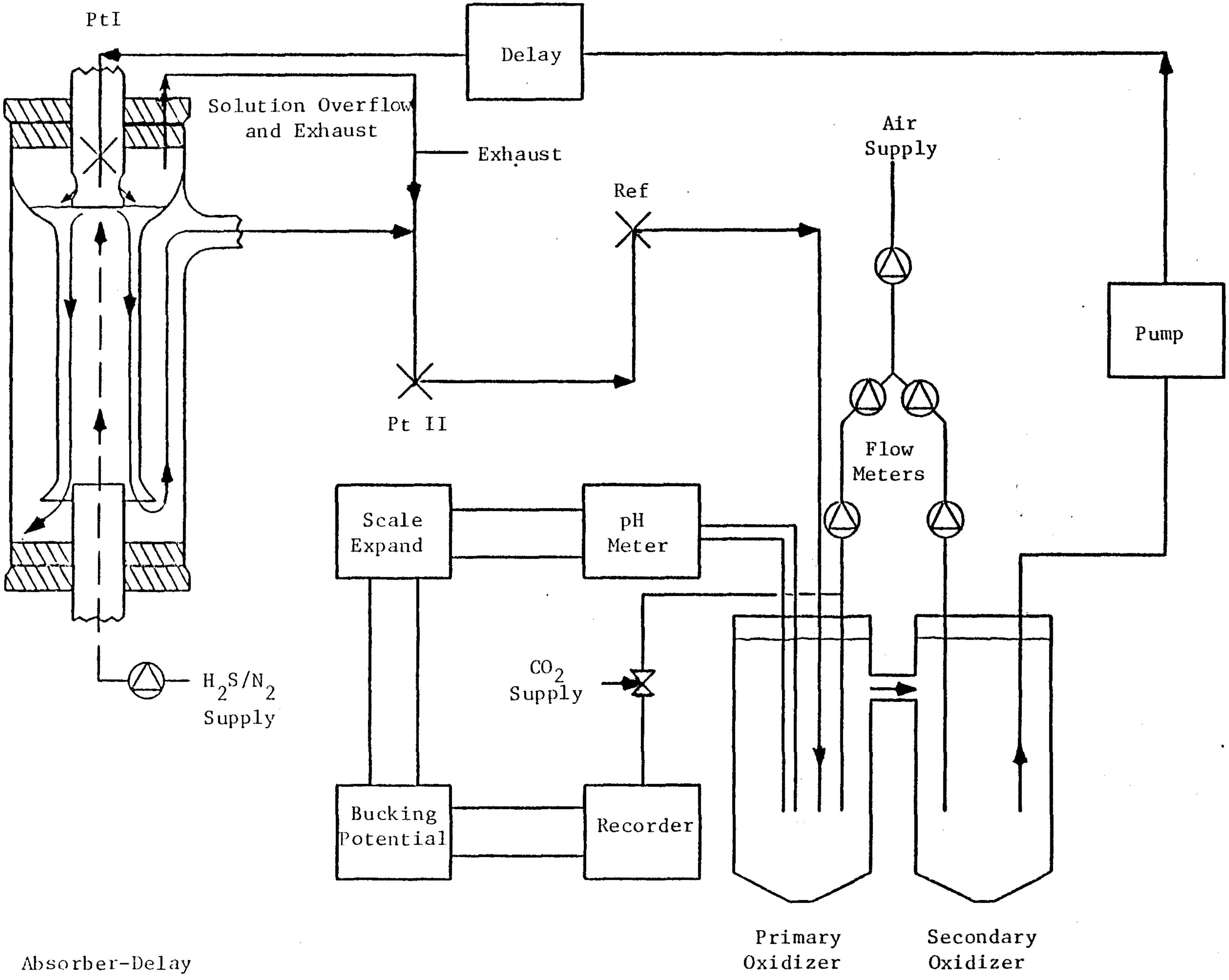
A1.2 pH Control Apparatus

The CO_2 inlet line is connected to a needle valve situated at the back of the recorder. This needle is controlled by a lever that extends from the needle valve to the pen carriage of the recorder. The pH meter sends a signal to the recorder causing the pen carriage to move so as to open or to close the needle valve. In this way, the CO_2 flow rate into the primary oxidizer is controlled. The bucking potential is a potentiometer that allows one to establish a balance point for the pen carriage and hence a balance pH for the solution. At pH values above this balance pH the servo motor in the recorder drives the pen carriage such that the needle valve opens and CO_2 is admitted into the solution. Once the balance is established the unit can maintain the solution pH to within 0.01 pH units. Figure A1.1.1 shows each component of this unit.

Figure A1.1.1. Mini-Pilot Plant Design.

Key:

◬	Needle Valves
⧖	Servo Meter
⇡	Gas Flow
↑	Stretford Solution Flow


PtI
Delay
Solution Overflow and Exhaust
Exhaust
Ref
Air Supply
Pump
Pt II
Flow Meters
Scale Expand
pH Meter
CO_2 Supply
H_2S/N_2 Supply
Bucking Potential
Recorder
Primary Oxidizer
Secondary Oxidizer
Absorber-Delay

Appendix 2

Design Aspects of the Coulometric Cell

Appendix 2

A2 Design Aspects of the Coulometric Cell

A2.1 Introduction

The flowing coulometry experiment involves the continous introduction of a solution, containing an electroactive species, into a well stirred electrolytic cell. The incoming solution displaces solution in the cell at an equal rate. The electroactive species is then removed from the cell by the electrochemical reaction and in the exiting solution. By comparison of the input and output solution concentrations at a constant flow rate, the rate of removal by electrochemical reaction of the species can be calculated.

A comparison of the rate of the electrochemical removal with the rate of introduction of the electrochemical equivalents gives a measure of the current efficiency. Given sufficient time, a steady state concentration will be attained in the cell which will be a function of the flow rate, the feed concentration, and the current flow through the cell. The calculation of the current efficiencies from the steady state concentration is simple and representative of the current efficiency at a specific pH and electrolyte concentration.

A2.2 Apparatus

The apparatus constructed for use in the flowing coulometry experiments is shown in Figure A2.2.1. The cell was constructed from a 400 ml Berzelius beaker and a tightly fitting rubber stopper. Four platinum gauze basket electrodes were carefully shaped to fit into the beaker with the basket leads passed through the stopper. The shaped electrodes were concentrically arranged in the cell to permit solution stirring. The electrodes were further arranged such that they could be used as an anode-cathode pair. The separation between the pair varied from 1 to 8 cm. One half of a glass fritted tube (the half containing the 18 mm medium porosity frit) was placed through the center of rubber stopper, extending far enough into the cell to reach the 250 ml. level. A cylindrical platinum basket electrode, 5 cm x 1.2 cm, was placed in the fritted compartment. The fritted electrode to shaped basket separation through the frit varied from 2 to 15 cm.

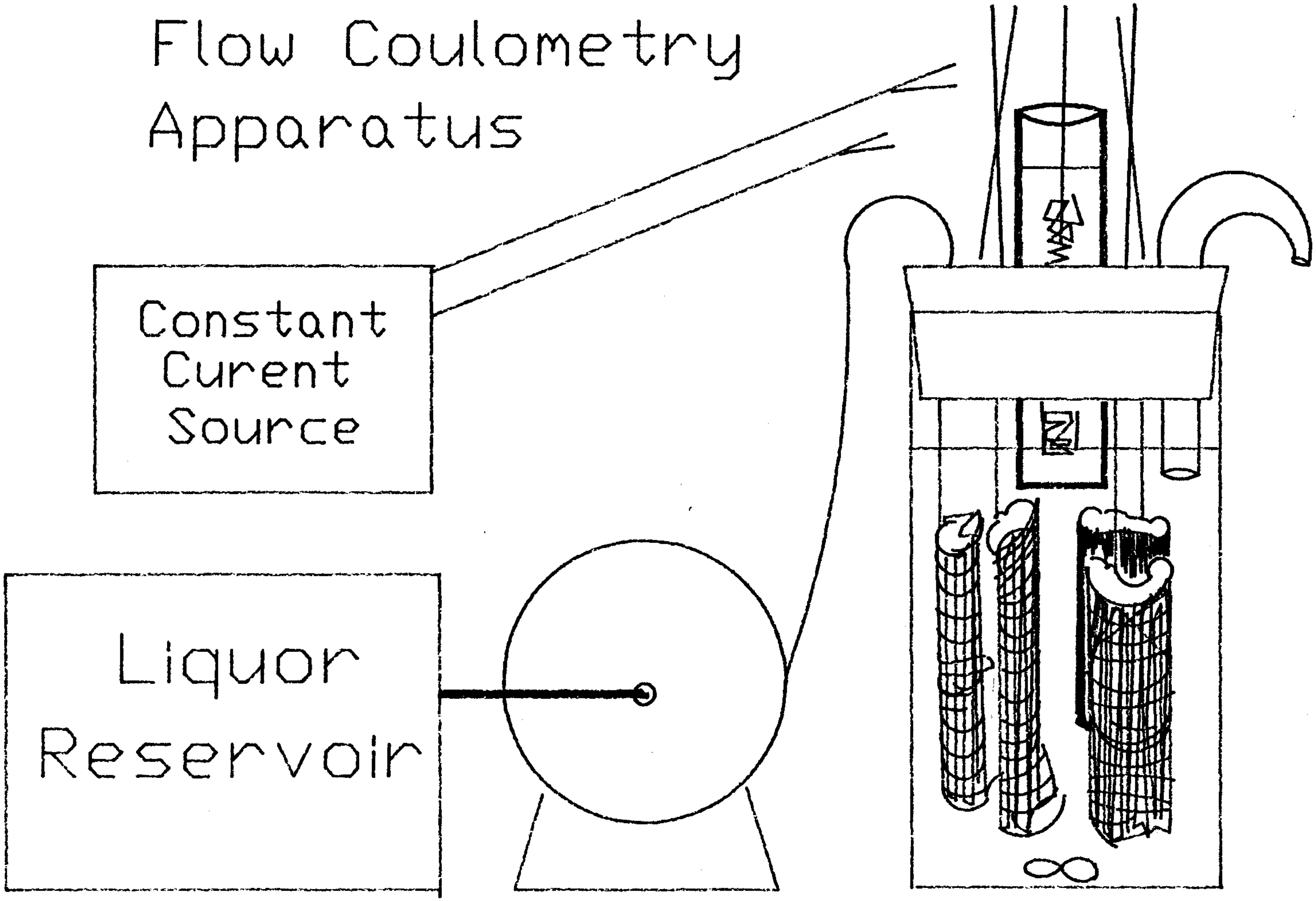
A J-shaped piece of 6mm glass tubing was positioned, with the long end in the stopper, to withdraw solution from the 300 ml level. The solution input to the cell was made through a 4 cm section of glass tubing which had been drawn thin enough to accomodate the 1.6 mm bore of the pump tubing. The process liquor was pumped from a 2 litre reagent bottle 'resevoir' into the apparatus by a peristaltic pump. The pump used was a Masterflex 7545 variable speed peristaltic pump fitted with a No. 7013 pump head. The pump maintained a pressure of 4 cm of liquor in the cell. The process resevoir was continuously flushed with laboratory nitrogen which had scrubbed in a gas cleaning apparatus.

The 0.2 amps of constant current used in the electrolyses was supplied by Sargent Model IV Coulometric Current Source.

A2.3 The Derivation of the Mathematical Model

Applying calculus to the problem of a well stired reaction

Figure A2.1.1 Continuous Flow Coulometry Apparatus



vessel with a feed, exit, and electrochemical mass flow rate yields a series of equations which model the operations of the experimental apparatus used. The variables used in developing these equations are listed below:

C_o = feed concentration

C_i = initial concentration

C_t = concentration at time t

V = electrolysis cell volume

R = solution flow rate

t = time

t_{ss} = time to steady state (approx)

E = current efficiency

M_t = moles in cell at time t

$= C_t V$

$C_t = M_t / V$

n = number of equivalents per mole

F = 96487 coulombs per equivalent

k = constant of integration

i = current

C_{ss} = steady state concentration

Using the mass balance, the mass in the reactor at time, t, is given by:

$$M_t = C_iV + C_oRt - itE/nF - \int (C_tR\ dt)$$

Substituting $C_t = M_t/V$ and differentiating with respect to time gives:

$$dM_t/dt = 0 + C_oR - iE/nF - M_tR/V$$

$$= (nFC_oRV - iEV - nFM_tR\ )/nFV$$

$$dt/nFV = dM_t\ /\ (nFC_oV - iEV - nFM_tR)$$

Integrating both sides:

$$t/nFV = [\ln\ (nFC_oRV - iEV - nFM_tR)]\ /(-nFR) + K$$

$$-tR/V = \ln\ (nFC_oRV - iEV - nFM_tR) + k$$

$$\exp(k)\ \exp(-tR/V) = nFC_oRV - iEV - nFM_tR$$

where k = KnFR and k' = exp(k)

$$nFM_tR = nFC_oRV - iEV - k'\exp(-tR/V)$$

$$M_t = C_oV - iEV/nFR - k'[\exp(-tR/V)]/nFR$$

$$M_t/V = C_o - iE/nFR - k'[\exp(-tR/V)]/nFRV$$

$$= C_t$$

If we apply the following boundry condition:

when $t = 0$ then $C_t = C_o$,

it is possible to solve for k'.

