National Library of Canada
Canadian Theses Service
Ottawa, Canada
K1A 0N4

Bibliothèque nationale du Canada
Services des thèses canadiennes

CANADIAN THESES

THÈSES CANADIENNES

NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30.

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30.

THIS DISSERTATION
HAS BEEN MICROFILMED
EXACTLY AS RECEIVED

LA THÈSE A ÉTÉ
MICROFILMÉE TELLE QUE
NOUS L'AVONS REÇUE

NL-339 (r. 86/06)

Canada

THE UNIVERSITY OF ALBERTA

An Electrochemical Study at 25°C. of the Leaching Behaviour of Gold and Silver in Inorganic and Organic Solutions

by

Christina J. Sayer

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF Master of Science

Department of Geology

EDMONTON, ALBERTA

Fall 1986

ISBN 0-315-32308-6

THE UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF AUTHOR	Christina J. Sayer
TITLE OF THESIS	An Electrochemical Study at 25°C. of the Leaching Behaviour of Gold and Silver in Inorganic and Organic Solutions

DEGREE FOR WHICH THESIS WAS PRESENTED Master of Science

YEAR THIS DEGREE GRANTED Fall 1986

Permission is hereby granted to THE UNIVERSITY OF ALBERTA LIBRARY to reproduce single copies of this thesis and to lend or sell such copies for private, scholarly or scientific research purposes only.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

(SIGNED) Chris Sayer

PERMANENT ADDRESS:

#1 Garnet Ave
Sherwood Park Ab
T8A 3S5

DATED Sept 12 1986

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled An Electrochemical Study at 25°C. of the Leaching Behaviour of Gold and Silver in Inorganic and Organic Solutions submitted by Christina J. Sayer in partial fulfilment of the requirements for the degree of Master of Science in Economic Geology.

Bruce E. Nesbitt

Supervisor

Samuel A. Bradford

H. Baadsgaard

Date May 26

Abstract

The leaching behaviour of gold and silver in aqueous solutions at 25°C was studied using the electrochemical techniques of Tafel Analysis and Cyclic Polarisation. Through these techniques and thermodynamic solubility calculations, the Eh-pH conditions and corrosion rates for transport of gold and silver were determined.

The inorganic solutes studied are 0.1M solutions of CN^-, SCN^-, Cl^-, $FeCl_3$, NH^{4+}, $S_2O_3^{2-}$, HS^-, S_x^{2-}, SO_4^{2-}, OH^-, CO_3^{2-}, and HCO_3^-. The organic solutes studied are phenol, benzoic acid, citric acid, methanol, and natural humic acid.

The results of the gold electrochemistry show three types of behaviour in the solutions. Firstly, CN^-, HS^-, and S_x^{2-} form soluble complexes with Au^+. Secondly, SCN^-, Cl^-, and $S_2O_3^{2-}$ form complexes with Au^{3+}. Thirdly, the remaining solutions showed no indication of significant complexing behaviour.

The overall corrosion rates determined by the electrochemistry indicate that transport of gold at 25°C is sufficiently fast that saturation will be attained in the solutions.

The conditions determined for gold oxidation at 25°C are as follows: CN^- oxidises gold under reducing alkaline conditions. SCN^- oxidises gold under oxidising neutral conditions. $AuCl_4^-$ oxidises gold under Eh conditions of 750 mV or higher and acid to neutral pH. Because of this high potential, it is unlikely that $AuCl_4^-$ will form a distinct blanket of enrichment. $S_2O_3^{2-}$ oxidises gold at intermediate Eh and neutral pH's; and HS^- oxidises gold under reducing conditions at neutral to alkaline pH's. Environments suitable for sulphide transport are: supergene oxidation of fresh sulphides, reducing bogs, or euxenic marine settings. Difficulty with humic acid extraction resulted in ambiguous data in the humic acid experiments.

Results of experiments with silver indicate that rapid oxidation occurs to form silver oxides, except in Cl^-, HS^-, and CO_3^{2-} solutions where silver chloride, sulphide and carbonate are formed. In all solutions mobility of silver is indicated by formation of a black Ag film on the platinum counter electrode. This mobility of silver explains increasing gold fineness with distance of transport.

Transport of gold by any of the above ligands may produce supergene enrichment and contribute to placer deposits of gold. Deposition of the gold is probably due in most cases to change in oxidation conditions.

Acknowledgments

I would like to acknowledge a number of people who helped me through this thesis. First of all, I would like to thank my supervisor Bruce Nesbitt who not only gave me a chance but was always positive even when things looked bleak. Secondly I would like to thank Peter Tremaine who allowed virtually free access to his lab and corrosion [illegible] and gave valuable advice and insight into the experimental techniques. I would also like to thank Linda Gray who was never too busy help me with the corrosion techniques and discuss the sometimes unfathomable results. Thanks are due to the members of my defence commitee; Dr. H. Baadsgaard, Dr. K. Muehlenbachs of geology and Dr S. Bradford of mineral engineering for their helpful critisisms and comments. I would like to thank Tony Cable of Fisons Horticultural products who, for no personal gain, gave and delivered unsterilised peat moss to me. Last but not least, I owe the deepest thanks to my fellow graduate students, Mark Brearley, Louise De St. Jorre, Mike Dufresne, Jane Evens, Darrel Fluet, Paul Lhotka, Greg Lynch, Pierre Maheux, Doug Rucker, Steve Swatton, Lori Walton and Xiamau Xhang, for drinking with me when I needed a drink, laughing when I needed to laugh, boosting my confidence when I needed it, and for valuable discussions and insights when it came to producing a thesis.

Table of Contents

List of Tables

List of Figures

List of Plates

I. Introduction

The solubility of gold and mechanisms of aqueous gold transport have been topics of experimental research since the turn of the century. This research includes the study of both inorganic and organic transporting agents. A review of the earliest work of this century is presented by Ogryzlo (1935).

In general, the point of studying aqueous transport of gold is to obtain a better understanding of gold transport in solution in order to facilitate the assessment of conditions needed to transport and deposit gold. As a result this information can be used to determine the characteristics which are required to cause decreased gold solubilty and result in an ore deposit. In this study transport of gold will be examined at 25°C in order to be applied to low temperature examples of gold transport and deposition.

A. Previous Work

Previous work on gold solubility has generally been conducted at temperatures above 100°C. This was done because the studies were to be applied to hydrothermal systems. Another factor of working at high temperatures is that the kinetics of gold reaction are faster, resulting in greater solubility. In this way the results were easier to evaluate.

Early work on gold solubility established the importance of chloride and sulphide species as complexing agents (Ogryzlo, 1935; Smith, 1943). This was determined through weight loss or etching experiments. With thermodynamic and electrochemical data Krauskopf (1951) was able to calculate Eh-pH conditions where gold chloride and sulphide complexes would be stable. Helgeson and Garrels (1968), also calculated the solubility of gold chloride complexes up to 300°C, whereas Henley (1973) experimented on gold chloride solutions up to 500°C. A major contribution on the stability of gold sulphide complexes was conducted by Seward (1973). It was generally concluded through the work cited above that gold is soluble under hydrothermal conditions by both chloride and sulphide complexes.

Although studied to a lesser extent, there are examples where gold complexing has been examined at 25°. Cloke and Kelly (1964), experimented with chloride complexes at low temperatures and detailed the conditions necessary for their formation. They also pointed out that gold chloride solubility is enhanced by the presence of Fe^{3+} or Mn^{4+}. The general conclusions to be drawn from the low temperature studies are: that chloride solutions will transport gold under conditions where pH is less than 4 and Eh at 800 mV or higher. Sulphide transport has not been examined at low temperatures as far as this author is aware.

Ligands other than chloride or sulphide have been proposed as complexing agents for gold as well. These include; CO and CO_3^{2-}, Kerrich and Fyfe (1981); NH_4^+, Skibstead and Bjerrum (1974); and the CN^- or SCN^- species, (Lakin et al., 1974).

The study of organic complexing of gold has not enjoyed the history of attention that inorganic processes have, but with the recent interest in organometallic compounds, there have been a number of studies conducted. An early study by Ong and Swanson (1969) suggested that gold was transported as organic colloids as opposed to complexes. This was later refuted by Baker (1978) who showed using polarographic solvent extraction and X-ray diffraction that Au-humic complexes were indeed formed. In addition, later work by Varshal et al. (1984) demonstr[illegible]d the existence of Au-fulvic acid complexes.

Ligands Studied

From the review of the literature regarding gold complexes, a list of ligands which might complex with gold and that are common enough in natural systems to be widely applicable was compiled, (Table 1), and used for this study.

To study organic complexing it was decided to examine examples from a number of organic groups that may be found in soils (Rose et al., 1979). These include: acetic acid as an example of a fatty acid; methanol as an example of an alcohol; phenol to study the behaviour of phenolic groups; and benzoic acid to look at carboxyl groups. Because humic and fulvic acids are made up of long chains of phenols, carboxyls, and alcohols (Ong and Swanson, 1969), the last three were studied to determine which functional groups in the organic acid are responsible for complexing. To study how these functional groups interact with each other, a simple analogue of humic acid was studied. This analogue, as suggested by Cronan and Aiken

(1985), was citric acid. Since Varshal et al. (1984) found that the best fulvic acids for gold complexation had molecular weights between 1500 - 5000, it was decided to extract organic acids from a natural source. All the ligands examined in this study are listed in Table 1.

Because of the common occurrence of silver-gold alloys (Boyle, 1979), it is important to understand the properties of silver transport in the same solutions as gold. This information can be applied to questions regarding changes in gold fineness with transport such as that seen in supergene and placer gold environment.

B. Purpose of Study

A single leaching study of both gold and silver with the ligands discussed above would prove very time consuming if it were done using standard weight loss methods. A quick effective alternative is to use electrochemical polarisation. Using this type of experiment, the Eh of a solution is varied so that the rates and mechanism of oxidation and dissolution behaviour of gold can be investigated.

The purpose of this study is to use electrochemical polarisation to study leaching behaviour of gold and silver with a variety of ligands at 25°C Through the results of this study, it will be possible to compare qualitatively the relative rates of metal oxidation with the different ligands. It will also be possible to determine absolute rates of oxidation of these metals with individual ligands. In some cases there will be problems distinguishing between oxidation of the metal to form soluble complexes or to form solid films. It is also possible that the ligands in solution may oxidise more readily than the gold, but these problems have been recognised and will be discussed. A record of the reactions experienced by the gold or silver is also sometimes left on the surfaces of the electrodes, and can be useful in understanding the processes of oxidation. In this paper the results of this study will be presented in the following manner:

1. An outline of the theory and methods of the electrochemistry will be presented.
2. Results of the inorganic experiments will be presented.
3. Results of organic experiments are presented.

Table I.1 List of ligands studied

CN^-
SCN^-
Cl^-
$FeCl_3$
SO_4^{2-}
$S_2O_3^{2-}$
HS^-
S_x^{2-}
CO_3^{2-}
HCO_3^-
OH^-
NH_4^+
Phenol
Benzoic Acid
Acetic Acid
Citric Acid
Methanol
Humic Acid

4. Surface features of the electrodes will be studied
5. A comparison is made between the experimental conditions of gold transport and natural examples.
6. Conclusions are drawn regarding oxidation of gold in various solutions under differing geological conditions.

II. Experimental Methods

A. Introduction

Because the basis of this study is electrochemical research, a review of electrochemistry is appropriate. Metal oxidation or reduction is caused by the loss or addition of electrons through chemical reaction. Because this reaction involves the movement of electrons, a current is produced and can be measured.

The advantage of measuring a current is that it is a direct means of counting the number of electrons passing through the metal-solution interface in a given time. In this way the absolute number of moles of oxidised metal can be measured. As a result, the rate of the reaction can be determined. Because currents can be measured to extremely low values, reactions which are very slow can still be studied. This is particularly useful in the study of noble metals such as gold, because it eliminates the need for great lengths of time to allow sufficient reaction to occur so that it can be observed. The reaction of interest usually occurs on a metal electrode surface in an aqueous solution where the current is transferred by the ions in the solution. In this solution, or on the electrode, there must be a corresponding reduction reaction for every oxidation reaction and vice versa to conserve electrons (Mortimer, 1978). The electrode which is studied is the working electrode. For the purpose of acting as an electron donor or acceptor there is usually a second metal electrode in the solution. This electrode is the counter electrode. Making an electrical connection between the two electrodes completes the circuit (Figure 1). The metal electrode where oxidation is occurring is the anode. Currents measured here will be positive. The electrode where reduction is occurring is the cathode where the current is negative (Mortimer, 1978)

With no outside influence, two dissimilar electrodes in a solution will spontaneously produce a current. This current is produced because each metal has a different standard potential E° at which its oxidised and reduced states are in equilibrium (Garrels and Christ, 1965). These potentials are measured in volts relative to the Normal Hydrogen Electrode which is assigned a potential of 0.0 V and is thie standard reference. To facilitate comparison

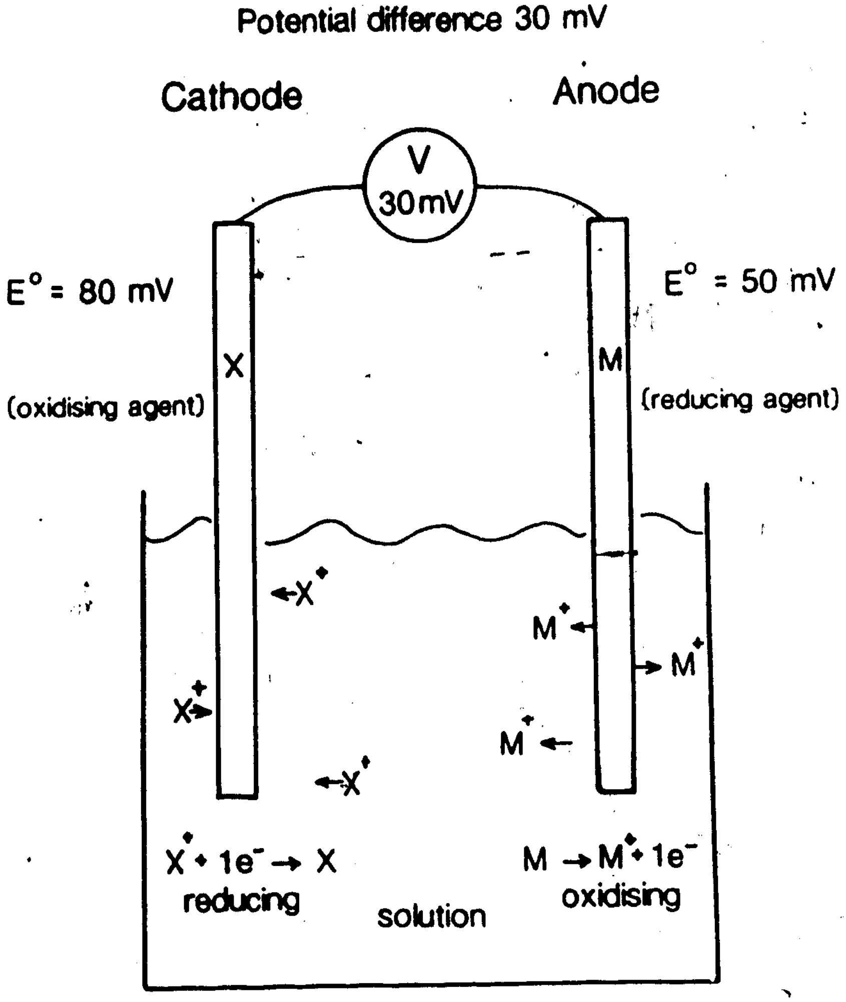


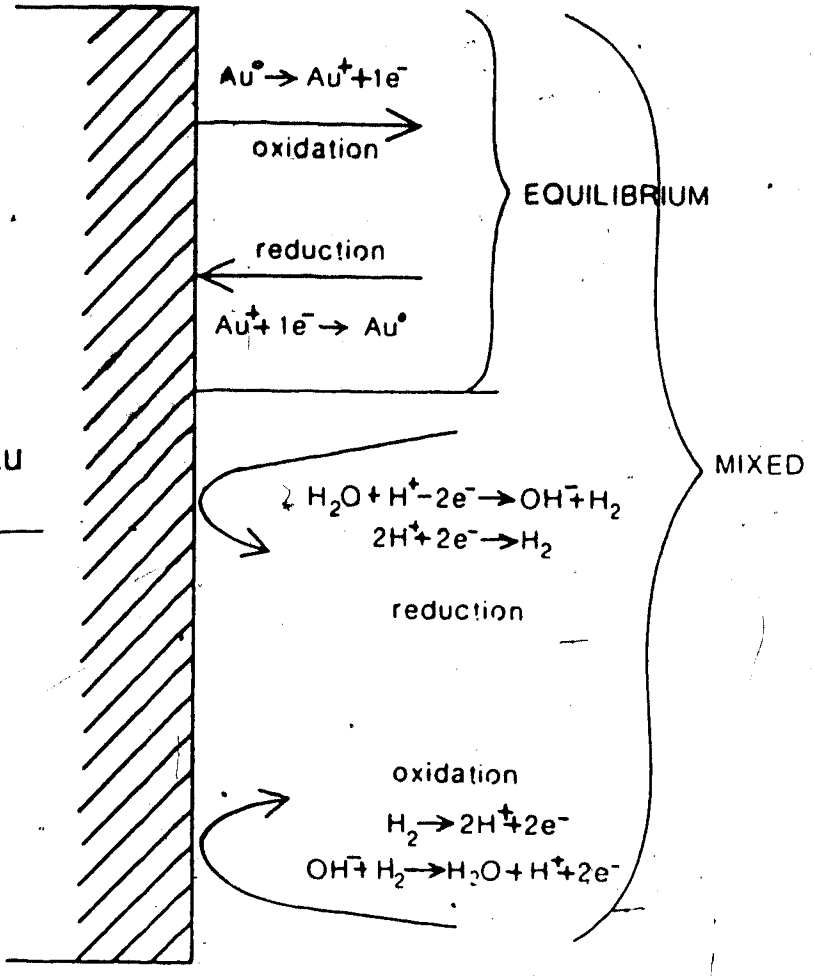
Figure II.1 A schematic diagram of an electrochemical cell. Emf or potential difference is 30 mV.