$$-iE/nFR - k'[\exp(0)]/nFRV = 0$$

It follows that $k' = -iEV$. The expression for the concentration in the reactor at time, t, then becomes:

$$C_t = C_o - iE/nFR + iE\,[\exp(-tR/V)]/nFR$$

The limit of C_t as t approaches infinity gives the concentration at the steady state.

$$C_{ss} = C_o - iE/nFR$$

This expression for the steady state concentration is a function of the feed concentration and the solution flow rate. The time to 95% of the steady state concentration, t_{ss}, occurs when the $iE\exp(-tR/V)/nFR$ term becomes equal to 5% of the steady state concentration as:

$$5\%\ C_{ss} = iE[\exp(-tR/V)]/nFR$$

$$t_{ss} = -(V/R)\ \ln(\,5\%C_{ss}nFR/iE)$$

A2.4 Summary of Flow Cell Equations

$$C_{ss} = C_o - iE/nFR$$

$$t_{ss} = -(V/R)\ \ln(\,5\%C_{ss}nFR/iE)$$

$$V_{ss} = Rt_{ss}$$

A2.5 The Current Efficiency Calculations

Rearranging the expression for the steady state concentration in the flow coulometry cell to solve for the current efficiency, E, gives:

$$E = (C_{ss} - C_o)nFR/i$$

where R = Flow rate (ml/sec), and concentrations are given in moles per ml. The expression can be rearranged to accomodate the flow rates in ml per minute, and the analysis data in moles per litre:

$$E = (C_{ss} - C_o)nFR/i * 60 * 10^3$$

If the analysis of vanadium (V) is performed using the coulometric titration, the expression for the current efficiency can be made to accomodate the titration times. In the coulometric titration, the concentration of vanadate is calculated from Faraday's law as:

$$C = i_{coulometry}t/nFV_{aliquot}$$

If the coulometric titration times for the vanadate concentration in the inflow and the outflow are given by t_{in} and t_{out}, the change in vanadate concentration due to the electrolysis is given by:

$$\text{Delta } C = i_{coulometry}(t_{out} - t_{in})/nFV_{aliquot}$$

The equation for the current efficiency becomes:

$$E = [\ i_{coulometry}(t_{out} - t_{in})/nFV_{aliquot}\ ]nFR/i$$

$$= i_{coulometry}(t_{out} - t_{in}) R / [V_{aliquot} * i]$$

For R given in ml/min this becomes:

$$E = i_{coulometry}(t_{out} - t_{in}) R / [V_{aliquot} * i]* 60$$

where $i_{coulometry}$ is the current employed in the coulometric titration and $V_{aliquot}$ is the volume of the vanadate solution used in the analysis.

Appendix 3

The Development of the Polarographic Techniques

Appendix 3

A3 The Development of the Polarographic Techniques

A3.1.1 Aim of Analysis

The evaluation of the modified Stretford process required an estimation of the anodic current efficiencies associated with the regeneration of the vanadium (V) in the process liquor. The current efficiency can be estimated directly by the disappearance of vanadium (IV) or by the appearance of vanadium (V) in solution. Ideally the two analyses should be complimentary. In the presence of sulphide, which reacts with vanadium (V), the current efficiency estimation must also allow for the disappearance of sulphide ion and the appearance of zero-valent sulphur. Lost current efficiency to oxysulphur anions and/or oxygen would complete the study. The ultimate analysis would be to quantify all electrochemical reactants and products in the process liquor. The minimal analytical requirement is for sulphide ion and either vanadium (IV) or (V). Solutions destined for analysis are buffered to pH = 9 and contain carbonate, citrate and one of the following combinations of inorganic ions:

V(IV), V(V)

V(IV), V(V), S^o, $S_2O_3^{2-}$, SO_4^{2-}

V(IV), S^{2-}, S_x^{2-}, S^o, $S_2O_3^{2-}$, SO_4^{2-}

S^{2-}, S_x^{2-}, S^o, $S_2O_3^{2-}$, SO_4^{2-}

A3.1.1 Survey of Analytical Techniques

There are many analytical methods for the determination of the species of interest. Few techniques, however, are applicable to the determination of all these species. This section outlines those techniques with the greatest analytical latitude.

The ring colourimetry and tlc techniques of Handra and Johri [40] allows the qualitative and semi-quantitative analysis of sulphide, sulphite, sulphate, and thiosulphate anions. The techniques were modified for use with a pilot plant run as outlined in Section 3.6.

The titrimetric/selective precipitation methods of Fetzer [20] are labour intensive and could not be made to accomodate the presence of vanadium species in solution. A comprehensive review [48] of sulphur chemistry failed to suggest modifications of Fetzer's methods to deal with vanadium.

Ion chromatography (IC) would be a useful technique for complete process liquor analysis were it not for the difficulties in the detection of the sulphur anions. Three major drawbacks have been identified. Firstly, the UV detection of sulphur anions requires instruments which are capable of operating in the low UV (185 to 200nm), and these are not generally available. Secondly, the use of conductivity detection of sulphide requires an eluent pH > 8 so as to assure a non-volatile and conducting sulphide species. However, solutions buffered to high pH increase the background conductivity, which decreases detector sensitivity, and cannot be used with all column types. Finally, specific electrochemical detectors suitable for sulphide detection are useful only for electroactive species.

The ion chromatographic analysis of vanadium (IV) and (V) or vanadium speciation could not be found in the literature. The results of initial investigations into IC analysis of process liquors is given in Section A3.1.3. A number of established IC techniques for the sulphur anions are described below.

Ion chromatography with ion suppression [49] has been used to separate a mixture of sulphide, thiosulphate and sulphate anions. The sulphate and thiosulphate anions are detected using a conductivity meter, whereas sulphide was detected by its absorption in the low UV (190 to 205nm). A commercially available IC [50] system employing single column ion chromatography with conductivity detection shows good separation of sulphate, thiosulphate, and bicarbonate at pH 3.7 in 4 mM potassium hydrogen pthalate. A change in column type facilitates citrate determination, but sulphide analysis has not been reported with this system. Ion chromatography with conductivity and amperometric detection [51] has been applied to sulphate and sulphide analysis. A Dionex AS4 anion exchange column, with a borate-carbonate mobile phase (pH 9), was used in the study. The authors reported the detection of sulphide down to 30 ppb. A post column reaction-detection system [52] has been used in the determination of thiosulphate, tri, tetra, and pentathionates. These species were detected by their redox reactions with Cerium (IV) yielding a fluorescent Cerium (III) species which is detected.

With low UV detection (210 to 220nm), Reeve [53] has been able to determine thiosulphate, di, tri, tetra, and pentathionate. Hydrosulphide, SH^-, could not be determined since it gave broad peaks possibly due to reaction with oxygen. With an eluent pH 7 the separation may have been complicated by the first acid dissociation of hydrogen sulphide, which was overlooked by the author. With UV detection at 254nm Reeve's methods have employed by Pitts [6] for the analysis of ADA isomers in our laboratory.

Polarography is a readily available analytical technique in our chemistry department. Its application to the analysis of process liquors may be useful in spite of its lack of specificity for carbonate, citrate, and sulphate anions. The usefulness of the technique is discussed below.

Alkaline vanadium (V) can be polarographically determined in the presence of vanadium (IV) [54], although there is some confusion regarding the cathode product in different electrolytes. Sulphide and thiosulphate, are also polarographically active [42,55]. The sulphide ion does not interfere with vanadium (V) determinations since the two are never simultanuously present. The thiosulphate ion does not interfere with vanadium (V) polarography.

Sulphide polarography is complicated by the deposition of insoluable mercury sulphide at the dropping mercury electrode (DME). This deactivates the DME and limits the useful analytical range of sulphide to concentrations below 2 mM. Thiosulphate ion has been reported by Canterford [56,57] to further limit the upper concentration limit of sulphide. The polarographic behaviour of polysulphide is similar to sulphide.

Carbonate, citrate, and sulphate ions are not polarographically active and can be used as inert electrolytes in the analysis.

A3.1.2 Modification of Analytical Techniques

The ring colourimetry and tlc method for sulphur anion determinations was modified to accomodate vanadium (IV) analysis by spraying the chromatograms with alkaline cupric chloride. This reagent produces a green spot for vanadium (V) and a brown-black spot or ring around a white spot for sulphide or polysulphide on a blue-green background. The vanadium (IV) present on the chromatograms is not visuallized.

The HPLC technique of Pitts [6] for ADA analysis was modified with the use of a Wescan 213A ion conductivity detector to accomodate the analysis of sulphate, thiosulphate, and vanadium (IV) and (V). The high concentration and equilibria of carbonate citrate buffer were found to complicate the separation with baseline fluctuations before and after the peaks. The high pH of Stretford liquor required eluent buffering (to protect the column) which decreased the sensitivity of the technique by increasing the background conductivity of the electrolyte. Decreasing the buffer concentrations increased the baseline fluctuations before and after the peaks. These complications, combined with the unknown effects on vanadium speciation and/or complexation in this column, influenced the decision to abandon this approach.

A3.1.3 Summary

No analytical technique surveyed appeared to be readily adaptable to the complete analysis of process-like liquors.

Polarography appeared to be the most promising technique for the minimal analysis of process liquors for a number of reasons. First the polarographic determination of both sulphide and vanadium (V) species has been reported in the literature. Second, vanadium (V) can be determined in the presence of vanadium (IV). Third, the liquor can be sampled directly. This is convenient since the analyte concentrations are acceptable and the speciation of sulphide is confined, at pH 9, to the hydrosulphide ion. Finally the thiosulphate ion, which is a possible by-product of the electro-oxidation process, is polarographically active.

The application of polarography to liquor analysis was felt to be especially promising for two additional reasons. Firstly, the literature seemed to lack clarity with respect to the polarographic responses of sulphide and vanadium (IV) and (V). Secondly, it was felt that the compilation of any electrochemical information about the electroactive species could prove invaluable to the project and should be a priority.

Sulphide and vanadium polarography are reviewed and presented, together with the results of some developmental work, in Sections A3.2 and A3.3.

A3.2 Sulphide Polarography

In an attempt to repeat Canterford's experiments and also to explore the combined responses and analytical ranges of sulphide, polysulphide, vanadium (IV) and (V), thiosulphate, cyanide, and sulphite, the polarographic responses of these anions were investigated in our laboratory. The discussion of vanadium (V) polarography is confined to Section A3.3. This section presents a brief history of sulphide polarography and describes the development of a new proceedure for polarographic sulphide analysis.

A3.2.1 Historical Development

The polarographic response of certain inorganic anions was first recognized by Revenda in 1934. He attributed their anodic waves to an enhanced oxidation of mercury forming mercury salts of varying solubility. The extent of salt solubility distinguishes between two predominate electrode mechanisms. Anions of the first type discharge to form soluable mercury salts which cause the surface dissolution of the Dropping Mercury Electrode (DME). Anions of this type include sulphite, thiosulphate, thiocyanate, cyanide, and hydroxide. The electrode reactions of these anions [42] are shown below (equations A3.93 through A3.97).

$$Hg + 2SO_3^{2-} = Hg(SO_3)_2^{2-} + 2e^- \qquad E(1/2)= -.01 \qquad (A3.93)$$

$$Hg + 2S_2O_3^{2-} = Hg(S_2O_3)_2^{2-} + 2e^- \qquad E(1/2)= -.15 \qquad (A3.94)$$

$$Hg + 2CN^- = Hg(CN)_2 \qquad E(1/2) = -.45 \qquad (A3.95)$$

$$Hg + 2OH^- = Hg(OH)_2 \qquad E(1/2) = +.08 \qquad (A3.96)$$

$$Hg + 2SH^- = HgS + 2H^+ \qquad E(1/2) = -.7 \qquad (A3.97)$$

Sulphide and hydroxide, at high pH, are anions of the second type. These anions anodically discharge to deposit insoluable mercuric sulphide and mercuric hydroxide at the DME (equations and). The deposition of these salts is self-inhibiting [42]. All evidence suggests that sulphide is not formally oxidized on mercury electrodes.

The polarographic behaviour of sulphide is not trivial. Half-wave potentials have been expressed by Duyckaerts [Bard [23: reference 21] as a function of pH and sulphide concentrations as shown below:

For pH < = 5:

$$E_{1/2} = -0.311-0.0591/2\ \mathrm{pH} - (0.0591/2)\log [Na_2S]/2$$

For pH 5 to 9.25:

$$E_{1/2} = -0.311 -(0.0591/2)\log (Na_2S/2 /(H^+(H^+ + 10^{-7.24}))$$

And for pH 9.25 to 13:

$$E_{1/2} = -0.525 -0.0591\ \mathrm{pH} /2 - (0.0591/2)\log [Na_2S]/2$$

The half wave potential for 10^{-3} M sulphide pH 9 is -0.6 volts (SCE) [42]. As many as four waves, some refered to as pre-waves, have been observed from -.7 to 0 volts (SCE). These waves overlap the half-wave potentials of cyanide, thiosulphate, and sulphite.

Polysulphide polarography has been studied by Konopik and Werner [Bard [23: references 32 to 34]. They attributed the polarographic response to the deposition of mercuric sulphide and elemental sulphur (equation A3.98).

$$Hg + S_x^{2-} = HgS + (x-1)\ S^o + 2e^- \qquad (A3.98)$$

In 1973, Canterford [56,57] reported that the total diffusion current, attained with as many as four anodic waves, varied linearly with sulphide concentration below 2 mM. At higher concentrations, the total diffusion current deviates from diffusion control and linearity. Canterford cautioned that since the four sulphide waves span nearly 650 mV, cyanide, sulphite, and thiosulphate anions which discharge in this interval, could interfere with the sulphide analysis.

Canterford's work effectively 'closed the book' on sulphide polarography. The limited analytical concentration range, the need to dilute sulphide solutions to below 2mM, the omnipresent threat of oxygen in the dilutions, and the large number of possible interferences have discouraged the use of Canterford's technique.

A3.2.2 Experimental

Concentrated stock solutions of sodium sulphide, sodium polysulphide, sodium thiosulphate, potassium cyanide, and sodium hydrogen sulphite were prepared using deoxygenated distilled water. The carbonate-citrate buffer was prepared by disolving 20 grams of sodium bicarbonate and 10 grams tri-sodium citrate in 1 litre of distilled water. The solutions were kept in stoppered flasks to minimize contact with aerial oxygen. The concentrated stock solution of vanadium (IV) was prepared by dissolving vanadyl sulphate in deoxygenated carbonate-citrate buffer and adjusting to pH 9 with sodium hydroxide.

Solutions subjected to polarographic analysis were prepared, in situ, by the addition of small aliquots of the stock solutions to a known volume of 0.24 carbonate, 0.034 M citrate buffer, which was previously de-oxygenated and continously blanketed with laboratory nitrogen. An Eppendorf Digital Pipette, model 4710, was used without calibration.

The polarograms were recorded with a Metrohm E506 Polarecord and an E505 polarographic stand. Two Ag/AgCl, saturated KCl, (Metrohm EA427) electrodes were used as the reference and auxillary electrodes. Drop times of 1 second were employed with the DC_t and AC polarographic modes.

Polarograms were recorded from -0.8 to 0.7 volts Ag/AgCl. This potential range encompases the onset of sulphide assisted mercury oxidation at E = -0.6 volts to well beyond the hydroxide assisted mercury oxidation peak at E = 0.0 volts.

The sodium hydroxide, potassium cyanide, and trisodium citrate used in the study were supplied by BDH (AnalaR). The sodium sulphide was supplied by Baker as the 'Baker Analysed' reagent. The solution of sodium polysulphide ion was prepared by dissolving BDH laboratory reagent grade flowers of sulphur in a sodium sulphide solution. The rate of dissolution was significantly enhanced in a Bransonic 220 ultrasonic cleaner. The anhydrous sodium thiosulphate and sodium hydrogen sulphite were obtained as the Fischer certified reagents.

A3.2.3 Results

The use of the current sampling technique in DC polarography has led, in general, to an enormous simplification in the interpretation of the polarographic response. It has not only increased the precision of diffusion current measurements, but has simplified multiple wave polarograms by visually presenting them in a more understandable manner. This simplification plays an important role in the investigation of sulphide polarography.

The DC_T polarogram recorded for 0.48 mM sulphide in a carbonate-citrate buffer is a case in point. The curve shown in Figure A3.2.1 can be compared with Canterford's 4×10^{-4} M sulphide in 1 M $NaClO_4$ [56]. The most evident feature of the DC_T polarogram is the discontinuous start of the diffusion wave at E = -0.698 volts. This discontinuous start is not observed in sodium hydroxide solutions and has been attributed to the specific adsorption of sulphide ion at the DME [56]. The inflection in the curve at E = −0.644 suggests that a prewave exists to the main wave which reaches a steady state diffusion current at E = −0.572 volts. Over the next 360 mV the diffusion current remains relatively constant. The constant current region gives way to a gentle wave with a half-wave potential of $E_{1/2}$ = −0.122 volts. In addition to these three waves, there is a sudden increase in diffusion current at E= 0.07 v. The current increases in small jumps (prewaves?) to merge with the hydroxide assisted mercury dissolution peak which starts at E = 0.13 volts. The hydroxide dissolution peak is shown clearly in Figure A3.2.2.

The first two waves are consistent with those reported by Canterford, and others, at this sulphide concentration. The small wave, at $E_{1/2}$ = −0.122 volts, may perhaps be attributed to a trace of thiosulphate in the solution.

The composite polarogram, shown in Figure A3.2.2, depicts curves recorded for successive (equal) additions of sulphide stock solution to a near constant volume of buffer. Notice that curve a shows only a narrow increase in diffusion current, with respect to curve b, due to incomplete stirring of the stock solution aliquot in the cell. Addition of the third aliquot, with subsequent stirring, yields a sulphide diffusion current which is appropriately three times the magnitude of the diffusion current in curve b.

The increases in diffusion current per aliquot, measured arbitrarily at E = −0.14v, are 2.3, 4.3/2 = 2.15, 4.3/2 = 2.15, 2.3, and

Figure A3.2.1 The DC_T Polarogram for 0.48 mM Sulphide in 0.24 M carbonate, 0.034 M citrate buffer, pH 9.

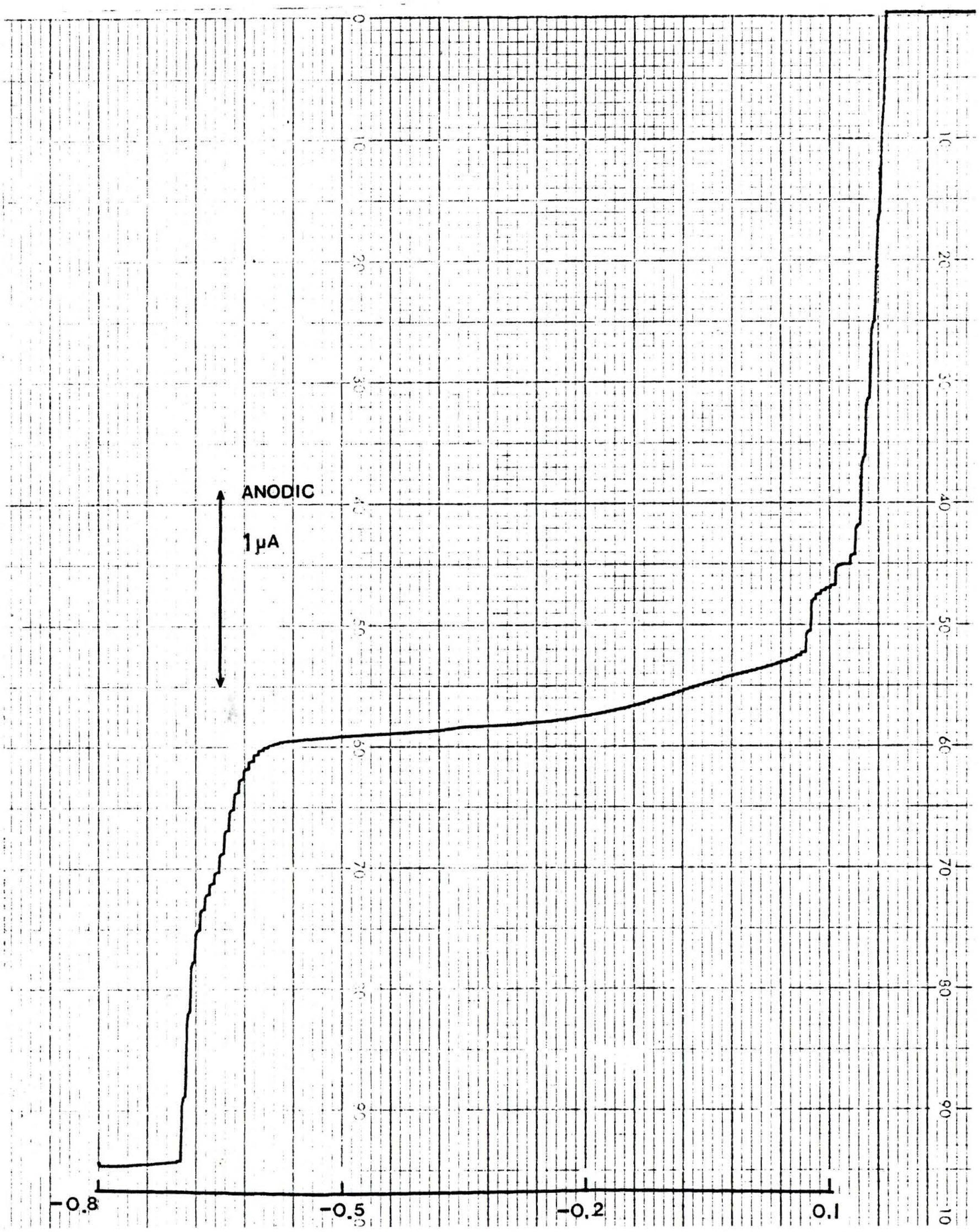
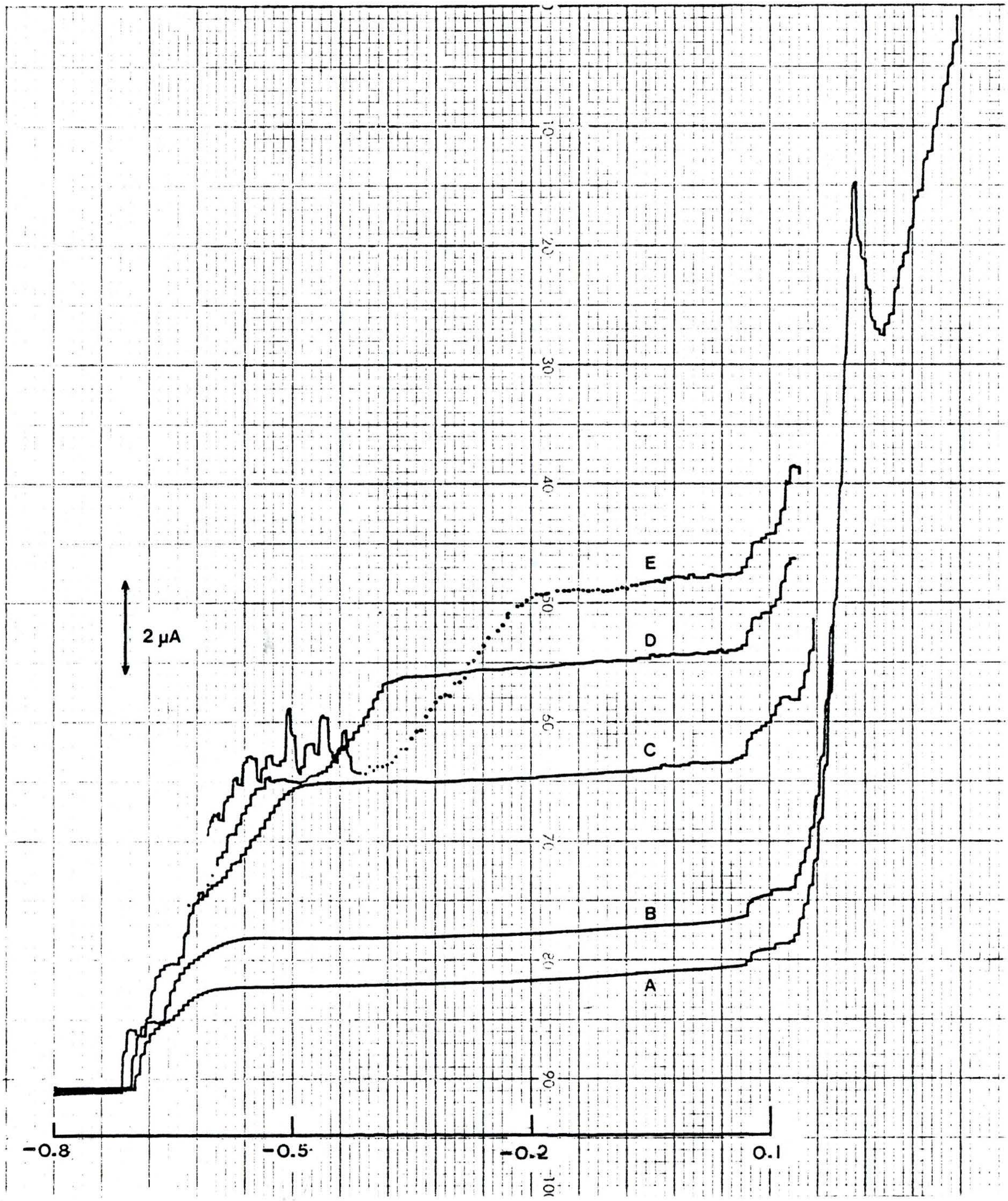

ANODIC
1µA
-0.8
-0.5
-0.2
0.1

Figure A3.2.2 A composite of polarograms for six sulphide concentrations: 0.48 (a), 0.96 (b), 1.44 (c), 1.92 (d), and 2.44 mM (e).