between oxidation potentials of different metals, each oxidation reaction of a metal is written as a half reaction in terms of the oxidised ion, the metal, and the electrons. All the half reactions of the metals are listed in a table in order of decreasing potential with the hydrogen reaction somewhere in the middle at 0.0 V. With the higher potentials the energy required to cause the metal to oxidise will be correspondingly high. The metals with lower potentials require less energy to oxidise. In an electrochemical cell containing two metals, the one with the higher potential will reduce while the one with the lower potential will oxidise. This is why the metal with a higher E^0 is known as the oxidising agent. The metal with the lower E^0 is the reducing agent. The difference in the E^0 of the two metals is called the potential difference.

B. Theory

Leaching of Metals

On the surface of a metal sitting in solution, there are a number of reactions which can occur. In the case where equilibrium is established, the reactions are oxidation and reduction of the metal at a potential (Figure 2). In cases where equilibrium is not established, the potential is produced by a mixture of reactions. These reactions will include the metal oxidation and reduction along with oxidation and reduction of H^+, OH^-, and water as well as any other aqueous species, (Figure 2). Each of these reactions will proceed at different rates but, with no outside influence, the electrode will assume a potential at which the net current produced by the reactions will be 0.0. This means that the net oxidation and the net reduction cancel each other, but corrosion of the metal is actively occurring. The potential at which the current is 0.0 is known as the rest potential or corrosion potential (Ecorr). To determine the rate of the metal oxidation reaction, at Ecorr a Tafel experiment is conducted then followed by a Tafel analysis. In this study the term Tafel experiment is used to describe a short duration experiment where 500 mV of potential are scanned, and the data used for a Tafel analysis. Strictly speaking this is not the precise name for this type of experiment, but it was adopted to distinguish it from the larger range Cyclic Polarisation experiment. From the Tafel



Figûre II.2 Oxidation and reduction reactions on the surface of a leaching metal.

experiment a corrosion current (Icorr) is determined. It is from this current that the rate of reaction is determined.

Calculation of Corrosion Rate

A short derivation of the corrosion rate, as found in the Princeton Applied Research Application Note 148 (1978), will illustrate how I is related to the rate of oxidation.

$$i\ (\text{current}) = Q(\text{coulombs})/t(\text{seconds})$$

$$1\ \text{coulomb} = 6.2 \times 10^{18}\ e$$

The measured current indicates the number of electrons passing through the circuit in a given time, therefore it allows calculation of how many ions are oxidised (i is +'ve) or reduced (i is -'ve) in that time.

$$\text{Total coulombs } Q = nFW/M$$

n = number of electrons in reaction

F = Faraday = 96,487 coulombs/M/n (g-equivalent)

W = total weight of metal g

M = atomic weight of metal g/mol

Rearranging:

$$W = QM/nF$$

$$Q = i(\text{current})\ t(\text{sec})$$

$$W = itM/nF$$

$$\#1)\ W/t = iM/nF$$

W/t is the corrosion rate in g/sec

To convert the corrosion rates to milli-inches per year equation 1 is divided by the density of the metal (d) in g/cm^3, and the area of the electrode (A); i/A = I (current density). Seconds are then converted to years and centimeters to inches:

$$W/t(mpy) = 0.13\ IM/nd$$

Current is controlled by the rate of the redox reactions. Generally, the greater the potential of the electrode, the higher the current, but if the kinetics of the oxidation or the reduction reaction are too slow, this relationship may not hold (Stern and Geary, 1957).

These rates are usually reported in the literature as milli-inches per year (mpy). This convention was also adopted in this study because the computer software provided with the experimental equipment calculated corrosion rates in mpy.

C. Experimental Procedure

The experimental methods used in this study are the Tafel experiment and Cyclic Polarisation. These are electrochemical experiments in which the potential or Eh of an aqueous system, in contact with a metal, is manipulated and the current measured. To conduct the Tafel experiment, the rest potential (Ecorr) is determined first without applied potential. This gives a reference potential from which to start the experiment. Then the working electrode is reduced by 250 mV from Ecorr and the applied potential is increased by 0.5 mV/sec until it is 250 mV greater than Ecorr. While the potential is being varied, the current density (I) is measured. Current density is the current measured over a unit area of the working electrode. In these experiments the unit area was 1cm^2. As the potential is moved further away from Ecorr, a plot of Ecorr vs log I should assume a straight line over one order of magnitude of current density (decade), in both the cathodic and anodic directions (Figure 3), (Stearn and Geary, 1957). The cathodic currents are negative, but for simplicity are plotted as positive values on the diagram. All results are plotted on potential (SCE) vs log I scales.

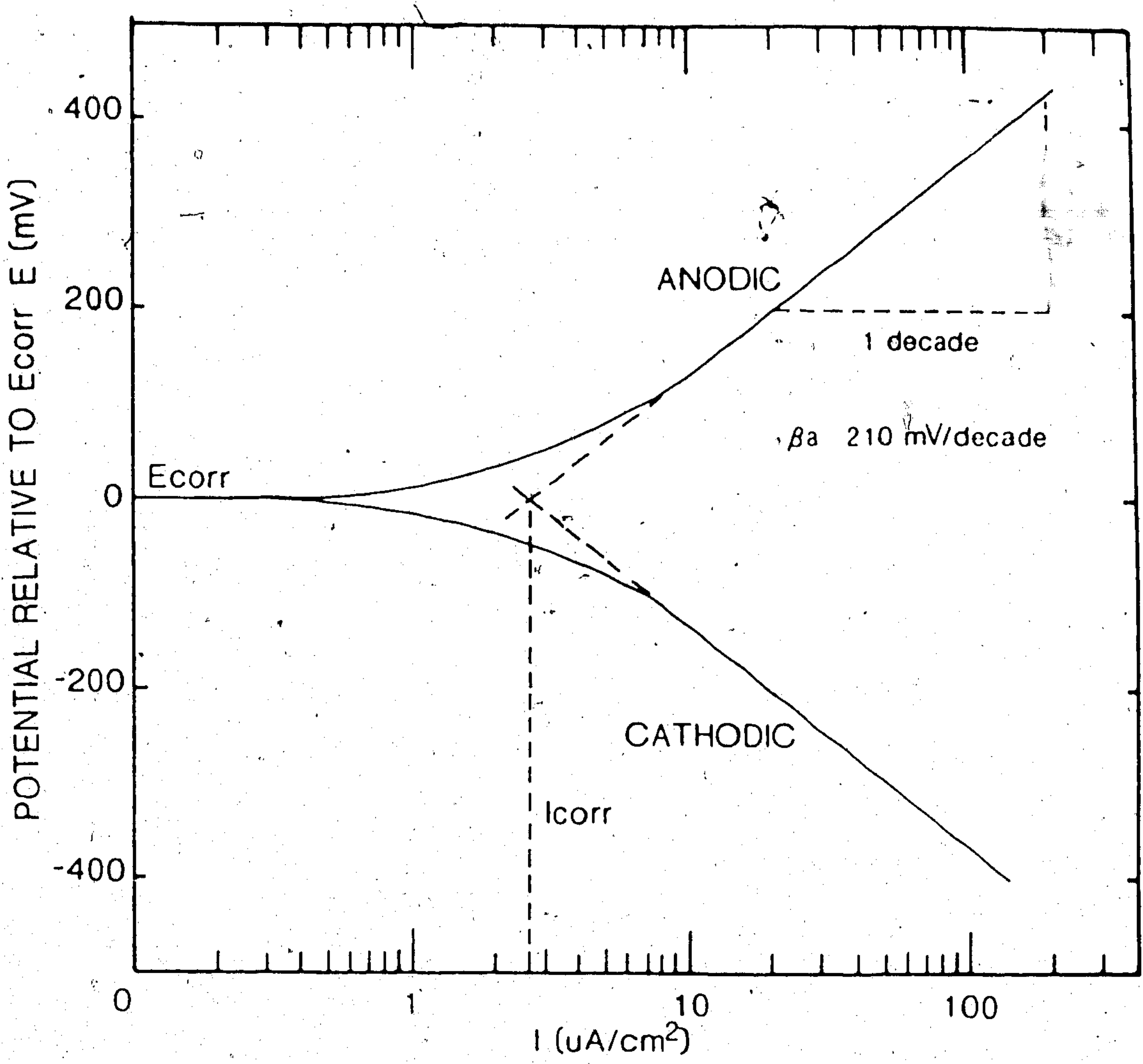


Figure II.3 Theoretical Tafel curve.

The slopes of the oxidation and reduction lines are known as Tafel constants; βc for the cathodic line and βa for the anodic line. A straight extension of these lines should intersect at Ecorr and at the corrosion current (Icorr), see Figure 3.

The following Tafel equations illustrate the relationship between the slope of the line, the potential, and Icorr.

$$a)\ \eta = \beta a \log \text{Imeas} - \text{Ired}/\text{Icorr}$$

$$b)\ \eta = -\beta c \log \text{Imeas} + \text{Iox}/\text{Icorr}$$

η = is the overpotential which is the difference between the measured potential and Ecorr.

The Tafel analysis will only work if the metal is known to be oxidising and the reaction occurs readily. This means that the Tafel constants, particularly βa must not be too high (Stern and Geary, 1957). For the results of this study, it was found that when βa exceeds 500 mV/decade it could be said that the reaction was not occurring readily. This high Tafel constant is interpreted to represent an inhibition of oxidation, or protection of the electrode from oxidation by formation of a film, or adsorption of an aqueous species. This is known as passivation (Wranglen, 1985). In this case, calculation of a corrosion rate will not give a rate for metal oxidation but rather for the passivating reaction. If the cathodic Tafel constant is too high, it may indicate that diffusion of species to the working electrode is too slow to keep up with the reduction reaction. This phenomenon is called concentration polarisation. In some cases concentration polarisation can be avoided by vigorously stirring the solution (Wranglen, 1985).

Following completion of the Tafel experiment, the Cyclic Polarisation experiment is conducted. This experiment like the Tafel Experiment is started at 250 mV below Ecorr, then the potential is swept at 2 mV/second up to about 1000 or 1200 mV above Ecorr. The Cyclic Polarisation is done to determine whether or not the oxidation reaction of the metal occurs at a higher potential than Ecorr, or if it occurs with a higher oxidation state of the metal. To determine corrosion rates from Cyclic Polarisation measurements the values of I at the potentials of interest can be used. To avoid influence from the cathodic reaction, however, the potential examined has to be at least in the linear region around Ecorr if not well away from Ecorr (Figure 3) A higher sweep may also show a drop in current indicating passivation.

After the potential reaches its maximum in both experiments, the experiment is repeated in the reverse direction at the same rate. In many cases, the plot of the reverse sweep does not follow the initial forward sweep. This implies that an irreversible process has occurred in the solution or on the electrode surface. Both techniques, the Tafel experiment and the Cyclic Polarisation were performed on all solutions.

D. General Behaviour of Metals

After completing a large number of experiments it is apparent that the metal behaviour in the various solutions tends to group itself into three styles of behaviour. These variations in behaviour can be explained through the general examination of metal corrosion in a solution containing its own cations. The metal corrosion of such a system is shown in Figure 4. The cathodic curve of Figure 4 shows reduction of the metal from metal cations in the solution. At the initiation of the experiments in this study, there are no metal cations in solution so the cathodic curve will show water reduction. If the pH is low it may be H^+ reduction to H_2, or if the pH is high it could be O_2 reduction to water (Wranglen, 1985). Differences in the style of curve produced in the experiments are controlled by the intersection of the water reduction curve, which is variable, and the metal behaviour curve, which is fixed. This intersection can occur at any point on the metal oxidation curve. Figure 5 illustrates the results produced by variations in intersections of the cathodic curves with the metal oxidation curve.

If the water reduction line intersects the cathodic region of the metal curve, a normal Tafel plot will result such as that seen in Figure 5a. These experiments are reversible and corrosion rates can be calculated in the region of Ecorr by the method outlined in the theory section. If the water reduction curve intersects somewhere in the passivation region the anodic Tafel constant is already extremely high so the resulting curve resembles the diagram in Figure 5b. In this region, the experiments are not reversible. Sometimes the passivation is a result of

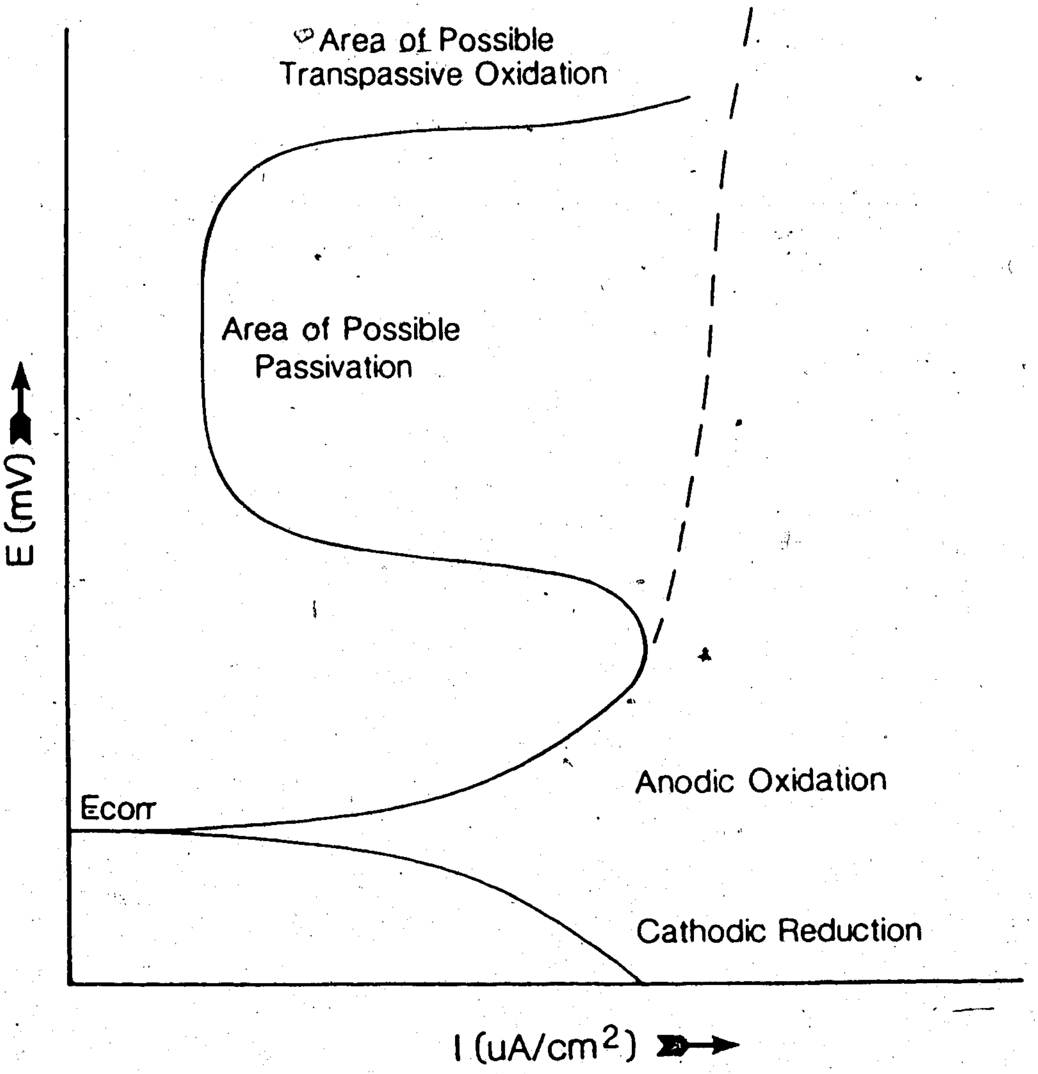


Figure II.4 Schematic diagram of general gold corrosion.