2 μA
E
D
C
B
A
−0.8
−0.5
−0.2
0.1
10
20
30
40
50
60
70
80
90
100

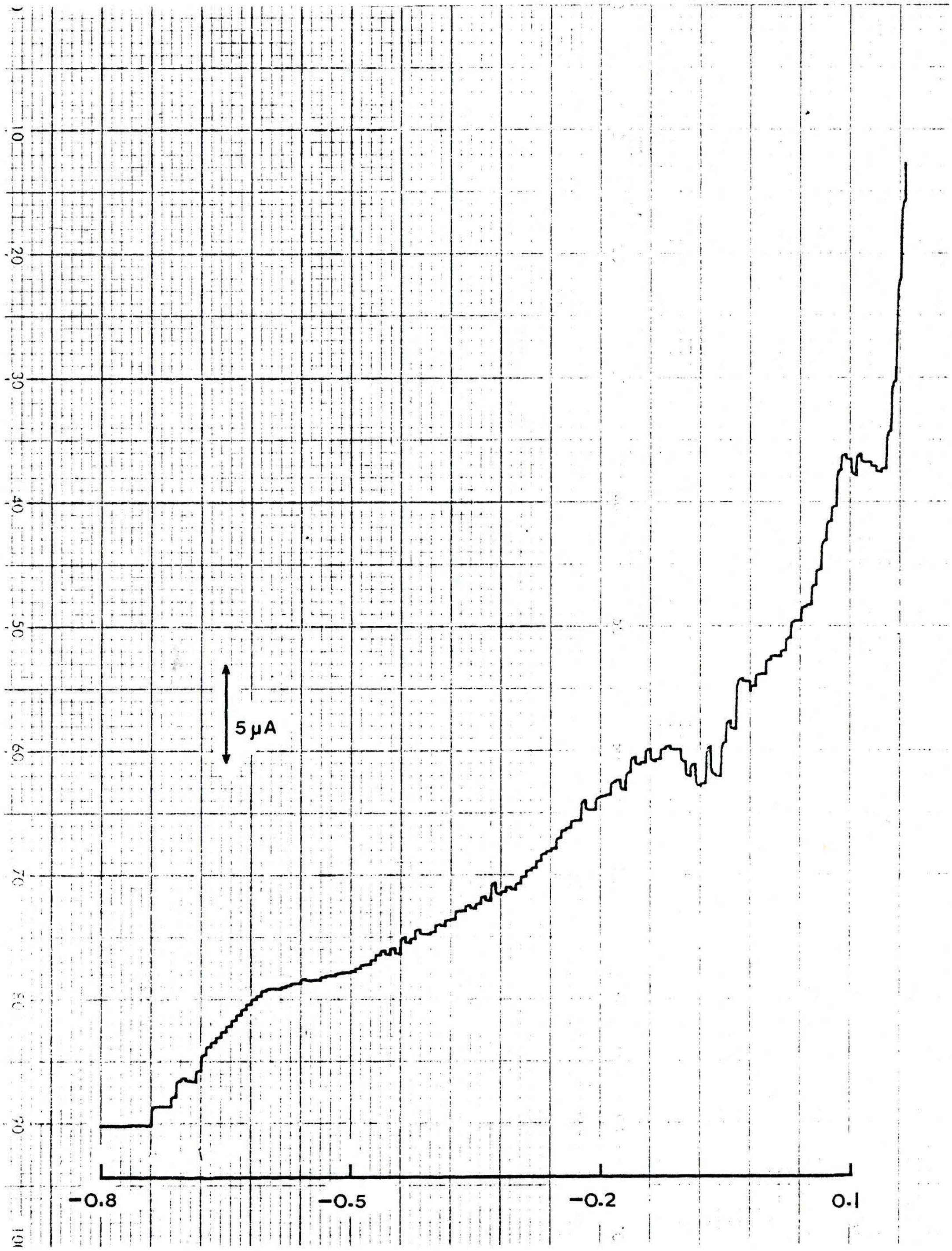
1.5 cm. The deviation at the highest sulphide concentration, 2.4 mM, from an otherwise linear relationship between concentration and diffusion current is in agreement with Canterford who reported deviations from linearity above 2 mM.

With increasing concentration, the first and second waves shift towards less anodic potentials. At a sulphide concentration of 1.44 mM (curve c) a third and fourth waves appear with half wave potentials of -0.632 and -0.56 respectively. The presence of these waves is in accordance with Canterford's observations of 1.5 mM sulphide solution. At 1.92 mM sulphide (curve d) the fourth wave shifts towards, and merges with, the third wave and a fifth wave is visible at E = -0.416 volts. The fifth wave shifts, by nearly 130 mV, with an increase in the sulphide concentration to 2.44 mM (curve e). The fifth wave has not been previously reported.

The polarogram shown in Figure A3.2.3 was recorded for 12 mM sulphide. The fifth wave has receded anodically and assumed a curvature that approximately matches the prewaves to the hydroxide peak. The gentle wave at E = -0.122 volts is not visible in this polarogram.

The shift of the fifth wave to more anodic potentials, with increasing sulphide concentration, and the overall shape of the 12 mM curve, including all irregularities and inflections, is consistent with the deposition of HgS and all the growing pains associated with the thickening of this layer. That the mercury drops are coated with HgS is immediately obvious from the spent drops which collect in the bottom of the cell. These do not coalesce as mercury normally does, but accumulate as a growing 'pool of beads'.

Figure A3.2.3 The polarogram of 12 mM Sulphide ion with Triton X-100.


5 μA
−0.8
−0.5
−0.2
0.1
10
20
30
40
50
60
70
80
90
100

The deposition of HgS at the DME should either inhibit, or retard, the electrochemical response of thiosulphate. On the contrary, the addition of as little as 0.6 mM thiosulphate causes a considerable increase in the current flow in the vicinity of the thiosulphate wave (curve b Figure A3.2.4). Increasing the thiosulphate concentration to 1.8 mM yields a discontinuously starting, but otherwise well defined, thiosulphate wave exhibiting a sizable diffusion current. By comparison with curve d, which is the polarographic response for 1.8mM thiosulphate alone, it is evident that there is an enhanced discharge of thiosulphate in the presence of sulphide.

The composite of polarograms shown in Figure A3.2.5 shows the response for sulphide ion in with sucessive additions of thiosulphate ion. In the presence of sulphide, every thiosulphate wave starts discontinuously from on top of the sulphide wave and undergoes the same short steep rise preceding the development of a current plateau. The constant plateau current increases in equal steps (linearly) with thiosulphate concentration. That the enhancement of the thiosulphate discharge occurs only once suggests that this is not a simple electrocatalysis.

The composite of polarograms shown in Figure A3.2.6 depicts the influence of successive increases in sulphide concentration on the enhanced response in the vicinity of the thiosulphate wave. The enhanced wave responds linearly with sulphide concentration. By comparison of Figures A3.2.5 and A3.2.6 it is evident that the increase in the diffusion current for 6 mM sulphide in the presence of either 3.68 mM or 9.2 mM thiosulphate are identical.

Figure A3.2.4 A composite of Polarograms for 12 mM sulphide and various thiosulphate concentrations. 0 (a), 0.6 (b), and 1.8 mM (c). The response of 0 (d) and 1.8 mM (e) thiosulphate ion in the absence of sulphide ion is shown.

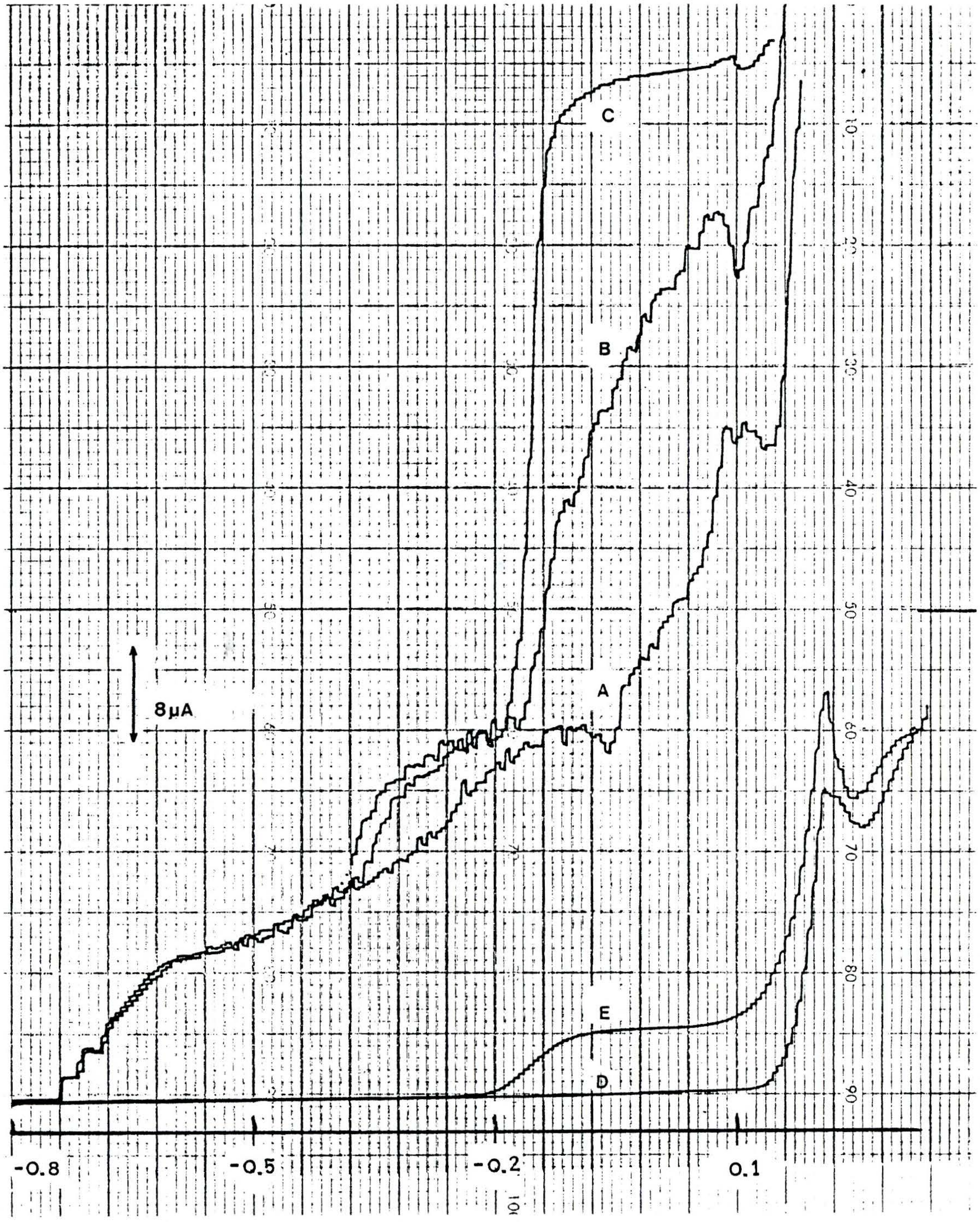

C
B
A
E
D
8μA
-0.8
-0.5
-0.2
0.1

Figure A3.2.5 The diffusion currents of 6 mM sulphide ion with sucessive thiosulphate spikes. The polarographic waves for 3.68 mM thiosulphate (a), 3.68 mM thiosulphate + 6 mM sulphide (b), and with sucessive increases in thiosulphate concentration in steps of 3.68 mM (c,d,e,f, and g).