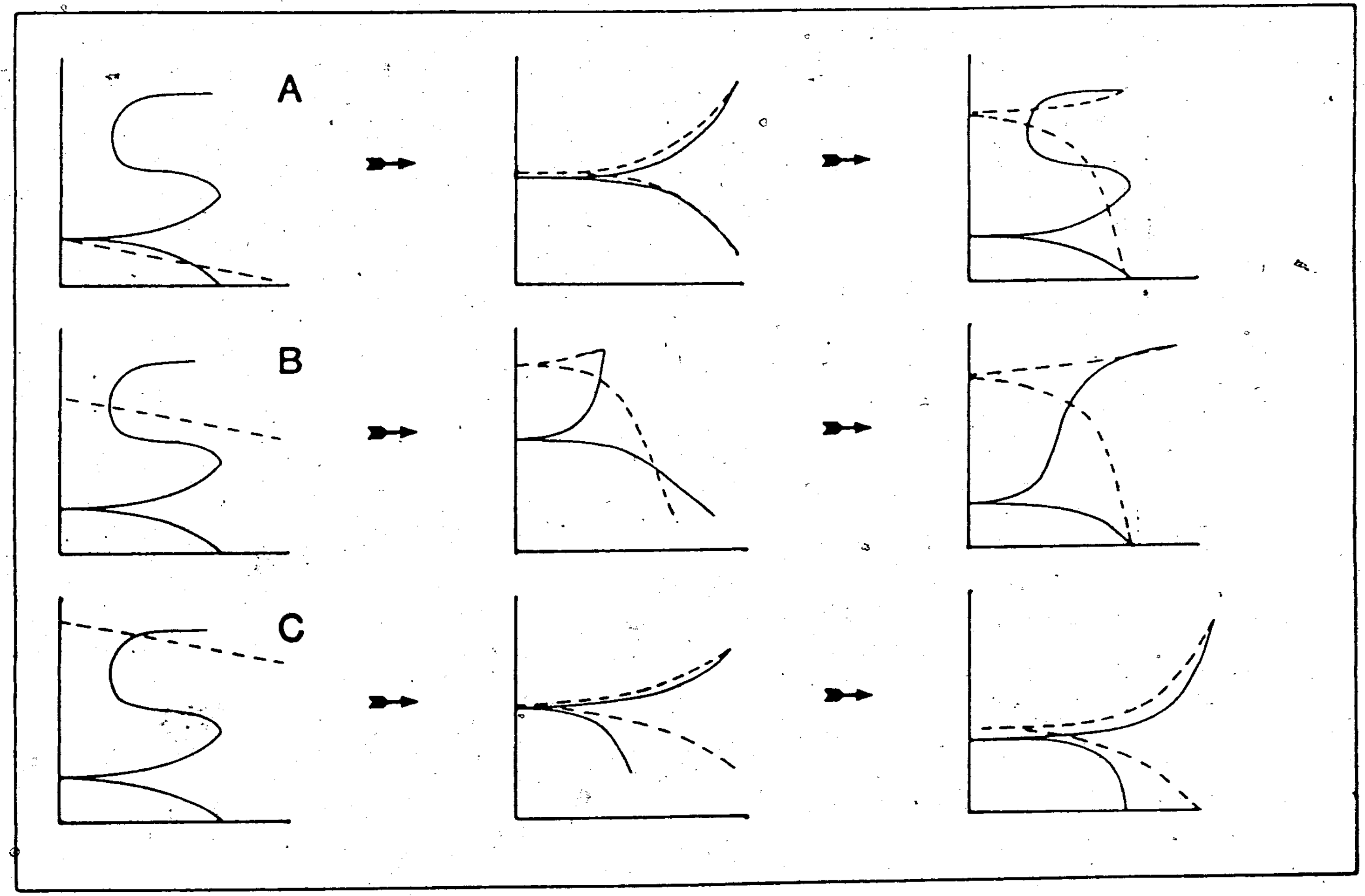


Figure II.5 Types of oxidation behaviour produced by different intersections of the cathodic curve with the metal oxidation curve. Forward sweeps in solid lines, all reverse sweeps in dotted lines. In the first column the dotted line represents water reduction.

Adapted from Harrel (1975).

adsorption of hydroxide on the gold surface. In some cases enough hydroxide is adsorbed that visible gold oxide species form (Hoare, 1984). In most cases the cause of passivation is not visible because the adsorption of the aqueous species may be on the order of an atom thick (Hoare, 1984). Passivation makes determination of the corrosion rate impossible in the region of Ecorr because, as already stated, βa is too high. If the water reduction curve intersects the transpassive region, extreme oxidation should result such as that shown in Figure 5c. It is also difficult to obtain a good corrosion rate from these results in the region of Ecorr because the cathodic curve is suffering from concentration polarisation.

Cyclic Polarisation sweeps should follow along the metal oxidation curve from the point where the hydrogen curve intersects it (Figure 5a-c). Transpassive oxidation may or may not be seen. If transpassive oxidation is not seen it may mean that the experiment did not go to a high enough potential, or that there is no major oxidation reaction that occurs.

If there is an oxidation reaction seen in the experiment, it has to correspond in some way to E^0 of that reaction. In the case that the behaviour of the system is like that shown in Figure 5a, it is Ecorr that reflects the reaction corresponding to E^0. By the same token Ecorr will correspond to E^0 in Figure 5c when it is at a higher oxidation state. In Figure 5b the transpassive oxidation corresponds to E^0. It has generally been found by the results of this study that the part of the curve that reflects E^0 of the reaction, whether it is Ecorr or a transpassive oxidation, is from 400-600 mV below the equilibrium E^0. The reason that the oxidation reaction in the electrochemical experiment is so much lower than E^0 of that suspected reaction is that the solution is not at standard state or in equilibrium.

E. Equipment

In this study a Princeton Applied Research Model K-37, three electrode electrochemical cell was used for all experiments. The working electrodes in this study were either gold or silver. Potentials were imposed on the working electrode and the resulting current measured. Alternatively, the current can be imposed and the resulting potential measured, but this was not done for this study. Control is accomplished by use of a Princeton

Applied Research Model 173 or 273 potentiostat, which is operated through an Apple IIE computer and software provided with the system. The computer software controls the potentiostat, assimilates and plots the data, and calculates the Tafel constants and Icorr. Tafel constants are calculated using a Stern-Geary best fit program. This process fits the entire Tafel experiment to the equations a and b on page 13 rather than just extending the straight part of the lines (Stern and Geary, 1957). The counter electrode was usually platinum but occasionally gold or graphite was used. In a three electrode cell, the potential difference is not measured between the working electrode and the counter electrode, but between the working electrode and a reference electrode of known E°. In this study the reference electrode is a Saturated Calomel Electrode (SCE), which has a potential of 244 mV (Garrels and Christ, 1965). Consequently, all recorded potentials are 244 mV higher than those recorded against the Normal Hydrogen Electrode (NHE). To compare results from this study to normal Eh-pH diagrams, 244 mV have to be subtracted from the results. All three electrodes are held in the solution by the glass cell, with no separation between the electrodes (Figure 6).

F. Solution Preparation

Solutions of the inorganic ligands were prepared by dissolving their sodium or potassium salts to 0.10M in deionized water. These solutions were then purged of oxygen by bubbling nitrogen through them for approximately an hour. The nitrogen was purified with regard to oxygen by passing it through a cylinder of copper shavings and alumina amalgam at 25°C. Ligands which can exist under different pH conditions were prepared at pH's 4, 7, and 10. Those ligands that were constrained by pH were allowed to buffer their own pH or, if the speciation of the ligand would not have been altered, the solution was adjusted to the nearest pH of 4, 7, or 10. To prepare bisulfide solutions, 0.10N NaOH solution was purged for one hour, then H_2S gas which had been cleaned of sulphate by passing it through a solution of $BaCl_2$, was bubbled through the NaOH solution until the pH was 7. This meant that there was 0.10M sulphide species present where HS^- was dominant. Polysulphide solution was prepared by mixing reagent Na_2S_4 in purged water (Giggenbach, 1974).

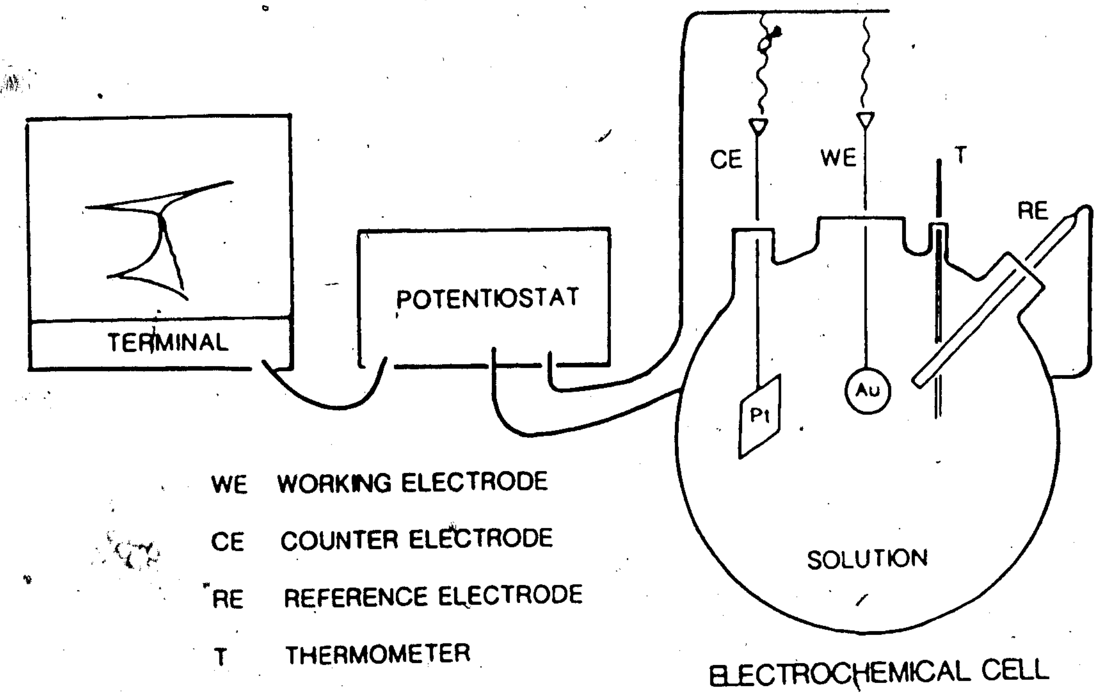


Figure II.6 A schematic diagram of the electrochemical cell and the equipment.

Most of the organic solutions for this study were prepared by dissolving their reagents to 0.10M in deionised water. The readily soluble ligands include methanol, phenol, acetic acid and citric acid. The benzoic acid was slow to dissolve but when added to 0.10N NaOH, it dissolved much more rapidly. As a result the NaOH was neutralised leaving 0.10M sodium benzoate.

Organic Acid Extraction

Peatmoss was used as a source of natural organic acids because peatmoss in general has little silt or other mineral matter in it, and it is rich in organic material (Rose et al., 1979). Because Boyle (1979) discusses a variety of examples where gold has been enriched in peat bogs it is also felt that peat moss is a valid choice for an organic reactant.

Organics were extracted from unprocessed peatmoss by the method outlined by M. Schnitzer (1982). The following is an abbreviated version of that method.

1. If carbonate is present remove it by effervescing with 0.10N HCl, (this was not necessary for the peatmoss in this study).
2. Rinse out acid with water.
3. Spread and dry at room temperature.
4. Add about 10 g of peatmoss per 100 ml of 0.10N NaOH, (the NaOH selectively extracts the organic acids).
5. Displace air in flask with N_2 then agitate for 24 hours.
6. Centrifuge for 10 minutes at 10,000 r.p.m.
7. Separate the supernatant.
8. (Optional) Add distilled water and centrifuge again.

In this study the resulting extractant was clear in that there was no visible matter suspended in it, but the colour was a very dark oily brown. The pH was 10 meaning that the NaOH was not completely neutralised. No attempt was made to characterise the acids in the solution.

After preparation the solutions were placed in the clean electrochemical cell. The solution was purged again for about 15 minutes.

Electrode Preparation

To prepare the metal electrodes for an experiment they were cleaned by polishing the surface of the metal disks with 360 grit, silicon carbide sandpaper. The dust was washed off with acetone. The disks fit into a teflon holder which exposes exactly 1 cm^2 to the solution and allows electrical contact with the potentiostat through a metal rod. This metal rod was isolated from the solution. At this point the cell was assembled and the experiments were conducted as explained previously.

III. Results

A. Results of Experiments With Gold in Inorganic Solutions

Cyanide Species

Because the cyanide species are well known complexing agents of gold, it was thought that these species would serve as a good model for oxidising electrochemical gold behaviour. The results of the experiments with cyanide solutions are shown in Figure 7. As anticipated, the CN^- and SCN^- ligands both show behaviour which indicates a high rate of reaction with gold. In the initial Tafel experiment the CN^- exhibits a fairly low anodic Tafel constant, accompanied by concentration polarisation. The SCN^- initially has a high anodic Tafel constant but this is followed by a current peak in the high sweep.

The results of the CN^- and SCN^- experiments show that one significant difference in their behaviour is the potential where oxidation starts. For CN^-, E° is -600 mV (NHE), (Latimer, 1952), which is -354 mV (SCE). The Ecorr in the CN^- solution is approximately -880 mV (SCE) which is the expected 500 mV below E°. This is followed by very high initial current acceleration. On the basis of work by Kirk et al. (1980), which shows $Au(CN)_2^-$ to form at approximately -700 mV (SCE), it would seem reasonable to assume that $Au(CN)_2^-$ is forming in this potential range in this study. There is a second peak at about -350 to -400 mV (SCE), (Figure 7) where there is a very thin film observed on the gold electrode but it disappears with higher oxidation. It has been shown by Kirk et al. (1980) that this peak is caused by Au^{3+}-oxide formation. Because the film disappears, the rest potential returns to its original value when the experiment is reversed. This indicates that the reducing species are those that were oxidised at the rest potential.