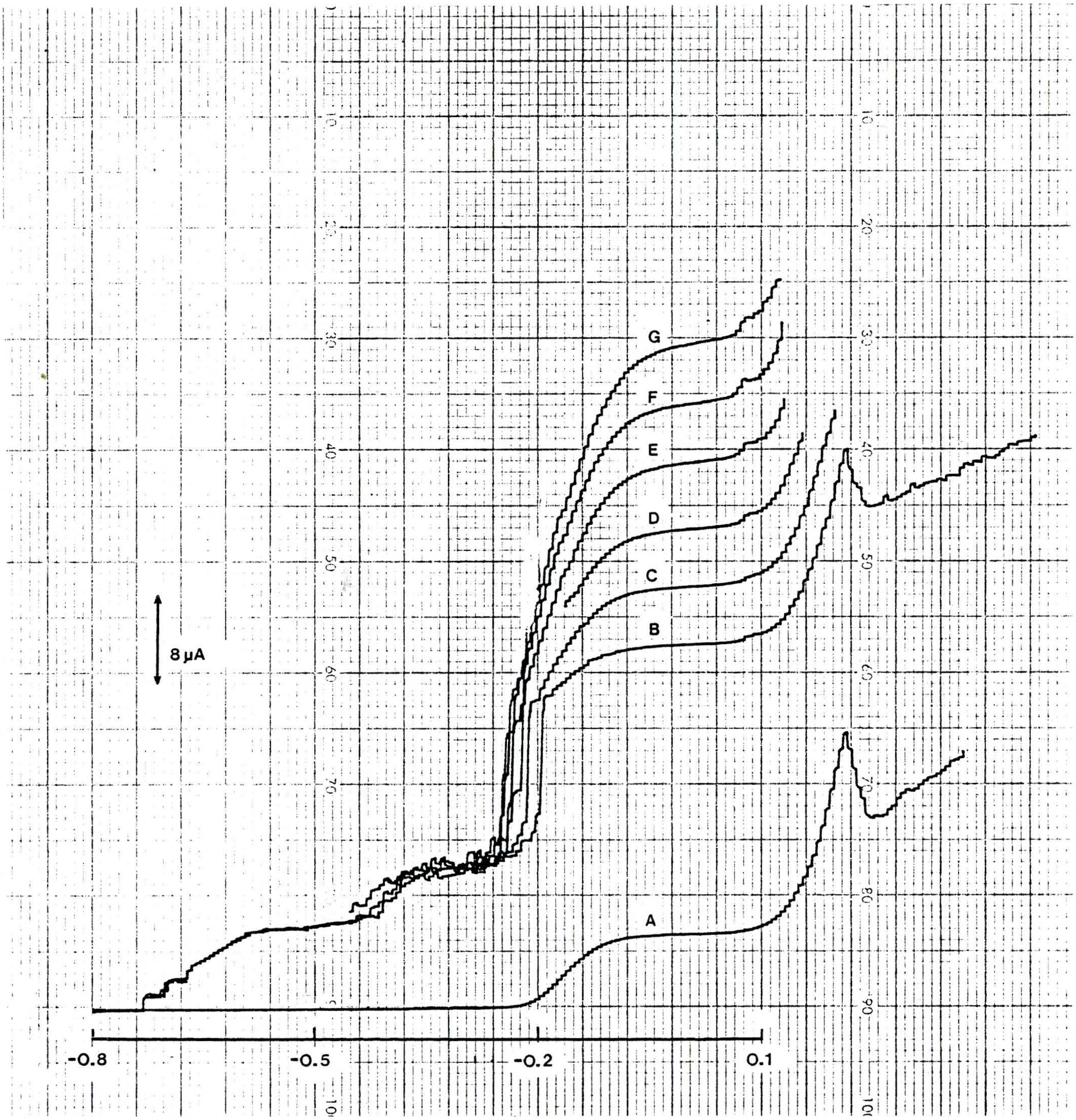
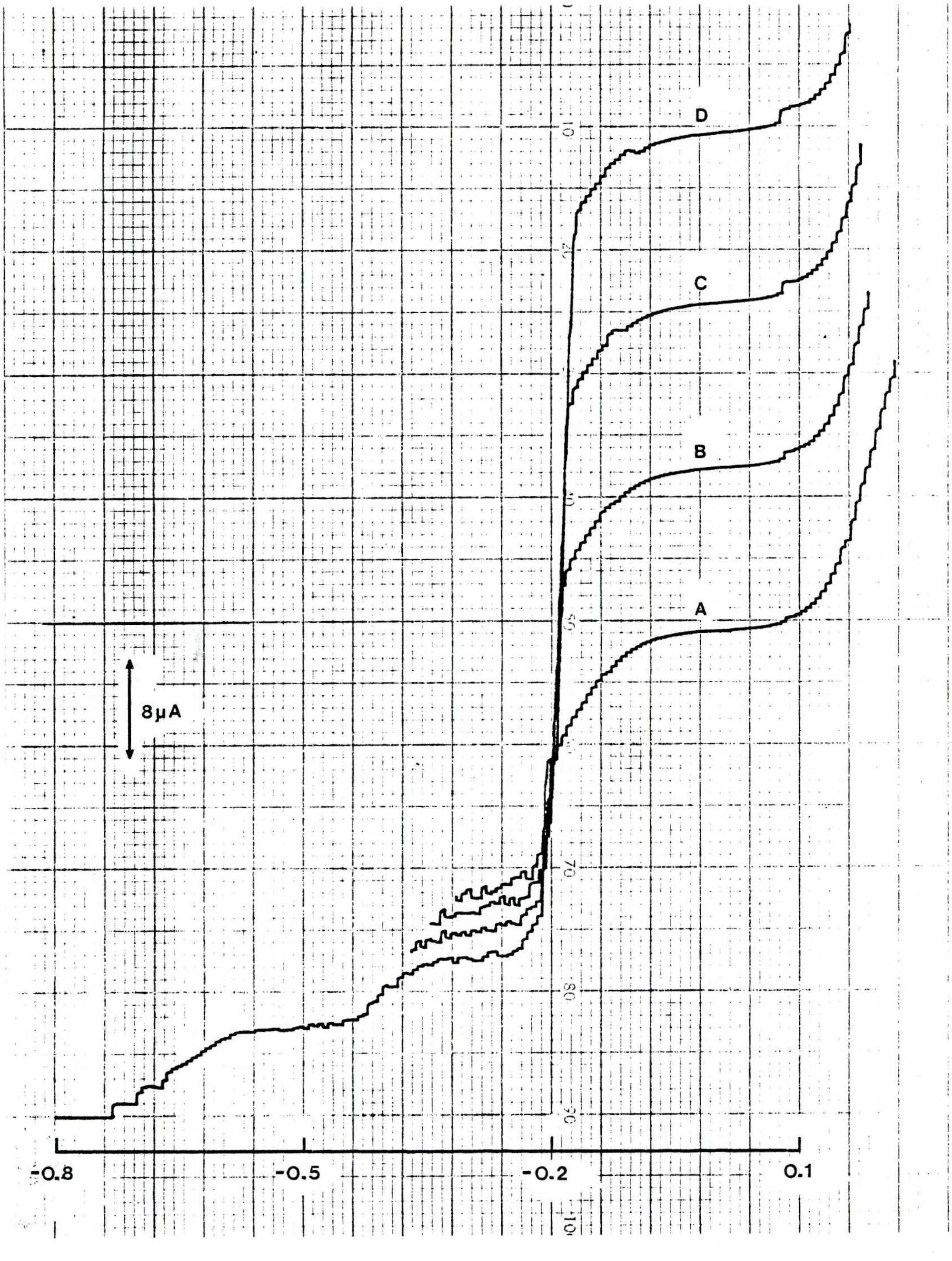

G
F
E
D
C
B
A
8 µA
-0.8
-0.5
-0.2
0.1
10
20
30
40
50
60
70
80
90
100

Figure A3.2.6 The diffusion currents of 9.2 mM thiosulphate with sucessive sulphide spikes. Curve a shows the response of 9.2 mM thiosulphate with 6 mM sulphide ion. The remaining curves depict the response for successive 3 mM increases in sulphide concentration up to 15 mM.


D
C
B
A
8µA
-0.8
-0.5
-0.2
0.1

An enhanced response for sulphide ion is not confered solely by thiosulphate ion. Similar responses are observed in the presence of cyanide ion (Figure A3.2.8), sulphite ion (Figure A3.2.7), and on the hydroxide plateau (Figure A3.2.9). Similar effects were observed with vanadium (IV) ion, but these were not entirely reproducible.

In addition, equal concentrations of sulphide and polysulphide ions show virtually identical enhanced waves. The phase selective AC polarogram of the enhanced waves (not shown) indicates that the response is faradaic in nature. The polarographic responses of polysulphide ion are shown in Figure A3.2.10.

A3.2.4 Discussion

The enhanced response for sulphide ion was first observed on the hydroxide plateau at potentials more anodic than 0.34 volts (vs Ag/AgCl, sat.KCl). The current flow on the plateau was found to vary with sulphide, cyanide, sulphite and thiosulphate ion concentrations. This was not identified in the literature search. On further investigations, the isolated enhancements were found to be coincident with the half-wave potentials for the individual ions. This was also as not identified in the literature search.

The anions which confer an enhanced response for sulphide share a common property -they anodically discharge at mercury to form slightly soluable mercury salts. These salts provide a mechanism with which to explain the phenomenon. The slightly soluable salts allow mercury to be anodically dissolved from the mercury drop surface into the electrolyte. There it reacts with sulphide ion to form mercuric sulphide. The mercuric sulphide formed in this manner does not passivate the DME.

Figure A3.2.7 The sulphite enhanced wave for 12 mM sulphide

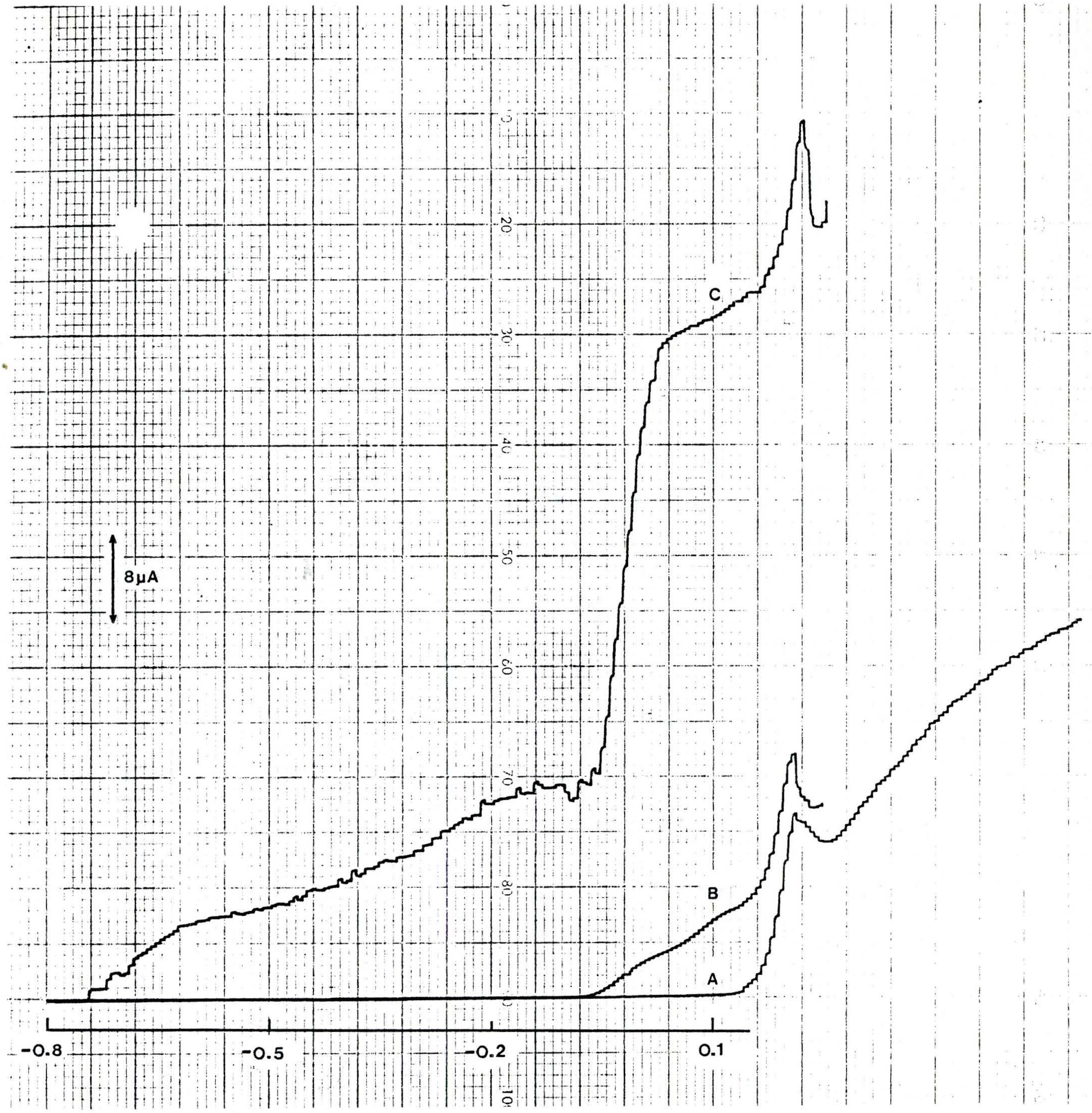

8μA
C
B
A
-0.8
-0.5
-0.2
0.1
20
30
40
50
60
70
80
10

Figure A3.2.8 The cyanide enhanced wave for 12 mM sulphide.

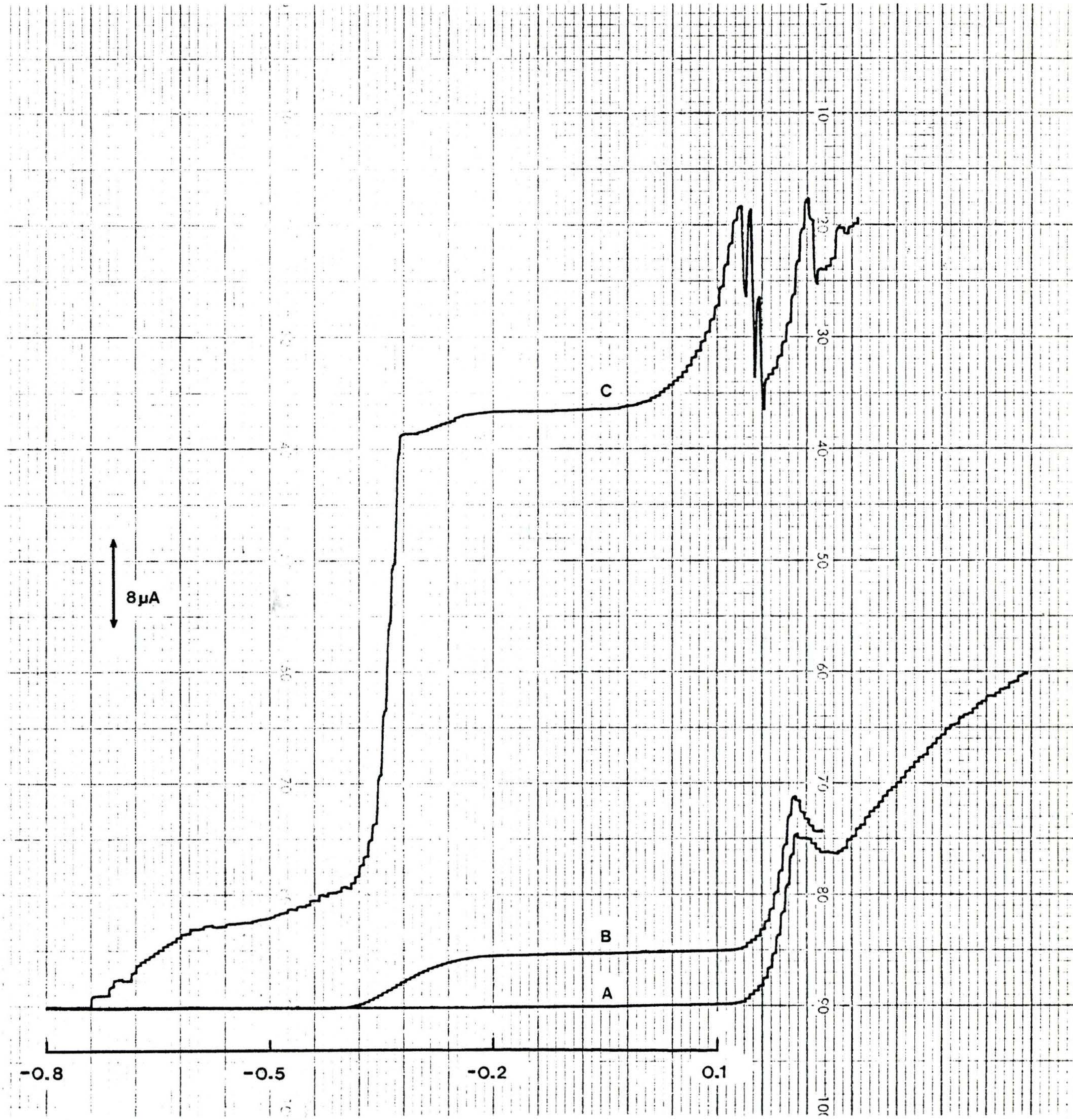

C
B
A
8 μA
-0.8
-0.5
-0.2
0.1

Figure A3.2.9 The hydroxide enhanced wave for 4 mM sulphide ion increments.