For the SCN^- solution, E° is 660 mV (NHE) (Latimer, 1952), or 884 mV (SCE). In the experiment the Ecorr is at -50 mV, which is far below E°. The current peak is at about 400 mV (SCE), which would indicate that $Au(SCN)_4^-$ is forming in the region of transpassive oxidation. In the SCN^- solutions a thick reddish film of unknown composition is observed. In

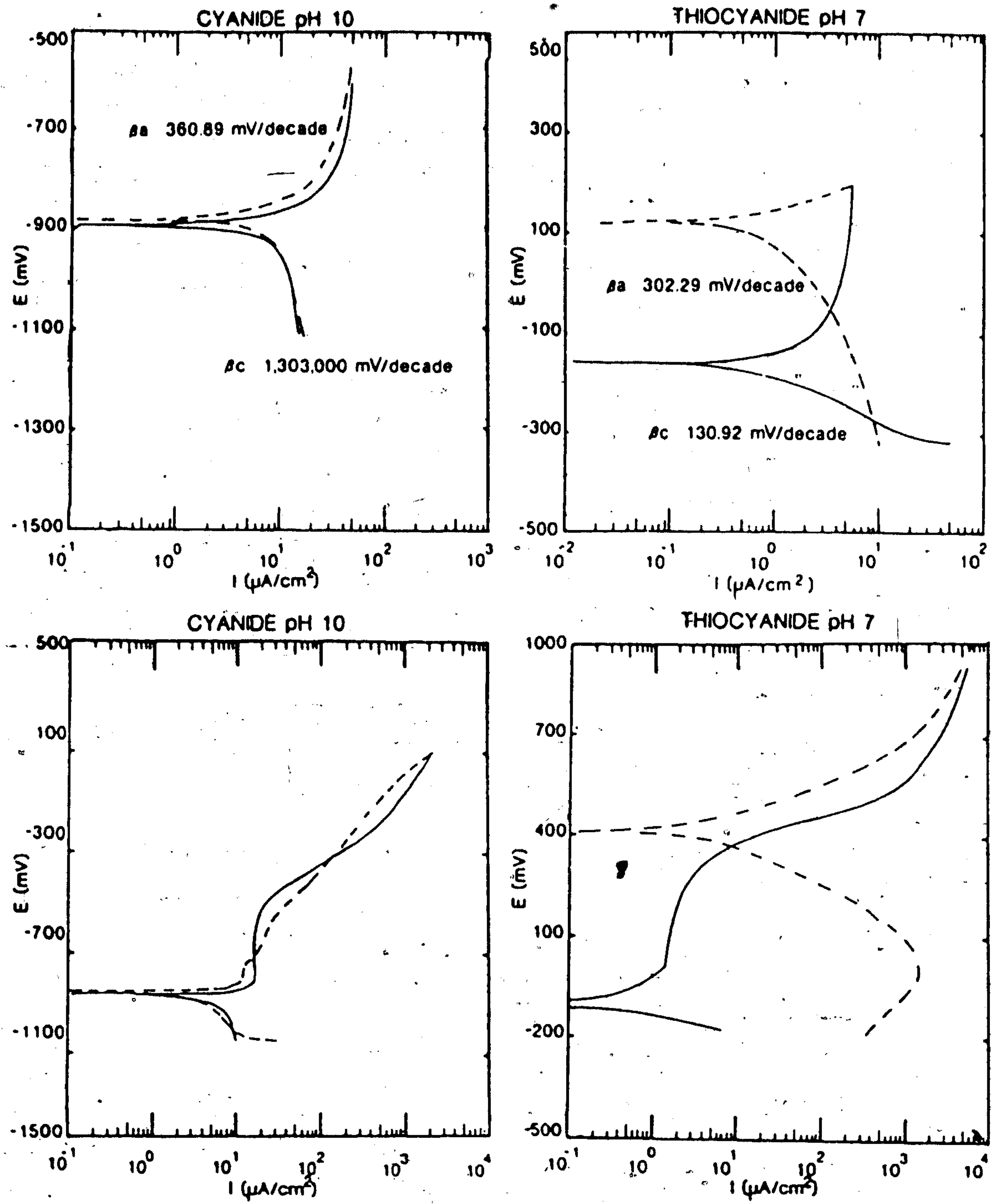


Figure III.7 Results of Tafel and Cyclic Polarisation experiments on gold with cyanide species.

this case the film persists which causes the reverse rest potential to be higher than the original rest potential (Figure 7). Values of I and corrosion rates for these ligands are found in Table 2. Overall the results of the cyanide experiments indicate oxidation of gold according to the standard E°'s for CN^- and SCN^- gold complexes.

Chloride Species

Chloride solutions appear to behave in much the same way as SCN^- solutions. If one inspects an Eh-pH diagram of the Au-Cl-O system as in Figure 8 (Garrels and Christ 1965), it can be seen that within the stability field of water at 25°C the stability field for $AuCl_4^-$ is dependent only on Eh and Cl^- concentration. It appears that the electrochemical experiments bear out this Eh-pH diagram very well. It can be seen from Figure 9 that the behaviour in the Tafel experiments is irreversible and the anodic Tafel constants are very high. Repeated experiments in these potential ranges failed to show any evidence of gold being deposited on the platinum counter electrode. As a result it is interpreted that this Tafel region is in the area of passivation, so no significant Au-chloride complex is forming. In contrast Figure 10 illustrates the results of the Cyclic Polarisation sweeps. These show a current peak for all Cl^- solutions at about 850 mV (SCE). This current peak is transpassive oxidation. These experiments usually cause the solution to turn light yellow in colour. It has been noted by many experimentors that $AuCl_4^-$ is yellow (i.e. Robinson and Frost, 1963). The E° for $AuCl_4^-$ formation is 1.00 V (NHE) (Latimer, 1952) or 1244 mV (SCE). As expected, the equilibrium potential is about 400 mV higher than the potential seen for $AuCl_4^-$ formation in the experiments. More evidence of complex formation is that gold is transported to the platinum electrode which aquires a thin but distinct coating of gold. A feature noted on the gold electrode is that with high oxidation in the chloride solution, a dark film is formed. This is interpreted to be a gold oxide (Gaur and Schmid, 1970). The formation of this film will be discussed in a later section.

The value of I from the sweep experiment at 994 mV (SCE) is about 6000 $\mu A/cm^2$ (Table 2). Strictly speaking this will not yield a true corrosion rate because both $AuCl_4^-$ and

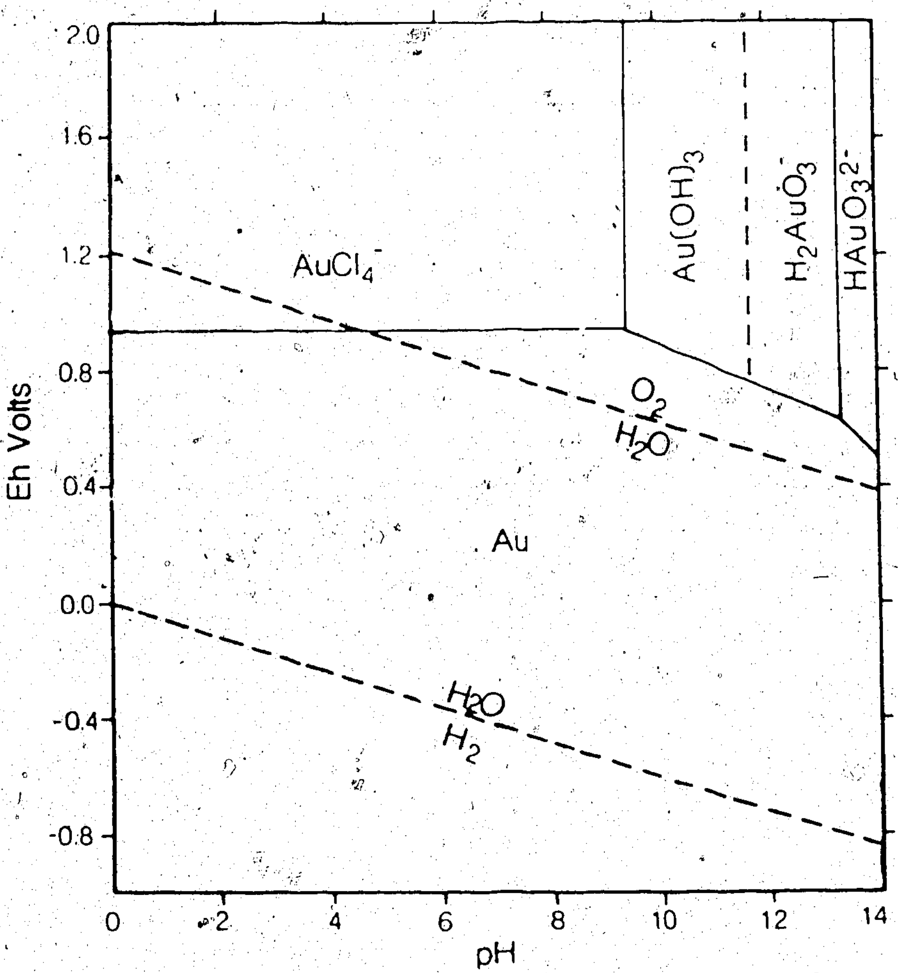


Figure III.8 Standard Eh-pH diagram of the Au-Cl-O system. Adapted from Boyle (1979).

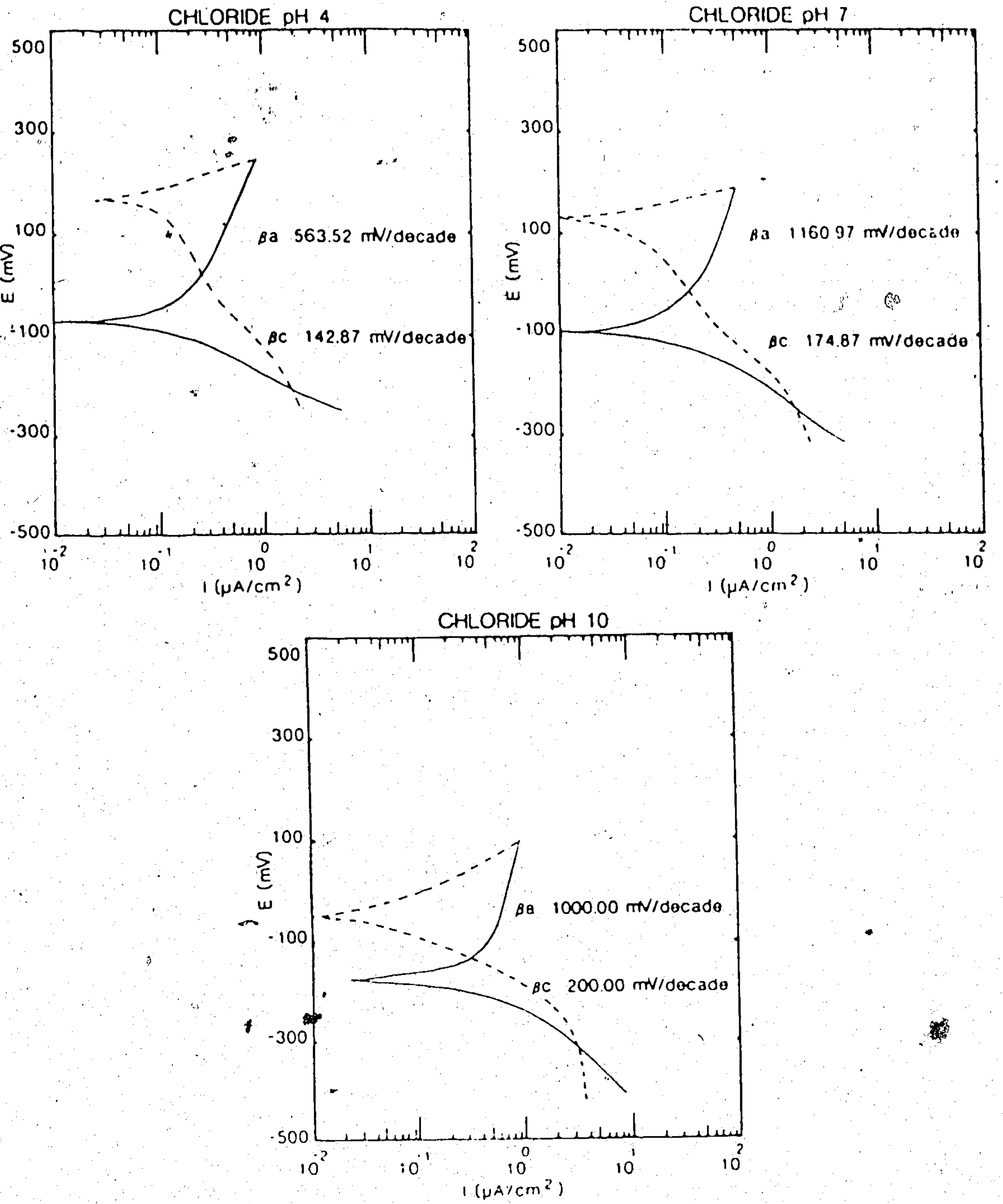


Figure III.9 Results of Tafel experiments on gold with chloride solutions at pH 4, 7, and 10.

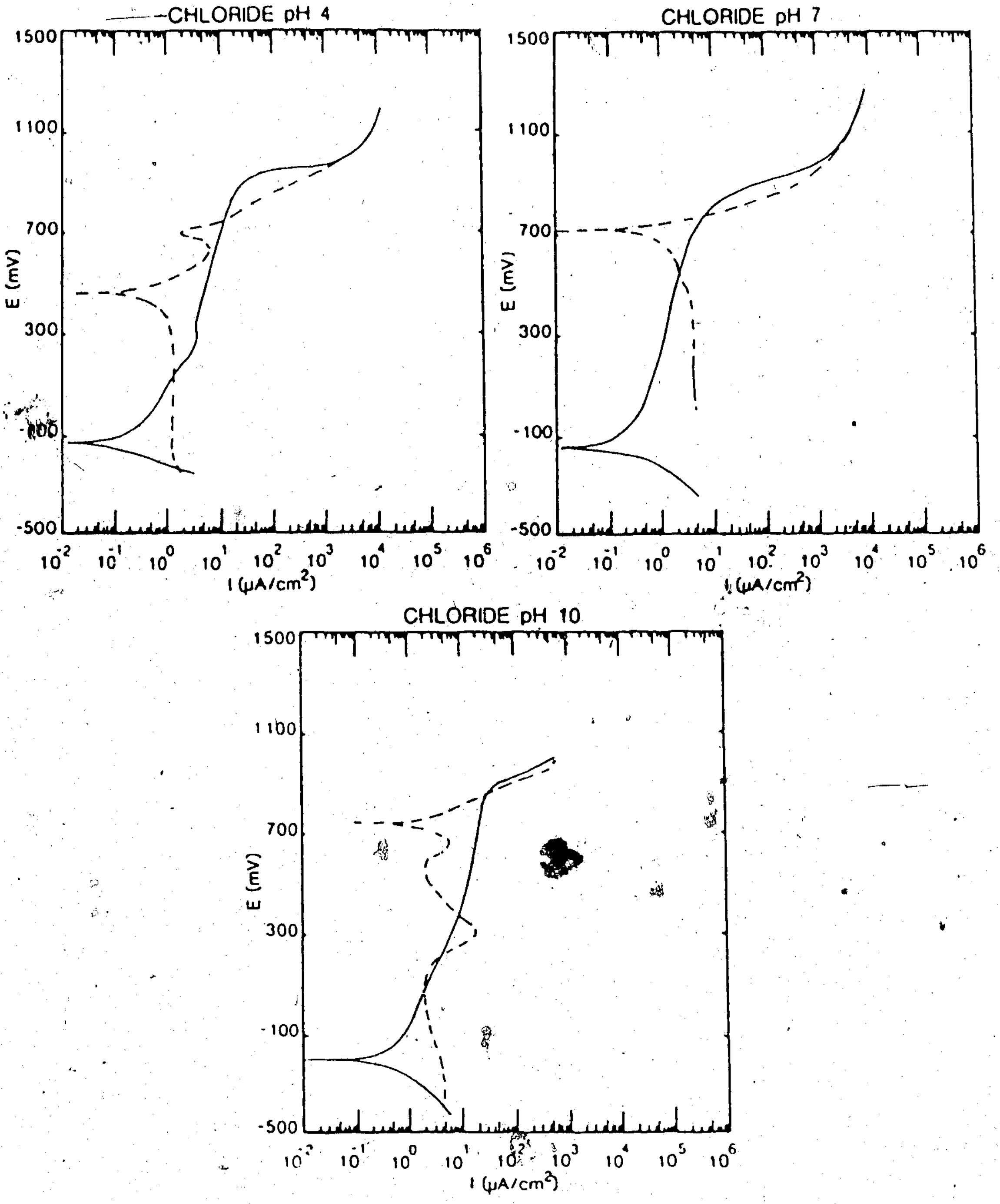


Figure III.10 Results of Cyclic Polarisation experiments on gold with chloride solutions at pH 4, 7, and 10.

Au-oxide are forming and it is impossible to distinguish how much of the current is being contributed to by each. As a rate of gold oxidation however, the corrosion rate is valid.

pH Effects

The main effect of pH variation in the Tafel experiments is that Ecorr is lowered slightly with increase in pH (Figure 9). This is due to the increase in the reduction of water with increase in pH, therefore this is a reflection of water stability (Garrels and Christ, 1965). It should be noted that the change is not as great as that indicated by thermodynamic calculations. This is probably because the presence of free H^+ or OH^- in the system is far less than 1.0M.

Presence of Fe^{3+}

Because Cloke and Kelly (1964) found that Fe^{3+} or Mn^{4+} in solution enhanced dissolution of gold, a solution of $FeCl_3$ was prepared at 0.10M Cl^- [illegible] examine this phenomenon. The Fe^{3+} hydrolises strongly which forces the pH to 2. Consequently, a Cl^- experiment was conducted at pH 2 for comparison. The results indicate that the solution with Fe^{3+} has a much higher Ecorr. This is probably set by the Fe^{3+} - Fe^{2+} couple. The Eh of Au^{3+} oxidation seems to be about 850 mV (SCE) for both (Figure 11). The main difference noted between the $FeCl_3$ and Cl^- solutions, is that there was significantly less oxide formed on the gold electrode in the $FeCl_3$ solution. The current densities, however, at 850 mV (SCE) are about 11μA/cm^2 for both solutions. This means that in the $FeCl_3$ solution almost all the current is produced by $AuCl_4^-$ formation whereas in the Cl^- solution $AuCl_4^-$ formation produces only a fraction of the current.

Numerous workers (i.e. Cloke and Kelly, 1964) suggest that Fe^{3+} and Mn^{4+} facilitate the oxidation of gold by acting as oxidising agents. From standard potential data (deBethune and Swendeman-Loud, 1964), it can be seen that the reaction of Fe^{2+} to Fe^{3+} occurs at a potential of 771 mV (NHE). Because this is a lower E^0 than 1.00 V (NHE) for $AuCl_4^-$, Fe^{3+} reduction could only oxidise a trace amount of gold. Using the Nernst equation it is possible

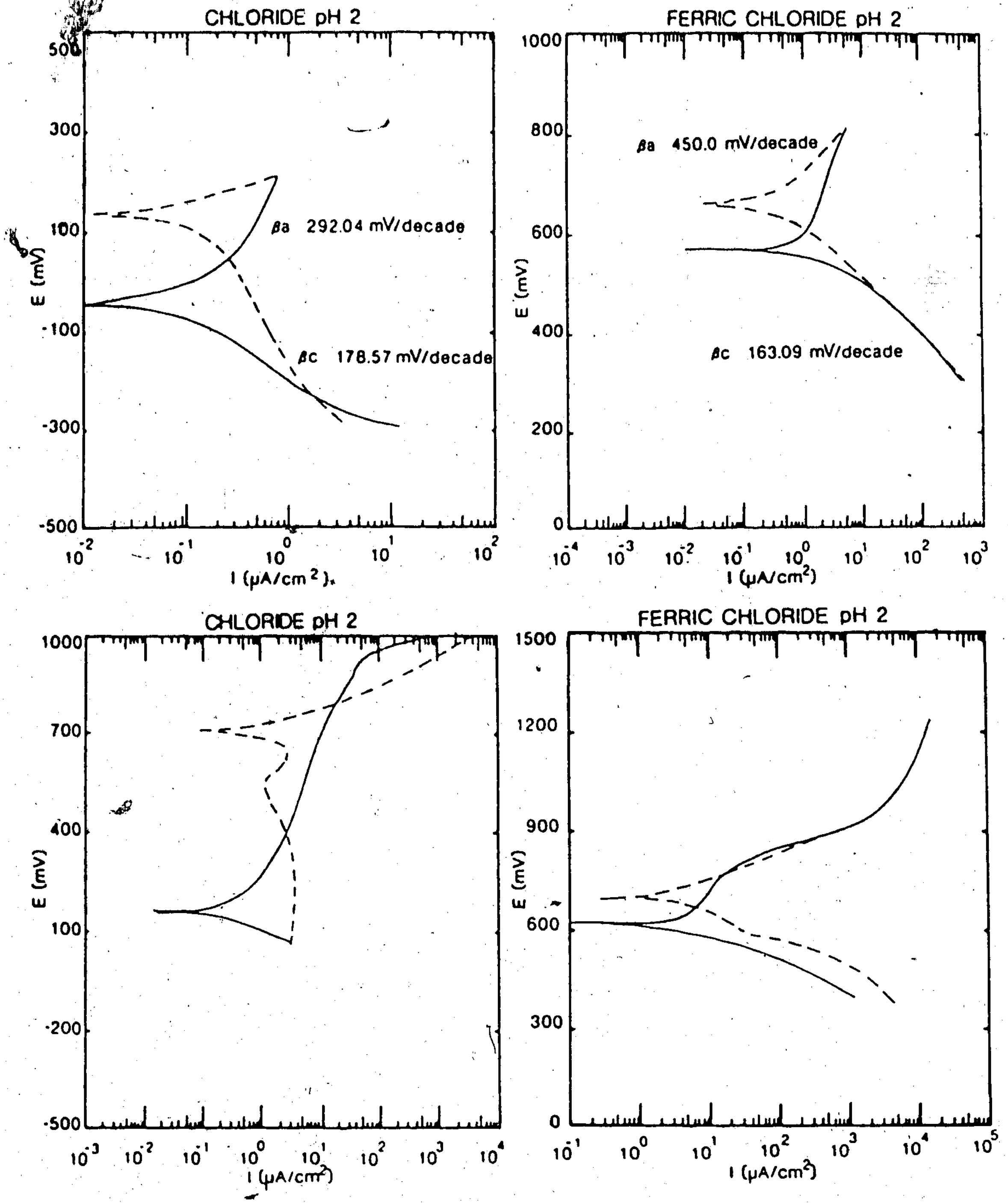


Figure III.11 Results of Tafel and Cyclic Polarisation experiments on gold with chloride and ferric chloride solutions at pH 2.

to calculate how much $AuCl_4^-$ could exist at an Eh of 771 mV (NHE) and thus be a result of reduction of Fe^{3+} That value turns out to be 8.05 X 10^{-5} ppt or 8.05 X 10^{-14} g/litre, see Appendix 1 for calculations. In a later section it will be discussed whether this content of $AuCl_4^-$ is significant. The Mn^{2+} to MnO_2 reaction may readily oxidise gold with a Eh of 1.23 V (NHE) (deBethune and Swendeman-Loud, 1964), but it is outside the stability of water so it is unlikely to occur in natural systems. In the electrochemical experiment it is probable that the reduction of Fe^{3+} to Fe^{2+} is forcing more gold to oxidise than would normally oxidise in a natural environment. This is because the electrochemical cell is an isolated system with no other metals available to oxidise. In Cloke and Kelly's experiments it is possible that the enhancement of gold oxidation that they observed was caused by a similar effect, but again in a natural environment it may not occur.

If, as suggested by Cloke and Kelly (1964), the stability between Fe^{2+}, Fe^{3+} and goethite can raise the Eh above the stability of water and therefore above 1.00V, then obviously $AuCl_4^-$ will form rapidly. Cloke and Kelly do point out however, that the conditions for this stability are extremely rare. At pH levels below 2 the hydrolised Fe^{3+} is dissolved. At higher pH's Fe^{3+} will precipitate as Fe-hydroxides, (Garrels and Christ, 1965). The commonly reported occurrence of Au in limonite or goethite (i.e. Mann, 1984) probably indicates that the iron may adsorb the gold causing it to precipitate with these minerals. The results of these experiments would indicate that although Fe^{3+} may oxidise gold to the pptrillion level, in a natural environment $AuCl_4^-$ is forced to form because the Fe^{3+} is reducing so rapidly.

Concentration Effects

As has been found by previous workers (Helgeson and Garrels, 1964), $AuCl_4^-$ is much more stable under acidic conditions than alkaline conditions. This is because the reaction:

$$Au + 4Cl^- + 3H^+ = AuCl_4^- + 3/2H_2$$

is dependent on H^+ being available. It is for this reason that experiments done to evaluate the effect of chloride concentration on electrochemical behaviour are all done at a pH of four. Chloride concentrations of 0.10M, 0.5M, 1.0M up to 2.5M by 0.5M increments were studied.

Because Ecorr is sensitive to slight pH and Eh variations in the solution, these variations can cause significant changes in Ecorr or the slopes of the lines. It is for this reason that it is impossible to reproduce the experiments exactly, therefore a quantitative comparison of concentration effects is not feasible. It can be said qualitatively, however, that an increase in the current occurs at all parts of the curves with increase in Cl^- concentration (Figure 12).

Ammonia

The results of the NH_4^+ experiments are similar to Cl^- results in that the Tafel experiment does not show any evidence of oxidation, indicating that it is in the region of passivation. The high sweep experiment, however shows a transpassive oxidation (Figure 13). The acceleration of current in the NH_4^+ is much less pronounced than in the Cl^- solution. Data of Skibstead and Bjerrum (1974) demonstrate the existence of a number of Au^+ and Au^{3+} - ammine complexes which form at 206, 325, or 563 mV (NHE). The current peak in the ammonia solution from this study starts at about 200 mV (SCE) or 444 mV (NHE). Data from deBethune and Swendeman-Loud (1964) show a standard potential of 110 mV (NHE), or 354 mV (SCE) for NH_4OH to N_2H_4. If the NH_4^+ solution follows the behaviour of the other solutions the current peak should be at least 400 mV below any known E^0 of oxidation. In this case the current peak is only 200 mV lower than the Au-ammine complex with the highest E^0. The peak may indicate that a gold-ammine complex is formed or that the NH_4^+ is oxidising but neither can be determined with any certainty.

Sulphur Species

With the high stability constants of $Au(HS)_2^-$ ($\log B_2 = 37.2$) and $Au(S_2O_3^{2})_2^{3-}$ ($\log B_2 = 29.4$ (Seward 1973)), there should be little doubt that gold will move in the presence of these species. The $S_2O_3^{2-}$ and HS^- curves are illustrated in Figure 14. The $S_2O_3^{2-}$ curve displays quite normal Tafel behaviour but is irreversible. This irreversibility is thought to be caused by oxidation of the solution rather than the gold. To test this hypothesis, the experiment was repeated twice, once with a platinum working electrode and once with a graphite working

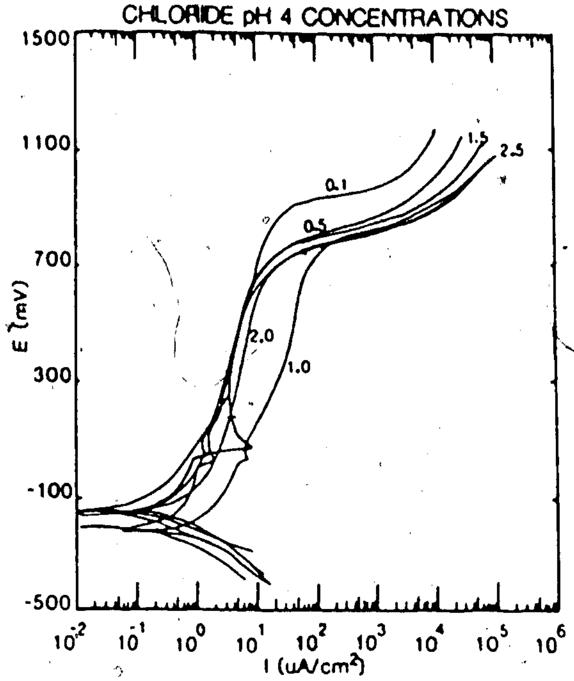


Figure III.12 Forward results of of Cyclic Polarisation experiments on gold with chloride solutions of differing concentration. Labelled concentrations in mol/litre.

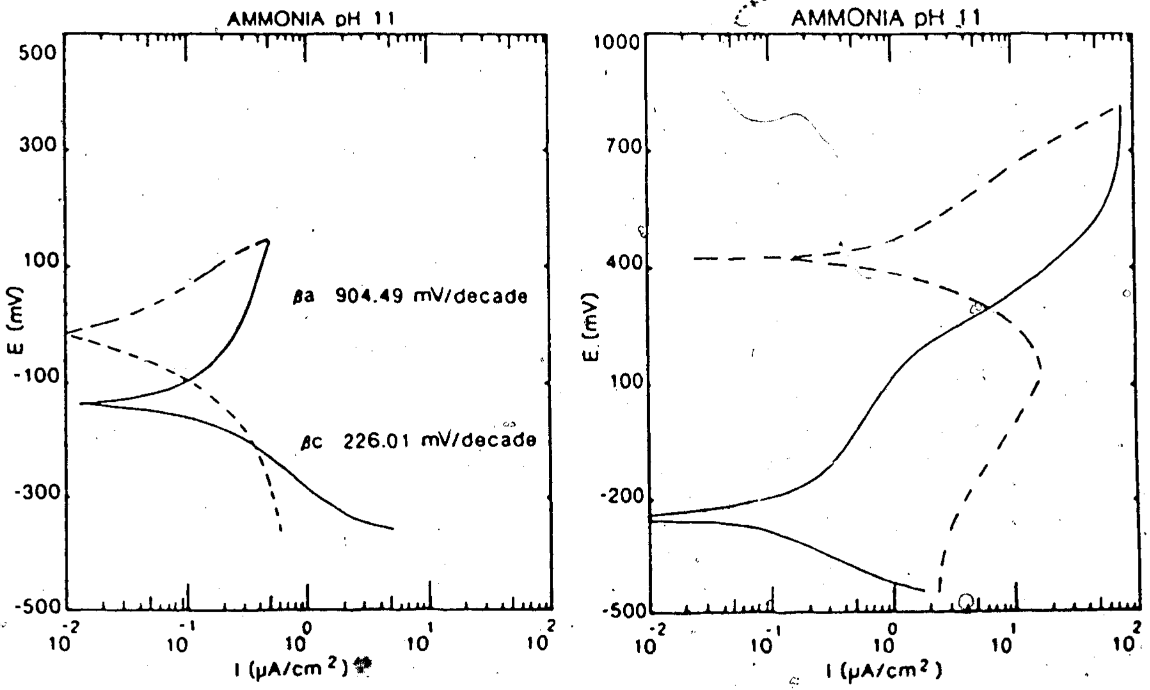


Figure III.13 Tafel and Cyclic Polarisation results of gold experiments with ammonia solution.