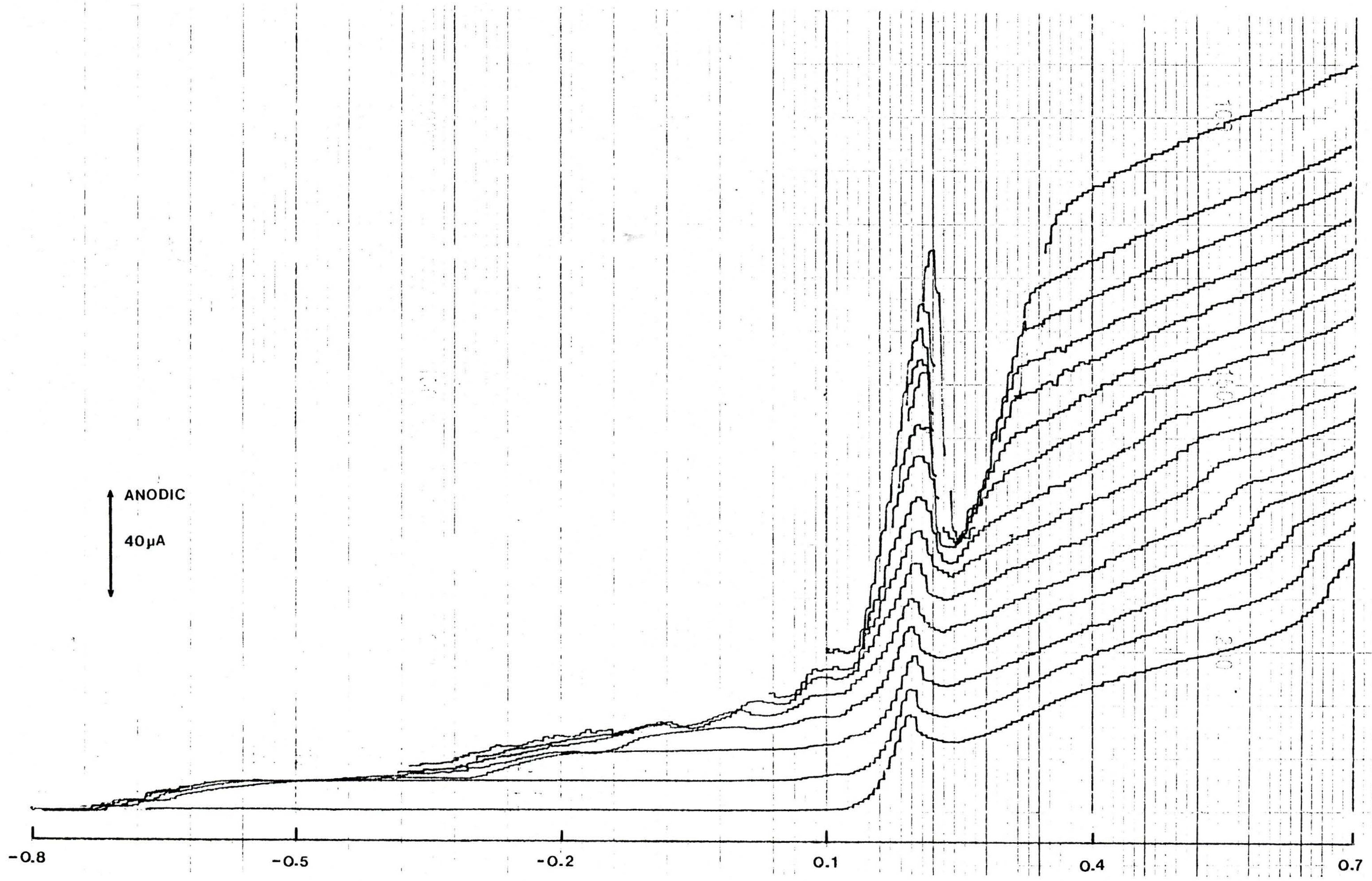
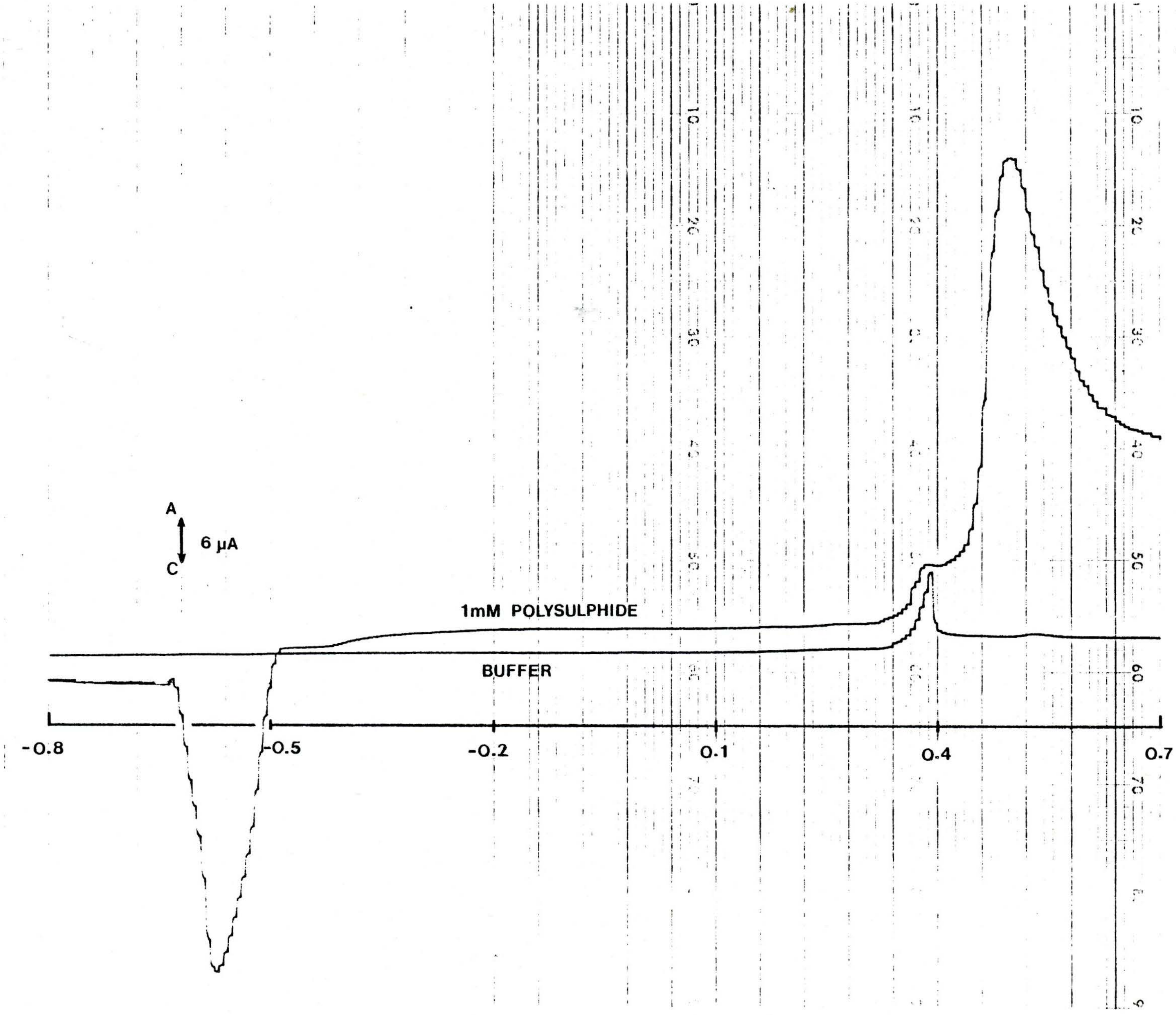

ANODIC
40μA
−0.8
−0.5
−0.2
0.1
0.4
0.7

Figure A3.2.10 The polarographic responses of polysulphide.


A
6 µA
C
1mM POLYSULPHIDE
BUFFER
-0.8
-0.5
-0.2
0.1
0.4
0.7

This mechanism can be summarized in the following form:

$$Hg + 2S_2O_3^{2-} = Hg(S_2O_3)_2^{2-}$$

$$Hg(S_2O_3)_2^{2-} + S^{2-} = HgS + 2S_2O_3^{2-}$$

$$Hg + S^{2-} = HgS$$

The formation of mercuric sulphide in the solution surrounding the mercury drop may explain why equal concentrations of sulphide and polysulphide give similar responses. The sulphide or polysulphide diffusion layer at the mercury surface will be dependent on concentration, but the diffusion coefficients for the mercuric complex and the isolated anions from this complex must influence the electrochemical response more than the sulphide and polysulphide diffusion coefficients. It should be noted that the cyanide and sulphite anions are unsuitable for enhancing polysulphide discharge since these species react with polysulphide to form thiocyanate and thiosulphate ions by the following reactions:

$$S_x^{2-} + CN^- = S_{x-1}^{2-} + SCN^-$$

$$S_x^{2-} + SO_3^{2-} = S_{x-1}^{2-} + S_2O_3^{2-}$$

Furthermore sulphite is generally unsuitable since the plateau currents are insufficiently developed before merging with the hydroxide assisted mercury dissolution wave. Hydroxide ion is also an unsuitable reagent since it gives rise to large plateau currents.

There are two requirements necessary to support the proposed mechanism. The sucession of new mercury drops allows the dissolution reactions to start on clean mercury surfaces at the requisite potentials. Heavily passivated mercury drops formed at lower potentials should be less reactive. Second, the formation of soluable sulphite, thiosulphate, or cyanide complexes of mercuric ion must be kinetically prefered over the deposition of mercuric sulphide at the mercury drop surface.

This type of polarographic mechanism for sulphide discharge should be observable with electroactive reagents which form soluable mercuric complexes. Two potentially useful reagents that were not investigated were EDTA, E(1/2) = -0.112 volts, and thiocyanate ion, E(1/2) = -0.18 volts. Citrate, carbonate, and bicarbonate anions may play a role in the dissolution reactions but are not electroactive at mercury.

The reduction maxima for polysulphide ion (Figure A3.2.10) may be attributed either to the reduction of polysulphide sulphur to sulphide or the reduction of chemically oxidized mercury. The reduction maxima should be investigated.

A3.2.5 Analytical Method

The proceedure used in the polarographic analysis of sulphide ion was derived from the method of Standard Addition. The response for sulphide is determined by measuring its combined response with thiosulphate, then subtracting the response of thiosulphate alone.

The diffusion wave height for the thiosulphate wave is measured, at a potential of -0.14 volts (Ag/AgCl, sat. KCl). This value was chosen as one closest to the half-wave potential of most of the enhanced thiosulphate waves. An arbitrary potential was chosen because of the irregular wave shape, even though it was recognized that the half-wave potential for thiosulphate is not a constant [42]. The current at this potential was taken as the difference between the extrapolated linear plateau of the enhanced wave and the current extrapolated from before the sulphide wave. The current flow prior to sulphide discharge is identical with the current flow in a carbonate citrate buffer in the absence of depolarizers.

A stepwise procedure for obtaining sulphide concentrations from polarographic data is described below:

Record the polarogram of an unknown sulphide solution. An enhanced wave verifies the presence of thiosulphate in the sample. (sensitive to approx 1 mM thiosulphate).

Record the diffusion wave, id 1, for the unknown sulphide solution with a measurable quantity of thiosulphate ion.

Record the diffusion wave, id 2, for the unknown sulphide solution with twice the measurable quantity of thiosulphate ion.

Record the diffusion wave, id 3, for the unknown sulphide solution with a measurable quantity of thiosulphate ion and a known quantity of sulphide ion (spike).

The difference in wave heights between id 1 and id 2 corresponds to the response of the measurable quantity of thiosulphide.

Subtracting the measurable quantity of thiosulphate from id 1 and id3 gives the response for sulphide present in the unknown and the spiked unknown respectively.