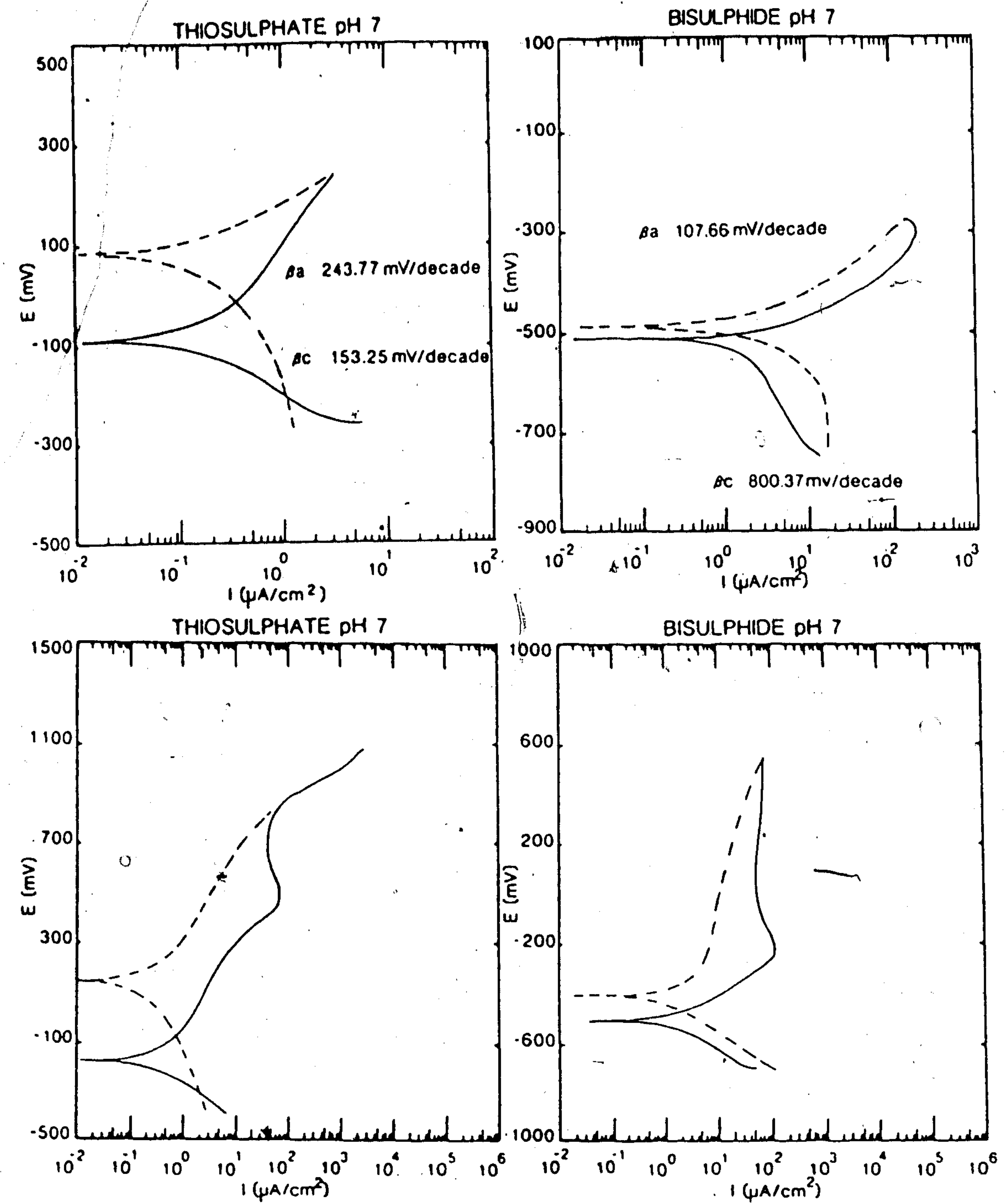


Figure III.14 Results of Tafel and Cyclic Polarisation experiments on gold with thiosulphate and bisulphide solutions.

electrode. In both cases the data were the same as they were with a gold working electrode. In the high cyclic sweeps there is a current peak at about 500 mV (SCE) with the gold electrode. This does not occur with the other two electrodes (Figure 15). This peak indicates that a reaction is taking place with the $S_2O_3^{2-}$ and gold that does not occur with platinum or graphite electrodes. Also, because the reverse sweep does not show a reduction at 500 mV, it indicates that whatever was formed is a soluble species not a surface species. Lakin <u>et al.</u> (1974) predict that $Au(S_2O_3)_2^{3-}$ forms at 600-700 mV (NHE) or 844-944 mV (SCE). If this potential is correct, the peak at 500 mV (SCE) could indicate that this complex is forming.

In an attempt to prove that a soluble thiosulphate species is forming, a series of 20 Cyclic Polarographs, as suggested by Plambeck (pers. comm.), was run from about 300 to 800 mV (SCE). To keep the oxidised species close to the electrode, the solution was not stirred and nitrogen was not bubbled into it. After this, a normal sweep was conducted. It was thought that if enough $Au\text{-}S_2O_3^{2-}$ species had formed the reverse sweep would show the reduction of those species at 500 mV. Instead, the result was that the peak disappeared (Figure 16a), even after vigorous stirring (Figure 16b). In a second attempt to prove that an $Au\text{-}S_2O_3^{2-}$ complex is formed, approximately 750ml of a 0.10M thiosulphate solution was spiked with about 10 ml of 0.025M $AuCl_4^-$ solution. Because the $AuCl_4^-$ solution is acidic and oxidising, addition of $AuCl_4^-$ caused the $S_2O_3^{2-}$ solution to oxidise somewhat, but again the ov[illegible] behaviour showed that the peak had disappeared (Figure 16). It is probable that, although the initial Cyclic Polarisation indicated that a soluble species was formed, the gold surface became protected during subsequent experiments. Because this protection also occurs with addition of $AuCl_4^-$, it would imply that whatever is protecting the electrode surface is a gold-thiosulphate species (Plambeck pers. comm.).

Because of the results with $S_2O_3^{2-}$, there was some suspicion that the HS^- solution would show the same behaviour. This suspicion was borne out by experiments using Pt and graphite working electrodes (Figure 17). These produce similar curves as the experiment using a gold working electrode. In the high sweeps a significant current peak is again found with the gold electrode (Figure 14). Fortunately, in the case of HS^- solution there is enough gold

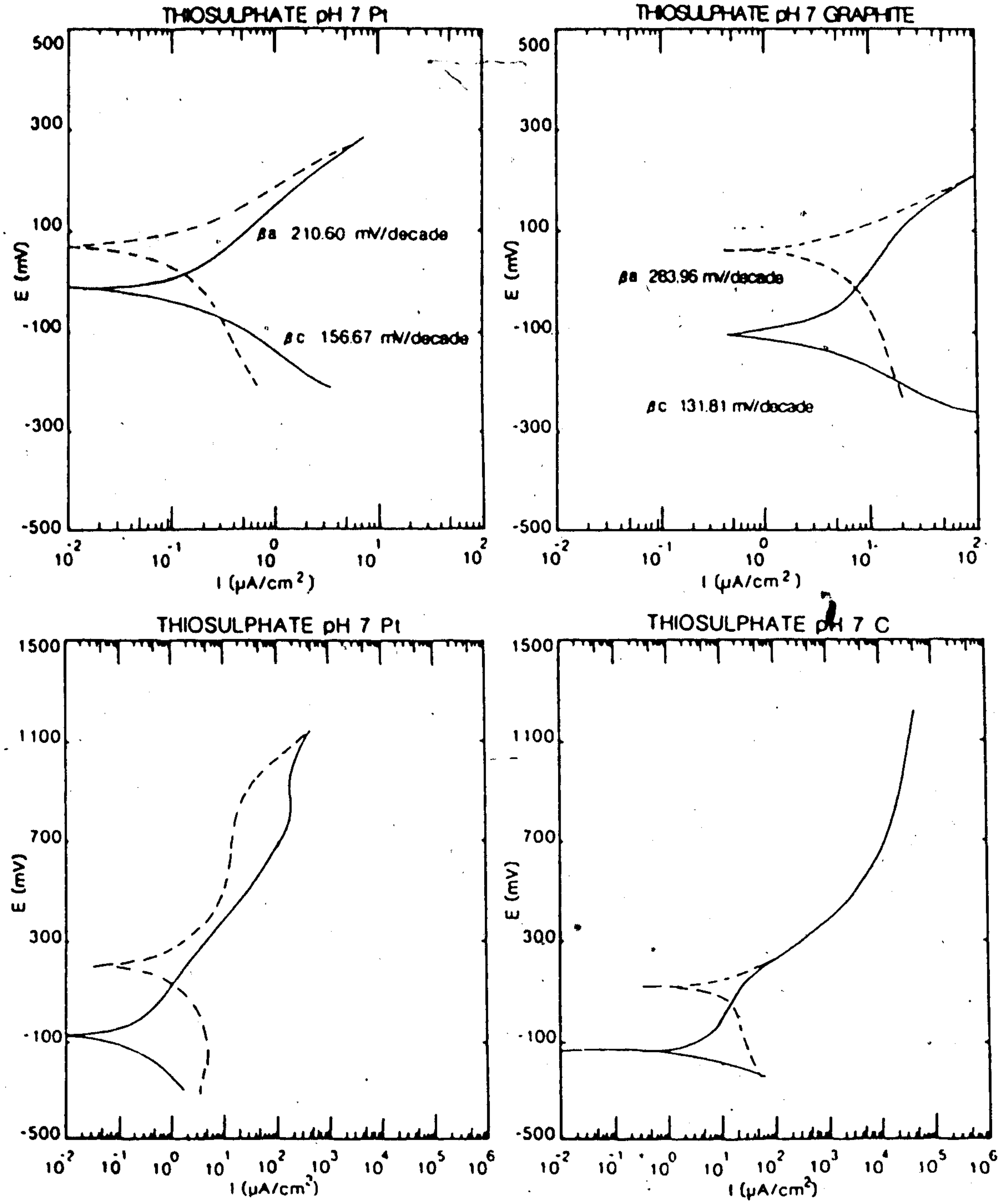


Figure III.15 Tafel and Cyclic Polarisation results of thiosulphate experiments with platinum and graphite electrodes.

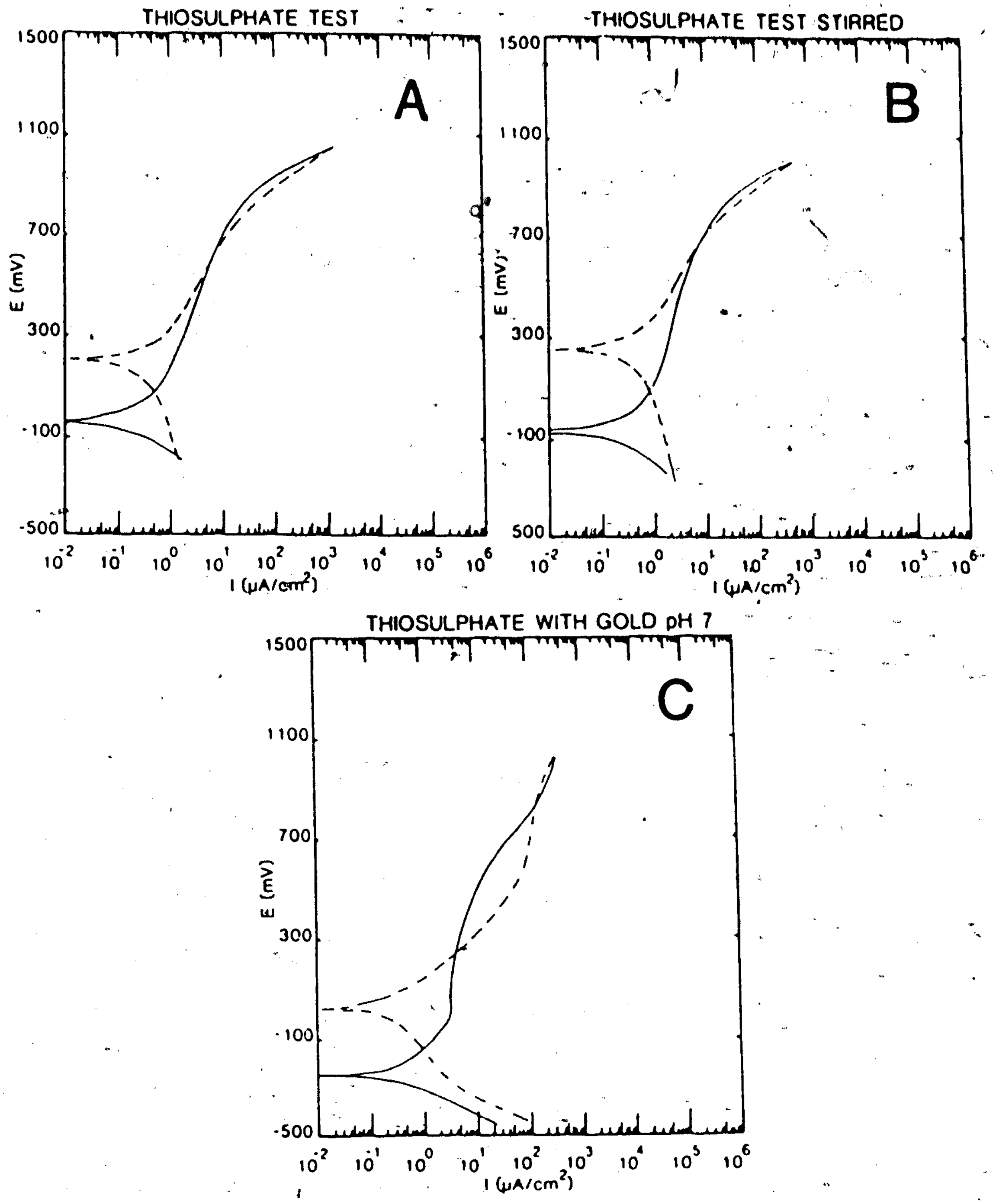


Figure III.16 Results of experiments in thiosulphate solutions, trying to prove the existence of a soluble Au-thiosulphate complex.

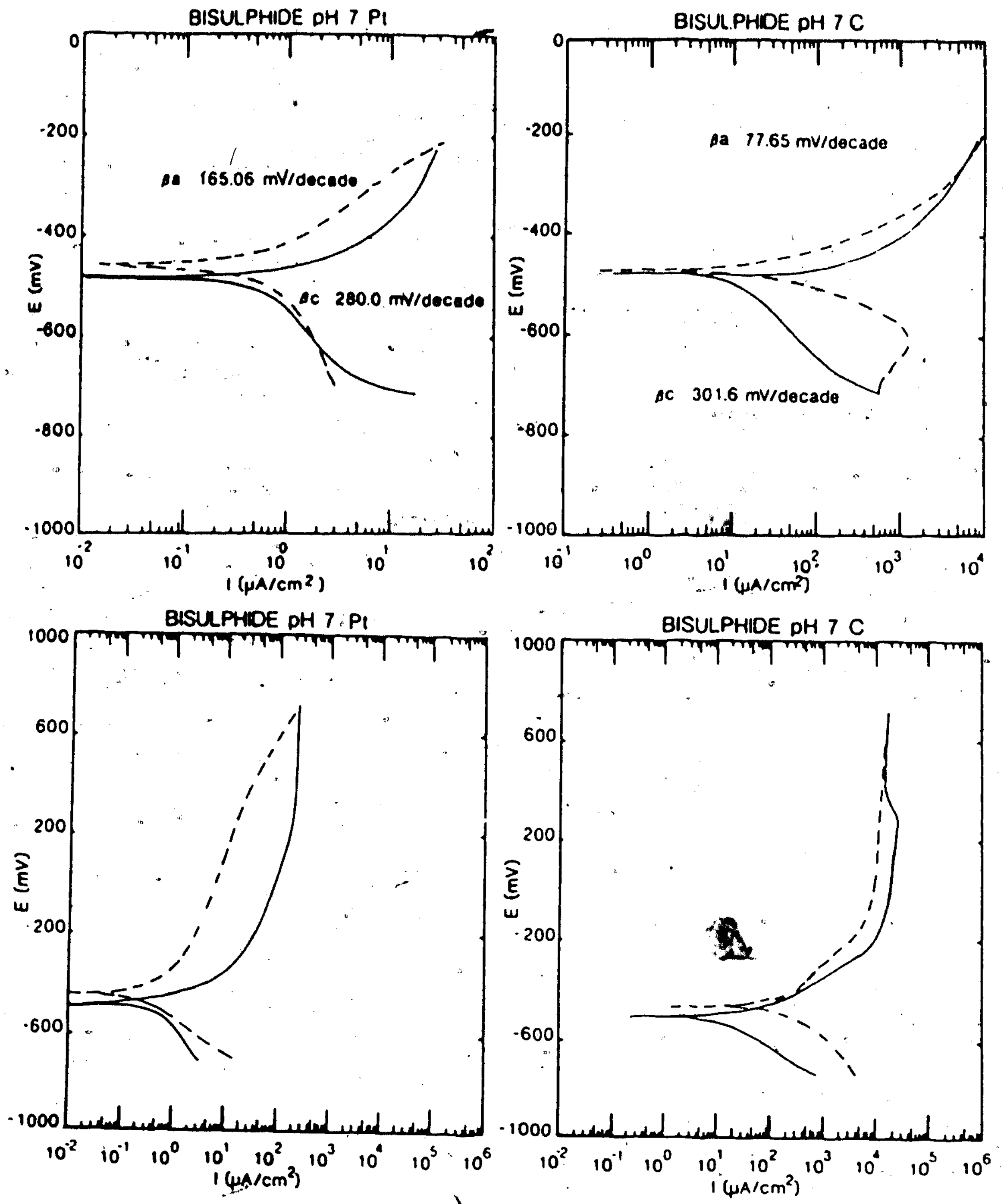


Figure III.17 Results of Tafel and Cyclic Polarisation experiments in bisulphide solutions with platinum and graphite electrodes.

movement that after a high sweep, the platinum electrode aquires a very thin layer of gold. This indicates that a soluble Au-HS^- complex was formed. The short cyclic sweeps were attempted with the HS^- solution but the behaviour of the bisulphide solution was so unstable that the peak could not be duplicated. The addition of $AuCl_4^-$ to the HS^- caused extreme oxidation with the probable production of polysulphides. The resulting experimental sweep, however, showed that the peak disappears as it does in the thiosulphate solution (Figure 18).

Figure 19 illustrates that the S_x^{2-} solution behaviour superficially resembles that of HS^- but it has a higher Ecorr. This may be a reflection of the overall more oxidised character of S_x^{2-} compared with HS^- (Giggenbach, 1974). [illegible] main characteristic of the S_x^{2-} solution is that at no point does the anodic Tafel curve [illegible] a straight line. These results could mean that the S_x^{2-} is oxidising to any of a numb[illegible]er longer polysulphide chains or other sulphur species altogether (Giggenbach 1974). It is also possible that an indeterminate amount of gold-polysulphide is forming as well. Because of the extremely unstable nature of the polysulphide solution (Giggenbach, 1974), the results are inconclusive.

On the whole, there is evidence to show that gold forms a complex with $S_2O_3^{2-}$ and HS^- but, there is no way to quantify how much current is produced by oxidation of the solution versus oxidation of the gold.

B. Non-Reactive Species

Sulphate

It was thought important for comparative reasons to understand the behaviour of solutions that did not significantly complex with gold. Sulphate solution was chosen for this purpose because of the low stability constant determined for $Au(SO_4)_2^-$, log β_2 = 6.1, (Peshchevitsky et al., 1970). The results of the experiments bear out these data (Figure 20). The Tafel experiment is not reversible and has a high anodic Tafel constant. The high sweep does not show any transpassive oxidation, nor is there any film formed or gold transferred to the counter electrode. This behaviour is the same at all pH's 4, 7, and 10; the only difference

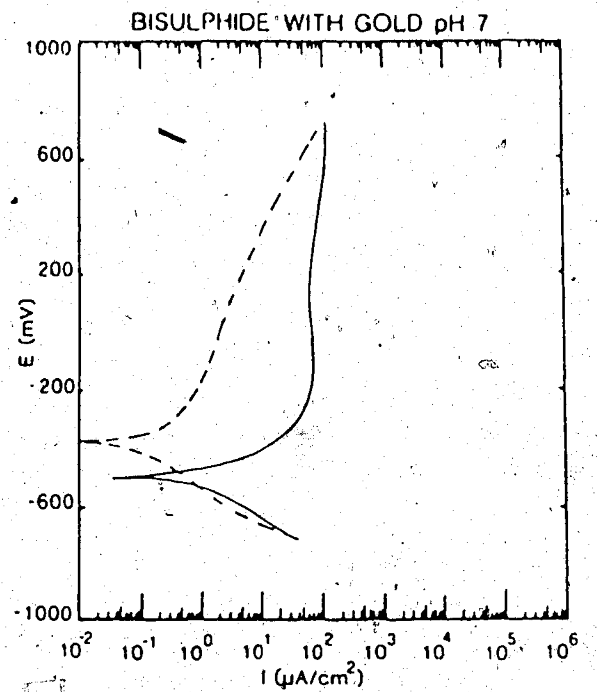


Figure III.18 Result of Cyclic Polarisation experiment on gold in bisulphide solution spiked with $AuCl_4^-$.

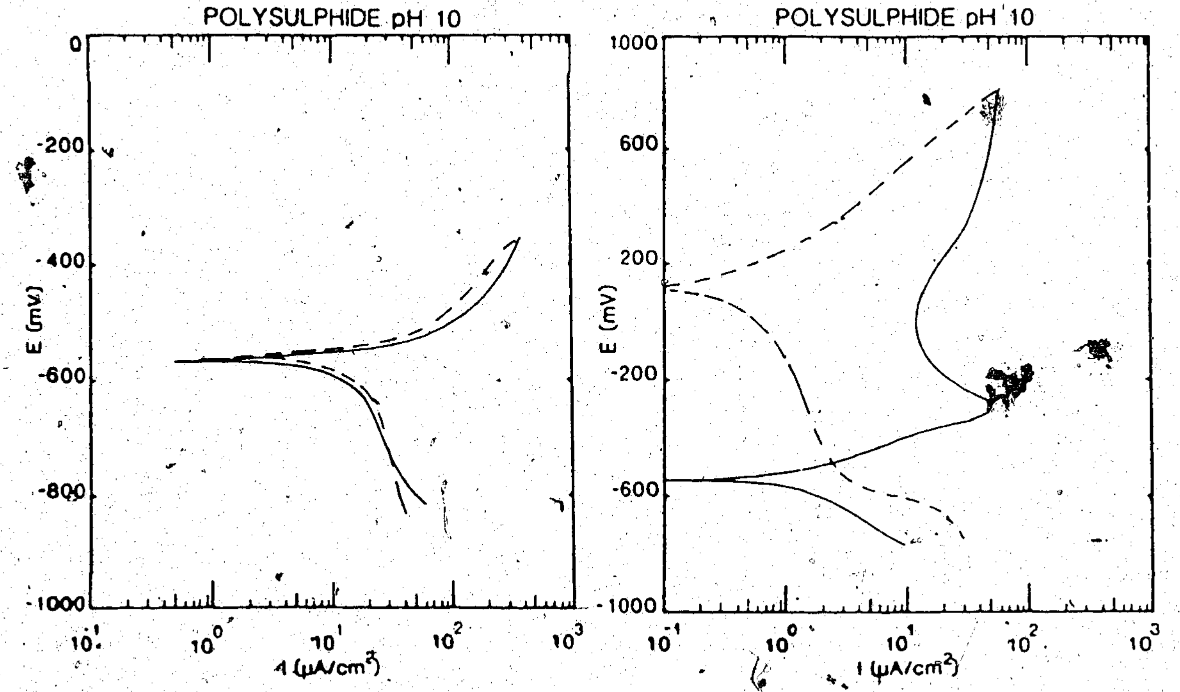


Figure III.19 Cyclic Polarisation results in polysulphide solution with gold.

being the slight reduction of Ecorr with increasing pH, as reported with the Cl^- solutions. The results obtained with the sulphate solutions as well as the following species are probably all water or water solute oxidation behaviour.

Hydroxide

Experiments with hydroxide solution were conducted to determine if the presence of OH^- would facilitate oxide growth. The results are negative (Figure 21). Because the OH^- solution behaves in the same way as the SO_4^{2-} solution at pH 10, it is interpreted that there is no significant complexing reaction occurring between gold and OH^-.

Carbonate

Results of experiments with both CO_3^{2-} and HCO_3^-, display the same evidence for lack of gold transport as SO_4^{2-}, (Figure 22). This seems to negate the idea proposed by Kerrick and Fyfe (1981), that gold may be transported as CO_3^{2-} complexes, although these experiments are at much lower temperatures than those proposed.

Mixed Solutions

The possibility that a mixture of solutions could enhance oxidation was also investigated. Solutions of 0.10M Cl^- with 0.10M CO_3^{2-}, $S_2O_3^{2-}$, and HS^- were examined. It appears that rather than exhibit a combined effect the behaviour of the solution is dominated by one of the ligands. By comparing Figure 23a with Figure 9, it is apparent that the shapes of the curves and the similaries in Ecorr indicate that in Cl-carbonate solutions the chloride behaviour dominates. Comparisons of Figure 23b and 23c with Figure 14 show that thiosulphate and bisulphide respectively dominate the behaviour when mixed with chloride. To study the behaviour of a natural solution with numerous components, a sample of North Saskatchewan river water was examined. This water had a pH of 8 and displayed almost identical behaviour to the bicarbonate solution, (Figure 24). According to Morel (1983), it is expected that in a multi-ligand solution the ligand which exhibits the fastest kinetic behaviour

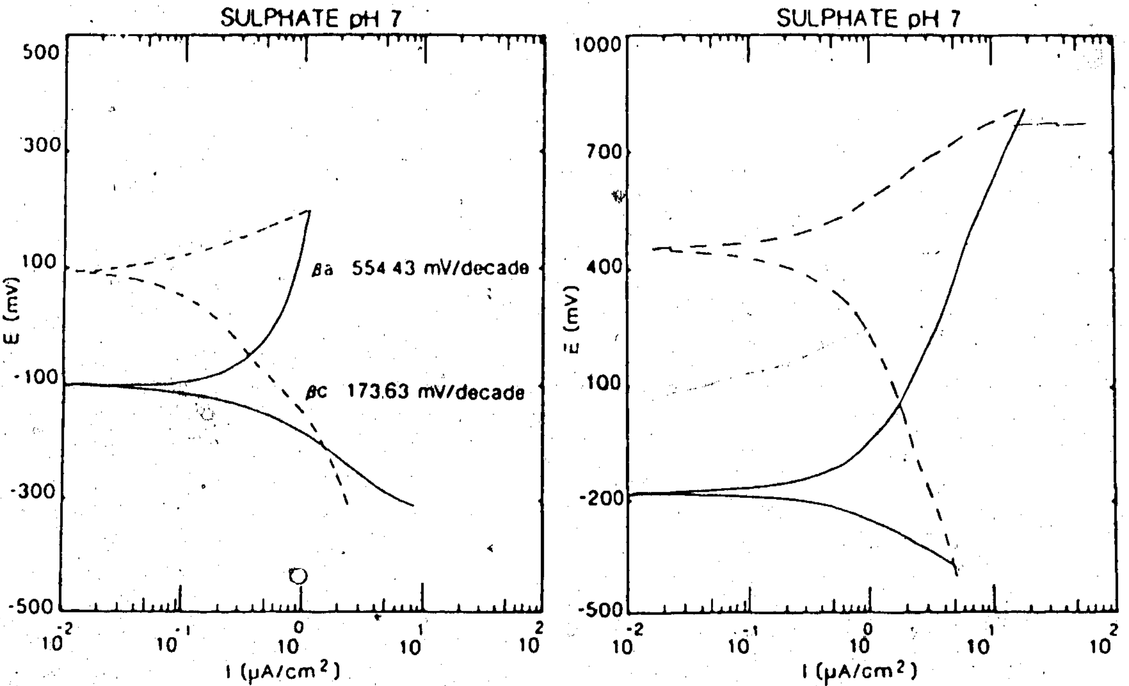


Figure III.20 Tafel and Cyclic Polarisation results of gold experiments in sulphate solution.

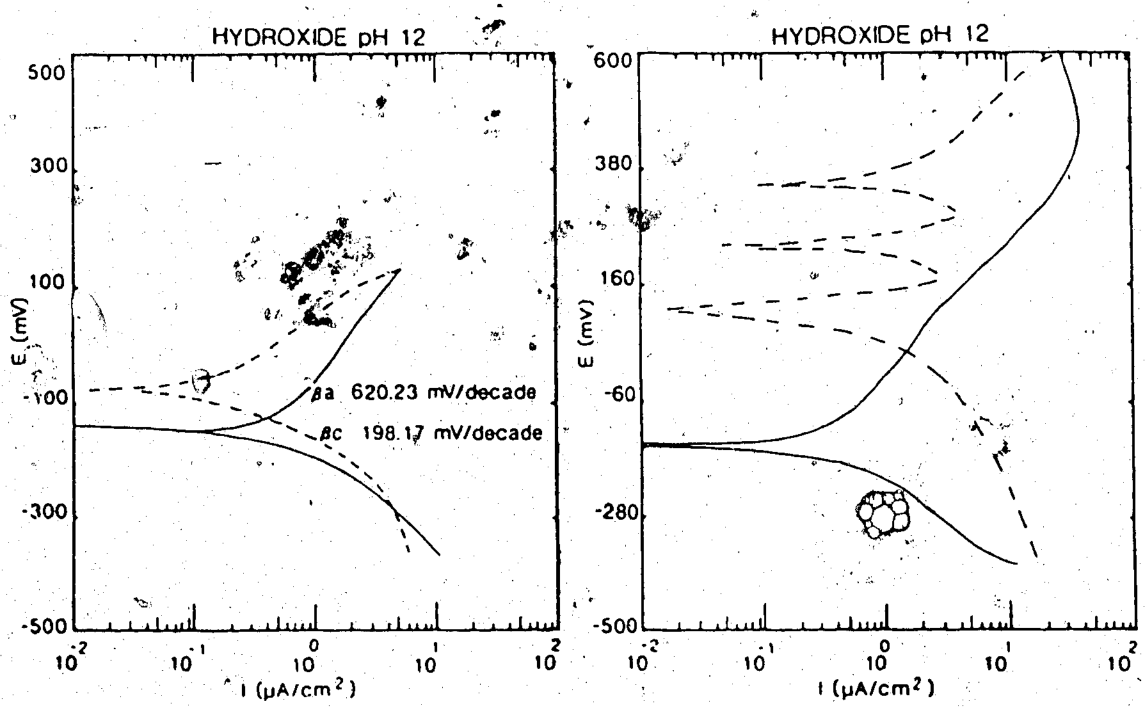


Figure III.21 Tafel and Cyclic Polarisation results in hydroxide solution with gold.

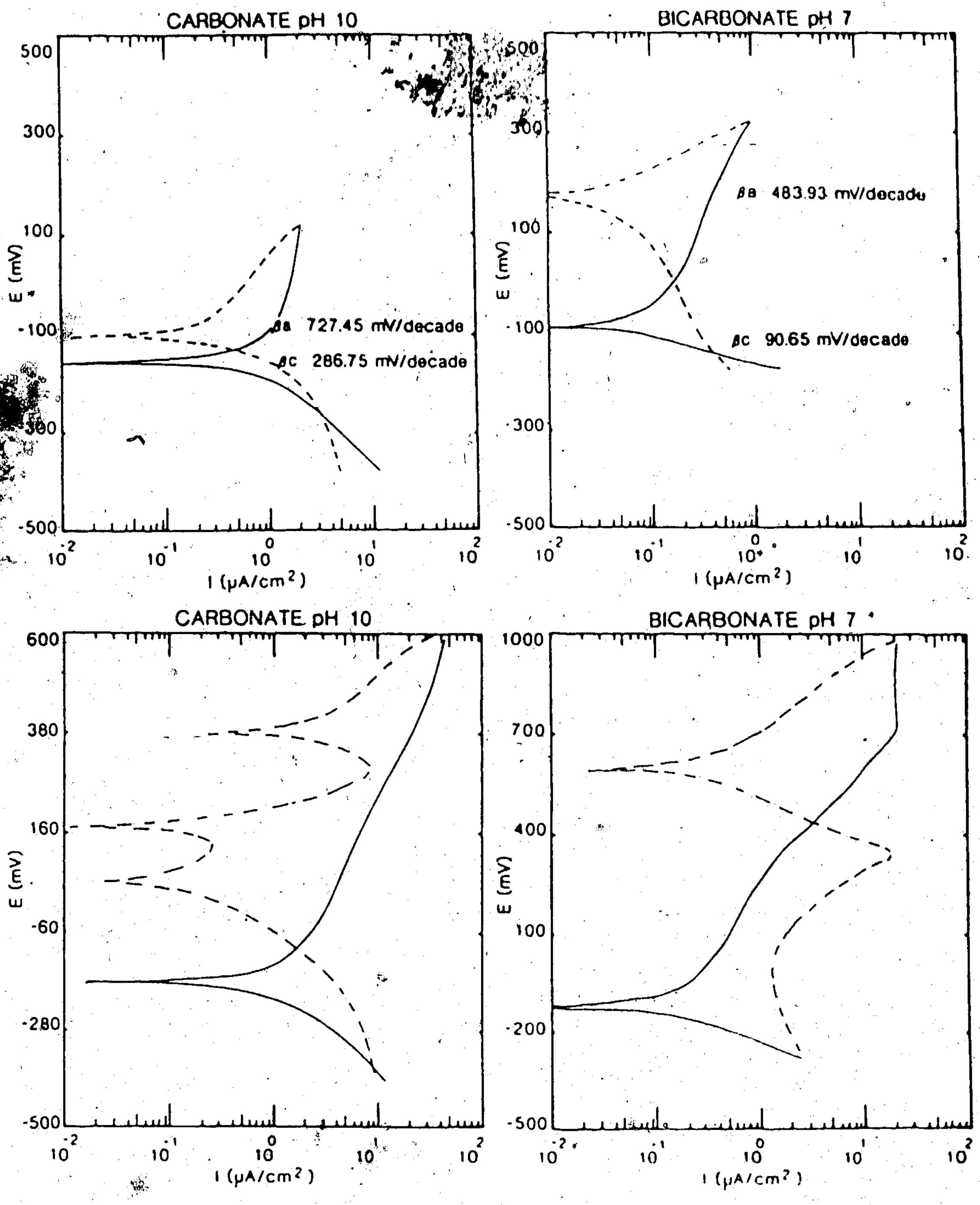


Figure III.22 Tafel and Cyclic Polarisation results on gold in carbonate and bicarbonate solutions.