The sulphide concentration can be calculated using the following equation:

$$[S^{2-}] = \frac{[id_{1s} - (id_{2s} - id_{1s})]\ C_s\ V_s}{(id_{3s} - id_{1s})\ V_{cell} + V_s(id_{3s})}$$

$$= \frac{[2id_{1s} - id_{2s}]\ C_s\ V_s}{[id_{3s} - id_{1s}]\ V_{cell}\ + id_{3s}\ V_s}$$

$$= \frac{[2id_{1s} - id_{2s}]\ C_s\ V_s}{[id_{3s} - id_{1s}]\ V_{cell}}$$

where

C_s= the concentration of the spiking solution

V_{cell}= volume in polarographic cell

V_s = volume of spiking solution

id_{1s} = diffusion current for unknown with thiosulphate spike

id_{2s} = diffusion current for unknown with two thiosulphate spikes.

id_{3s} = diffusion current for unknown with sulphide and thiosulphate spikes.

A3.2.6 Summary

The study revealed a previously un-reported catalytic response for the determination of sulphide and polysulphide anions. The catalytic response arizes from the anodic dissolution of mercury by cyanide, sulphite, or thiosulphate anions which forms slightly soluable mercuric salts and mercuric complexes in solution. These complexes are thought to react with sulphide or polysulphide ion to form mercuric (poly) sulphide and regenerate the complex anion.

The thiosulphate is the anion most suited to reveal the true response of sulphide since cyanide and sulphite ions are consumed in the presence of polysulphides. The analytical range of sulphide parallels that of thiosulphate. By the same mechanism, thiosulphate concentrations of approximately 2 mM can be detected in the presence of sulphide ion.

It must be noted that there was a tendency for sulphide and thiosulphate solutions to react with elemental mercury which accumulates in the polarographic cell. For this reason, the solutions were deoxygenated then placed at the DME station for analysis.

The anions which confer an enhanced response for sulphide share a common propertyµ they anodically discharge at mercury to form slightly soluable mercury salts. These salts provide a mechanism with which to explain the phenomenon. The slightly soluable salts allow mercury to be anodically dissolved from the mercury drop surface into the electrolyte. There it reacts with sulphide ion to form mercuric sulphide.

In retrospect, it is apparent that Canterford's four wave analysis of sulphide is an ad hoc approach to a complex problem. The discharge of sulphide at mercury procedes with the autosuppression of the response. Any substance which discharges on the surface and leads to a dissolution of mercury will remove the suppression. It is ironic that the Canterford's attention to improving sulphide solution purity decreased the likelihood of observing the enhanced responses.

A3.3 Vanadate Polarography

A3.3.1 Introduction

The polarographic oxidation of vanadium (IV) ion is well documented with reported half-wave potentials of -0.51 to -0.22 volts (S.C.E.) in different media (Table A3.3.1). The electrode reaction has been attributed to the oxidation of vanadium (IV) to vanadium (V).

The polarographic responses of vanadium (V) are more diverse. The reduction potentials for vanadium (V) vary with the electrolyte, the presence of complexing reagents, and the reduction product. In most media, the vanadium (V) is reduced sucessively to vanadium (IV) then tho vanadium (II) at potentials more negative than -1 volts. In 1 M NaOH, 1 M KCNS, or 0.3 M triethanolamine + 0.1 M KOH, vanadium (V) is reduced a potentials of -0.39, -0.49, and -0.34 volts (Ag/AgCl, sat KCl) respectively [54].

The final oxidation state for the cathodic reduction of vanadium (V) was reported by Filipovic, et al. to be vanadium (II) [58]. This was infered, in part, from the enhancement of the -1.1 volt wave by nitrate ion. Specifically the enhancement was attributed to the πcontinuous oxidation of +2 vanadium (produced by electroreduction).π It should be noted that Selbin [9] has attributed the unsucessful synthesis of nitrato vanadium (IV) salts to the πease with which the oxidation of vanadium (IV) by nitrate ion occurs.π The ramifications of this inconsistency to vanadium polarography are difficult to access.

The final product in the polarographic reduction of vanadium (V) has been identified in a number of ways including the comparison of the reduction waves for vanadium (IV) and vanadium (V) ions. In the majority of the tabulated [59,60] reduction potentials, the apparent reducibility of vanadium (IV) may be attributed to the lack of precaution against aerial oxygen and the presence of vanadium (V) in solution. The vanadium (IV) ion is not reducible in sodium hydroxide or carbonate buffers, but the existence of a double wave for vanadium (V) or a single wave for vanadium (IV), near -1.1 volts, in ammonia/ammonium buffers apparently confirms the reduction to the vanadium (II) ion [61].

A3.3.2 Results and Discussion

The voltamograms recorded for vanadium (V) in 0.24 M carbonate buffer, pH 9, show well defined diffusion waves at -1.06 volts (Ag/AgCl, sat KCl) in Figure A3.3.1. In 1 M carbonate buffer the half-wave potentials are shifted to -0.869 volts. The addition of Triton X-100 is necessary to supress a polarographic maxima. The linear variation of diffusion wave height with vanadium (V) concentration and the negligible effect of the vanadium (IV) ion on the wave confirms the usefulness of the response in vanadium (V) analysis.

The observation of a current maxima, with a half-wave potential of 0.3 to 0.35, in front of the vanadium (V) reduction wave is in agreement with the observations of Filipovic, et al. The magnitude of the current flow in the current maxima varies with vanadium (V) and carbonate concentrations. The maxima is shifted anodically at the higher carbonate concentrations and can be entirely suppressed with thiocyanate ion (although thiocyanate ion has a minimal effect on the wave at -1.06 volts). The maxima may be attributed to the electrochemical reduction of mercuric ion formed from the chemical oxidation of mercury by vanadium (V) [12,61,58].

It is quite suprising that the polarographic response of added vanadium (IV) should terminate and blend so smoothly with the vanadium (V) maxima as shown in Figure A3.3.3. (In the absence of vanadium (V), the vanadium (IV) wave terminates at the buffer only baseline). This may imply that the vanadium (IV) oxidation wave arises from the assisted oxidation of mercury and not the formal oxidation to vanadium (V). Further study is required to resolve this conflict.

Figure A3.3.1 Successive 5 mM additions of vanadium (IV) in 0.24 M buffer.

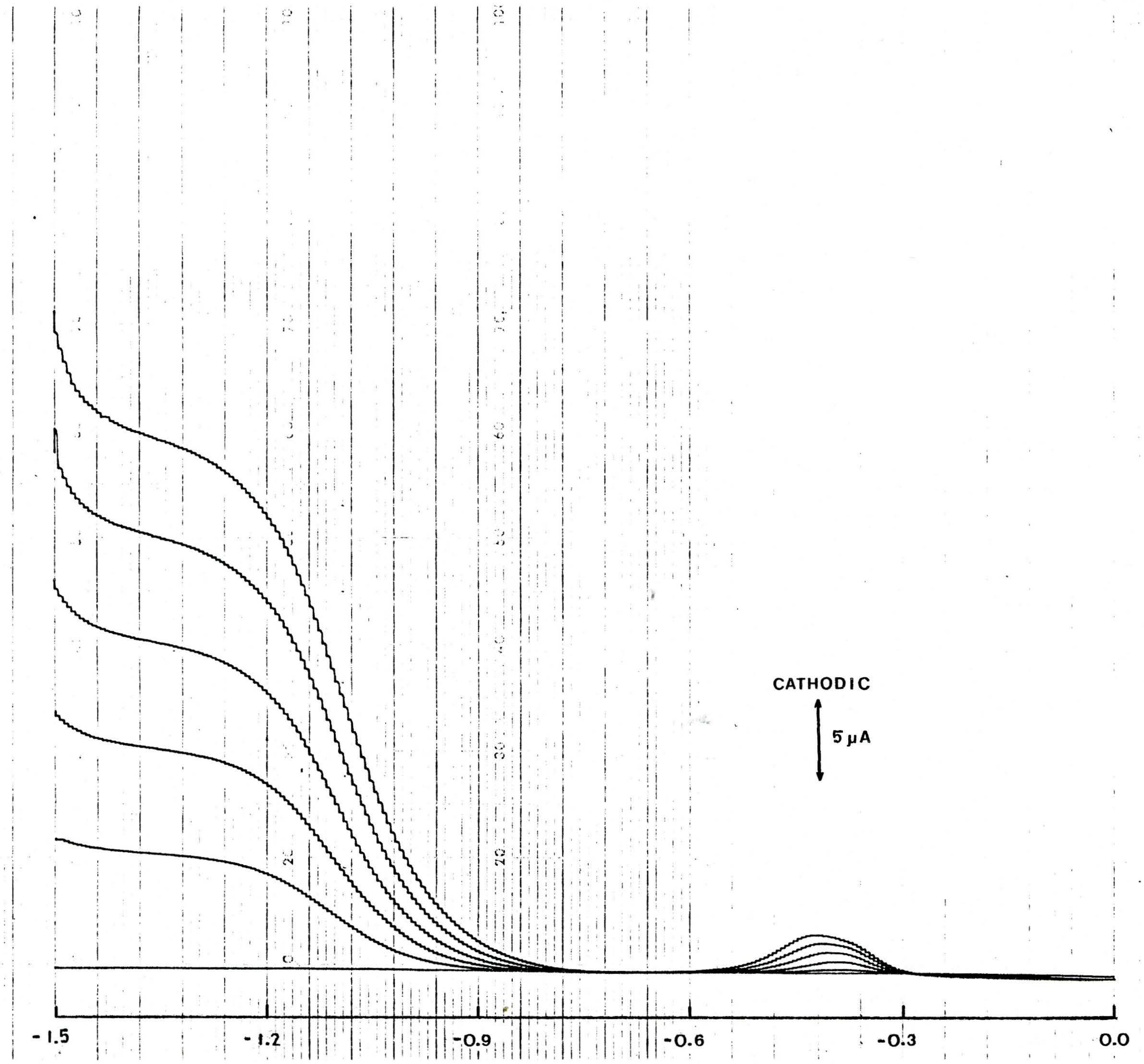

CATHODIC
5 μA
-1.5
-1.2
-0.9
-0.6
-0.3
0.0

Figure A3.3.2 Successive 5 mM additions of vanadium (IV) in 1.2 M buffer.

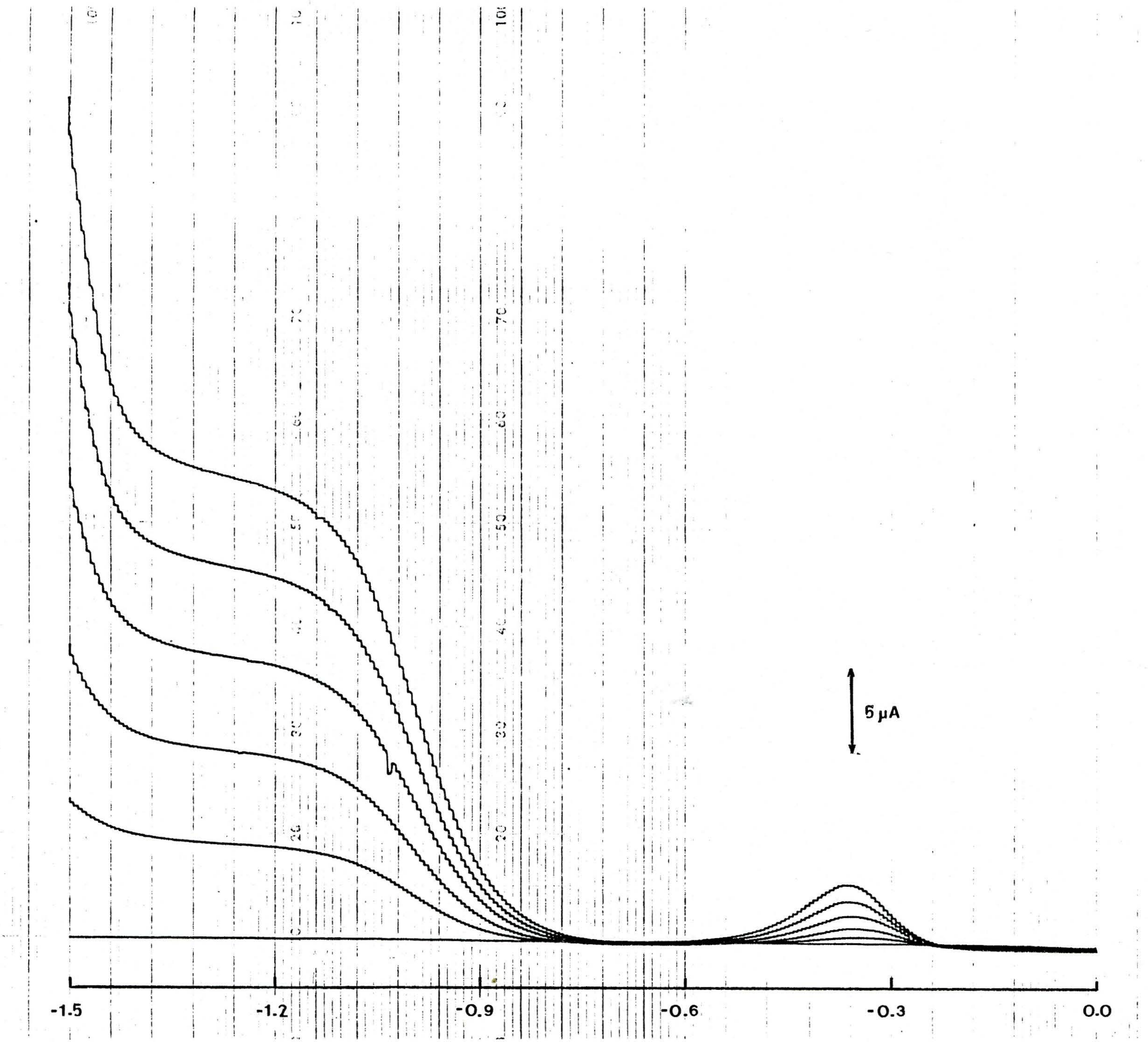

5 μA
-1.5
-1.2
-0.9
-0.6
-0.3
0.0
20
30
40
50
60
70

Figure A3.3.3 25 mM vanadium (V) with successive 5 mM additions of vanadium (IV) in 1.2 M buffer.

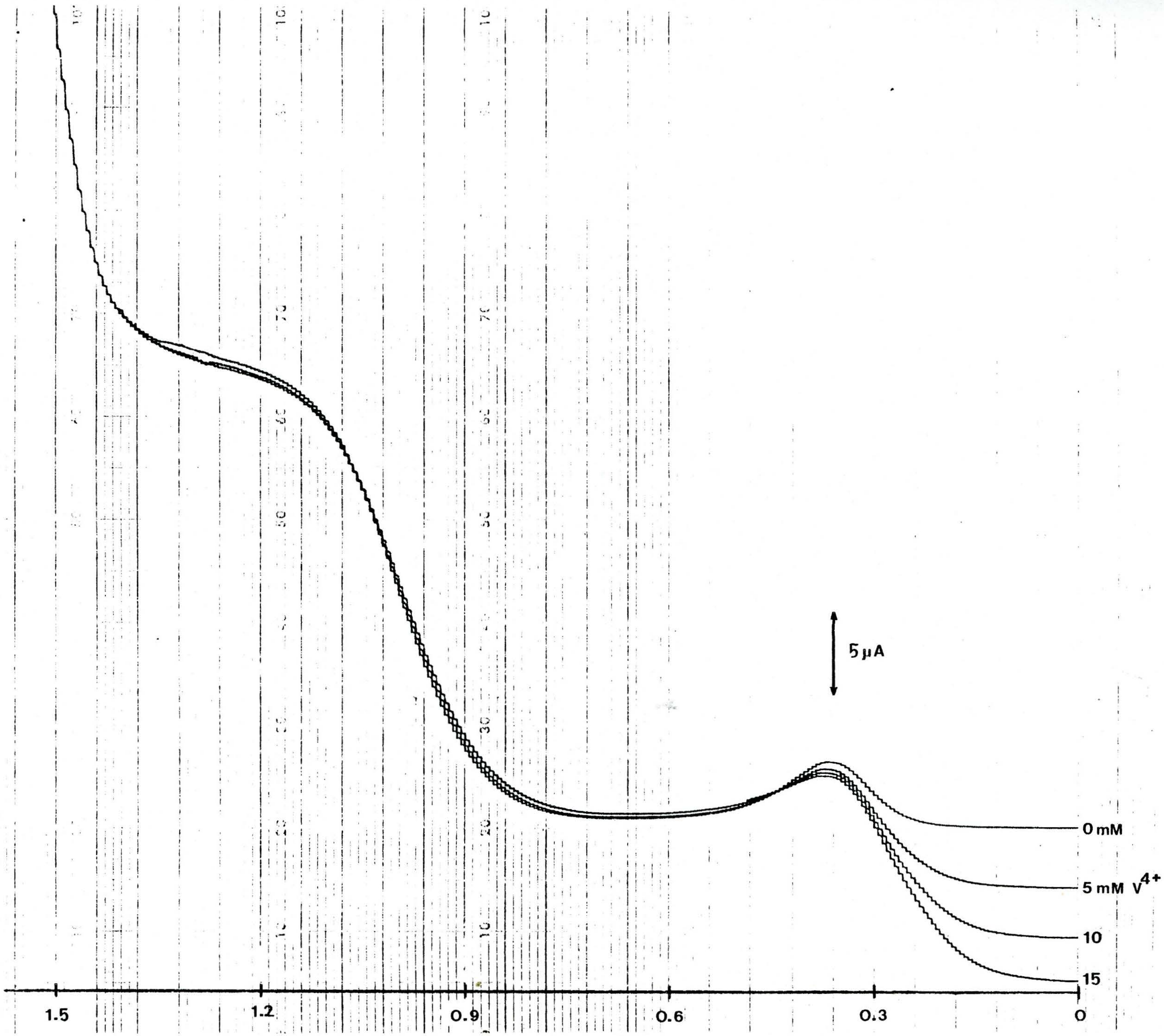

5 μA
0 mM
5 mM V4+
10
15
1.5
1.2
0.9
0.6
0.3
0

Table A3.3.1

Polarographic studies of Vanadium (IV) and (V)

Species	Product	E(1/2)	Comments
v(IV)	v(V)	-.432	1 M NaOH [61]
		-.22	1M bicarbonate pH 7.6 [58]
		-.41	0.25 M tartrate, 2 M NaOH [60]
		-.342	0.5 M carbonate, 0.5 M bicarbonate pH = 9.4 [62]
		-.30	1 M NaOH, 0.08 M sulphite, 1 M KSCN [62]
		-.32	1 M NH_3/1 M NH_4Cl, 0.08 M sulphite [61]
		-.38	1 M malonate, 0.2 M carbonate, 0.2 M bicarbonate, pH=10.0 [59]
		-.44	1 M malonate, 1 M NaOH [59]
		-.51	1 M Lactate, 1 M NaOH [59]
v(IV)	v(II)	-1.2	1 M NH_3/1 M NH_4Cl, 0.08 M sulphite [61]
		-1.17, -1.59	(prewave) 1 M malonate, 0.2 M carbonate, 0.2 M bicarbonate, pH=10.0 [59]
		-1.68	1 M malonate, 1M NaOH [59]
		-1.70	1 M lactate, 1 M NaOH [59]

Table A3.3.1 continued

Species	Product	E(1/2)	Comments
v(V)	v(IV)	-1.8	1 M NaOH [61]
		-1.86	0.25 M tartrate, 2 M NaOH [60]
		-1.3	Carbonate buffers, pH 9 to 12 [58].
v(V)	v(II)	-1.07,	1 M NH_3/1 M NH_4Cl [61]
		-1.22	Stepwise reduction to V(II)
		-1.18,	1 M malonate, 0.2 M carbonate,
		-1.59	2 M bicarbonate, pH=10.0,
			stepwise reduction to v(II) [59]
		-1.67	1 M malonate, 1 M NaOH [59]
		-1.71	1 M Lactate, 1 M NaOH [59]
v(V)	v(IV)	volts	vs Ag/AgCl, sat. KCl [52]
		-1.11,	
		-1.29	1 M NH_3, 1 M NH_4Cl
		-1.09	1 M KCl
		-1.18	1 M KCN
		-1.00	1 M NaF
		-1.10	1 M HCl
		-0.39	1 M NaOH
		-1.02	0.1 M KNO_3
		-0.49	1 M KCNS
		-0.34	0.3 M triethanolamine, 0.1 M KOH

APPENDIX 4

THE DETERMINATION OF VANADATE BY COULOMETRIC TITRATION

This section describes the apparatus used in the coulometric titration of vanadate ion. This was section was extracted from the second and third year analytical chemistry laboratory manuals used at McMaster.

Appendix 4

A4 The Determination of Vanadate by Coulometric Titration

A4.1 Apparatus

Figure A4.1.1 presents a schematic diagram of a simple coulometric titration apparatus. The generator circuit (left-hand side) incorporates a constant current power supply that is activated by a double-throw switch that simultaneously activates a timer. As current flows through the sample solution in the titration cell, Cu_+ is generated at G_2. The Cu_+ reacts with vanadate anions (the analyte) in the solution. After all the vanadate is consumed, the concentration of Cu_+ begins to increase linearly with time. The indicator circuit is used to measure the concentration of Cu_+ in solution. The current measured by the ammeter is proportional to $[Cu_+]$.

A4.2 Computer Control

An additional feature of this apparatus is the use of an Apple microcomputer. It is used to perform the titration in three stages.

Warm-up: The magnetic stirrer and indicator circuit voltage will be turned on and allowed to stabilize.

Start titration: The generator circuit switch will be closed to apply constant current to the titration cell.

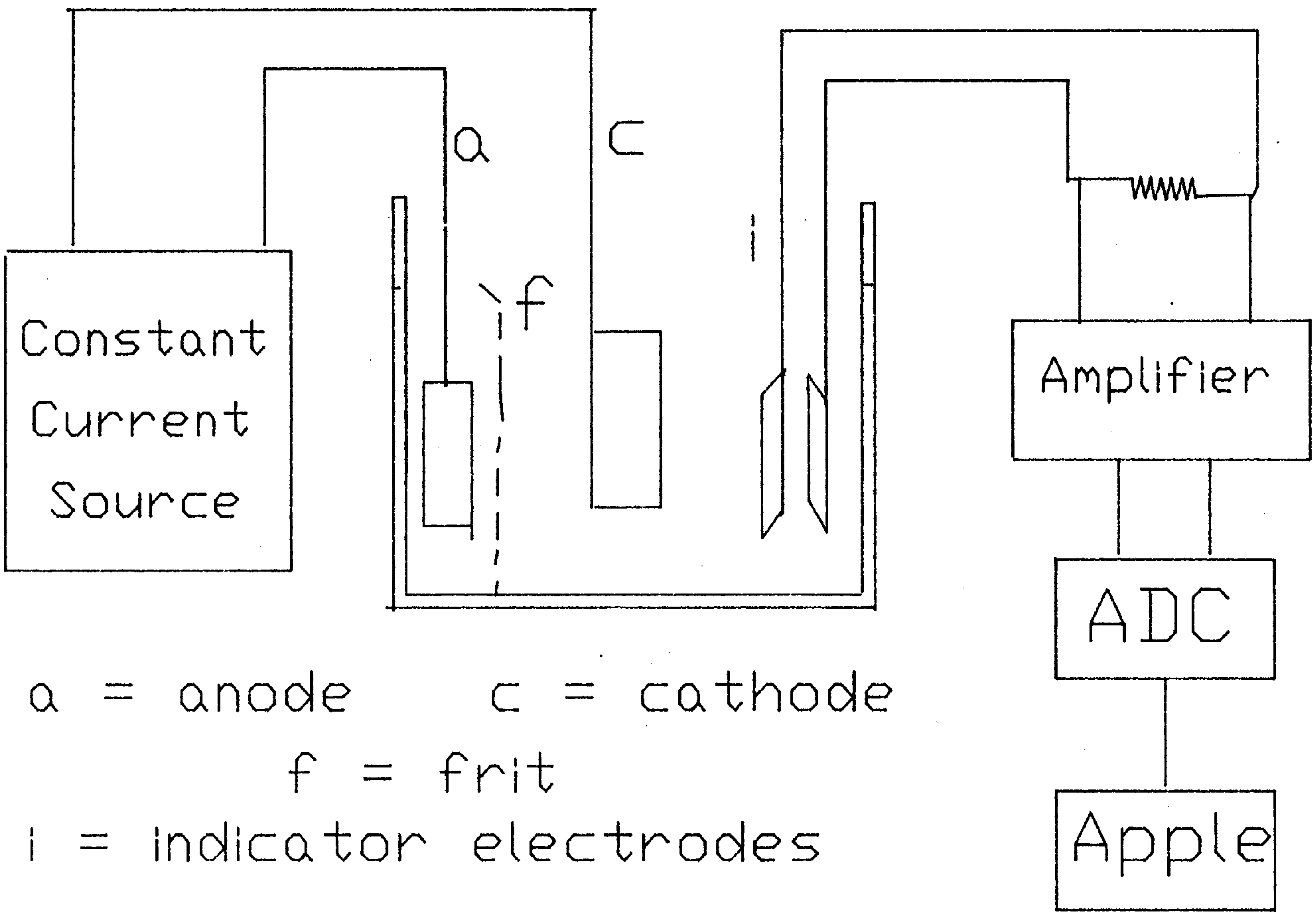
Data acquisition: Current in the indicator circuit and time elapsed in the titration will be read and stored in the computer memory.

Stop titration: The generator and indicator circuits and the magnetic stirrer are shut off when the titration is complete.

Data interpretation: Data stored in the memory of the computer will be analysed interactively with the aid of the graphics display capability of the computer.

Stages 1, 2, and 4 are accomplished by the computer opening and closing relays. These relays ate turned on by a high signal of 5V. and turned off with a low signal of 0V. These high and low voltages are generated with a digital-to-analog (DAC) that resides within the computer. During the analysis the computer dispatches digital signals of either 0 or 255 to any one of the three channels available of the DAC. A signal of 255 to the input side of a particular channel will result in 5 volts appearing on the output side. This voltage is held until a signal of 0 causes it to drop to and remain at 0 volts.

Data is aquired by the computer using an analog-to-digital converter (ADC) to measure the current in the coulometry indicator circuit. This is accomplished indirectly by first converting the current to a voltage by placing a 200 ohm resistor in the indicator circuit. Since the current in the indicator circuit is in the range of 0 to 50 microamps, the potential drop across the 200 ohm resistor will be 0 to 10mV. This value is too low for the the ADC to measure, so an amplifier is used to boost the potential to the 0 to 5 volts range. The resulting potential is then presented to the ADC for conversion to digital values.



a = anode c = cathode

f = frit

i = indicator electrodes

Figure A4.1.1 Coulometric titration unit