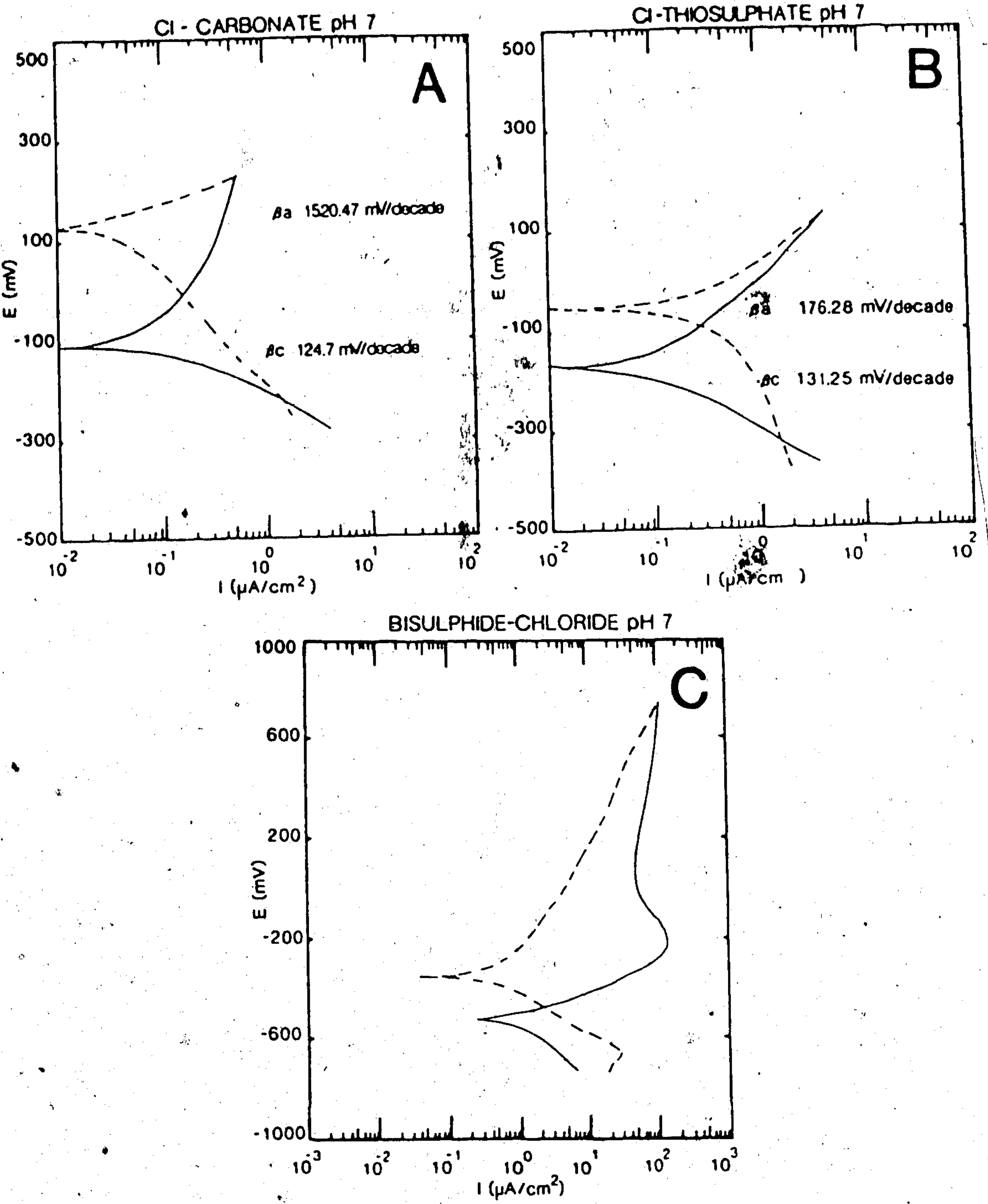


Figure III.23 Results of gold experiments with: A, Cl-carbonate B, Cl-thiosulphate and C, Cl-bisulphide solutions.

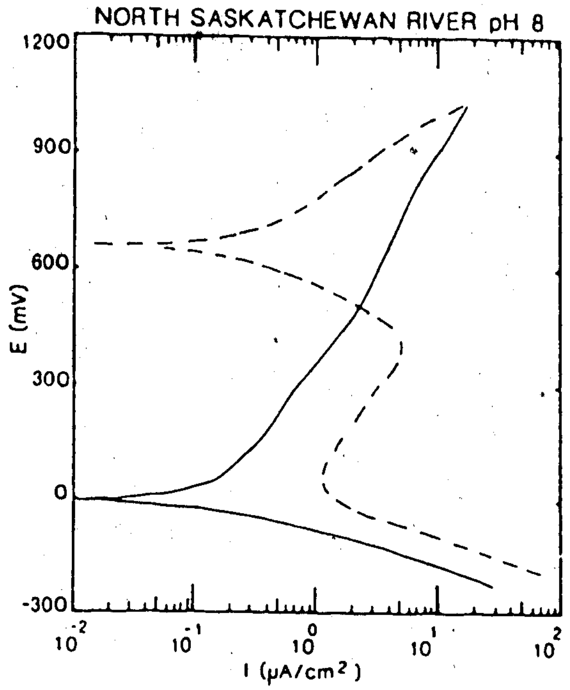


Figure III.24 Cyclic Polarisation result of gold experiment in North Saskatchewan River water.

will dominate the behaviour in the experiment.

C. Results of Experiments With Gold in Organic Solutions

The behaviour of gold is very similar in all the organic solutions studied, except for the humic extract. Three of the solutions had a pH of 3 or 4. These were acetic acid, citric acid and phenol. The Tafel regions of these are shown in Figure 25. For all three solutions, the rest potential is between 100 mV and -100 mV. They all have very high anodic Tafel constants as well. It is interpreted that there is no oxidation occurring in this potential range.

In the sweep experiments (Figure 26), there is more variability in Ecorr but overall the three organic solutions behave in a similar manner. In all three solutions, there is a very slight current inflection at about 500 mv (SCE). It is possible that this is a result of a slight adsorption of hydroxide (Hoare, 1984). Because of the lack of transpassive oxidation and lack of observed gold mobility, it is interpreted that these experiments indicate that no significant oxidation of gold is occurring.

Two other organic solutions had a pH of 7. These were benzoic acid and methanol (Figure 27). It can be seen by comparing both their Tafel regions and high sweeps with Figures 24 and 25, that the behaviour is again almost exactly the same for all five solutions. The conclusion to be drawn from these experiments is that all these organic solutions behave in a similar manner regardless of pH and that they do not seem to complex with gold. This is not surprising since Varshal <u>et al.</u> (1984) found that the more effective fulvic acids for complexing had molecular weights between 1500 and 5000. Obviously the phenol and carboxyl with molecular weights of 94.11 and 122.12 respectively are far too light if this relationship holds. Also, the citric acid with a molecular weight of 210.12 is too light as well.

The results of the humic extract are shown in Figure 28. The Tafel region seems to have a similar Ecorr to the other organic experiments, but the anodic Tafel constant is quite normal. The experiment is, however, irreversible which led to a suspicion that the solution was oxidising instead of the gold. The cyclic sweep experiment shows a fairly high and steady current increase with oxidation which indicates that an oxidation reaction is occurring but the

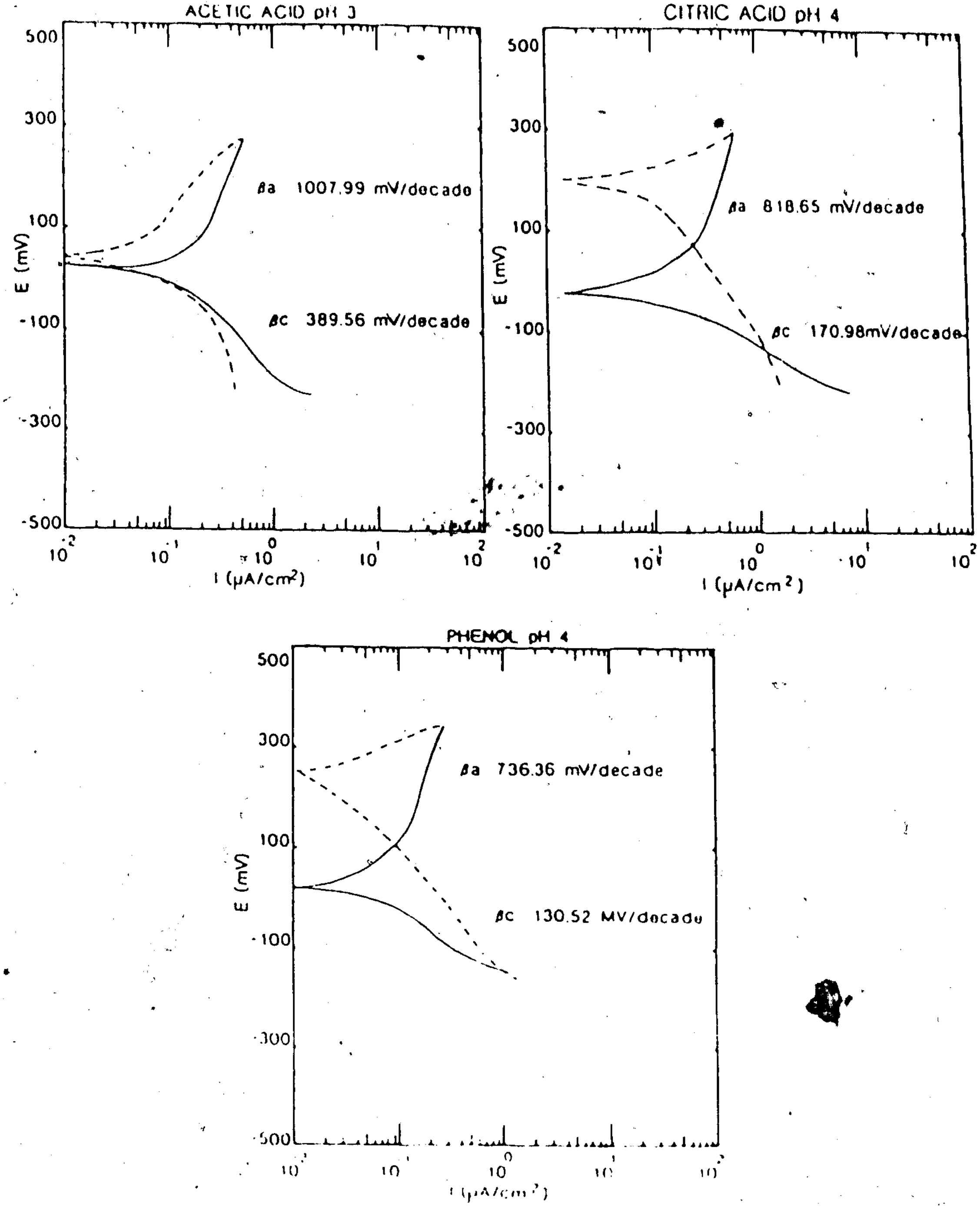


Figure III.25 Results of Tafel experiments with gold in acetic acid, citric acid, and phenol.

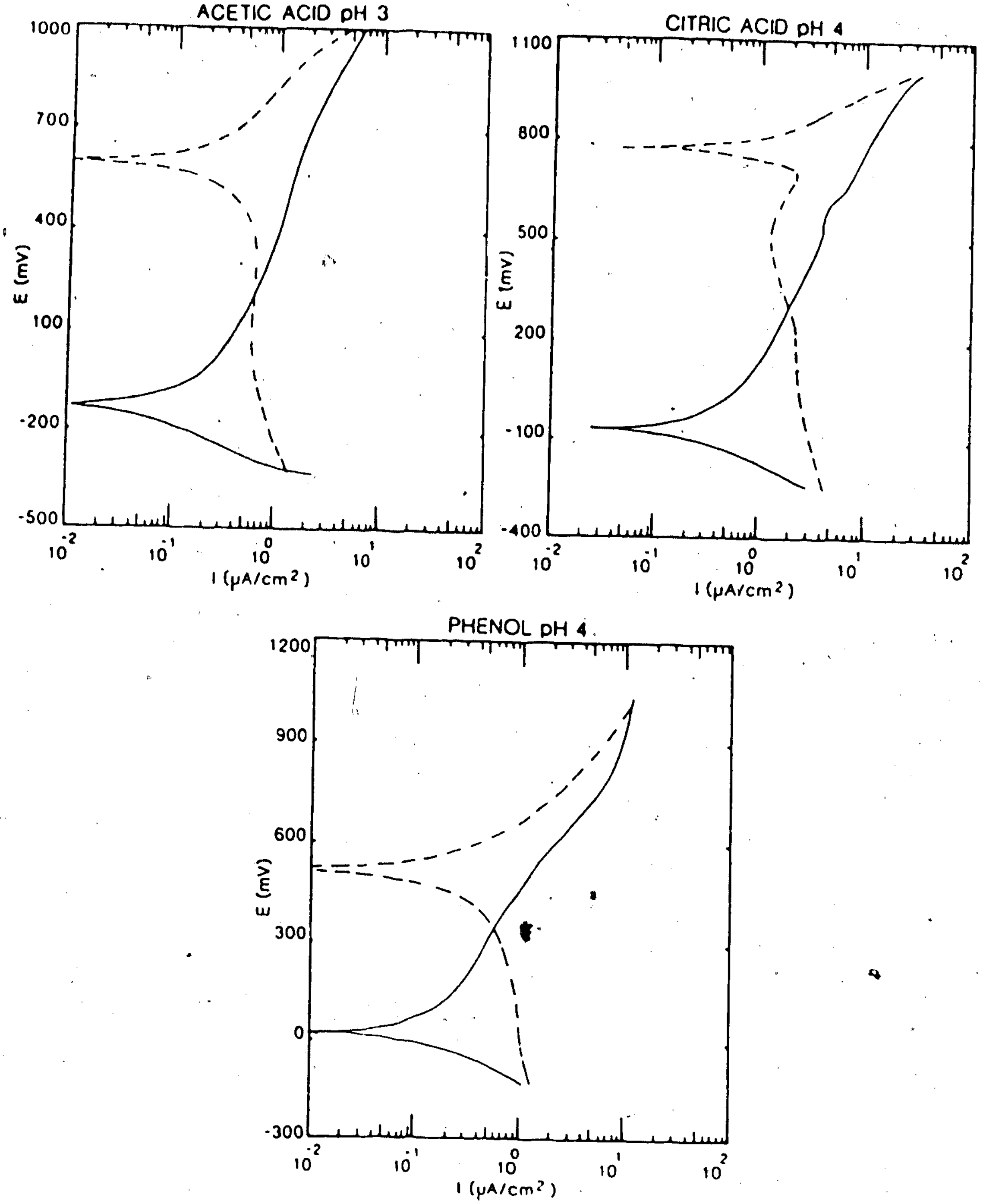


Figure III.26 Cyclic Polarisation results with gold in acetic acid, citric acid, and phenol.

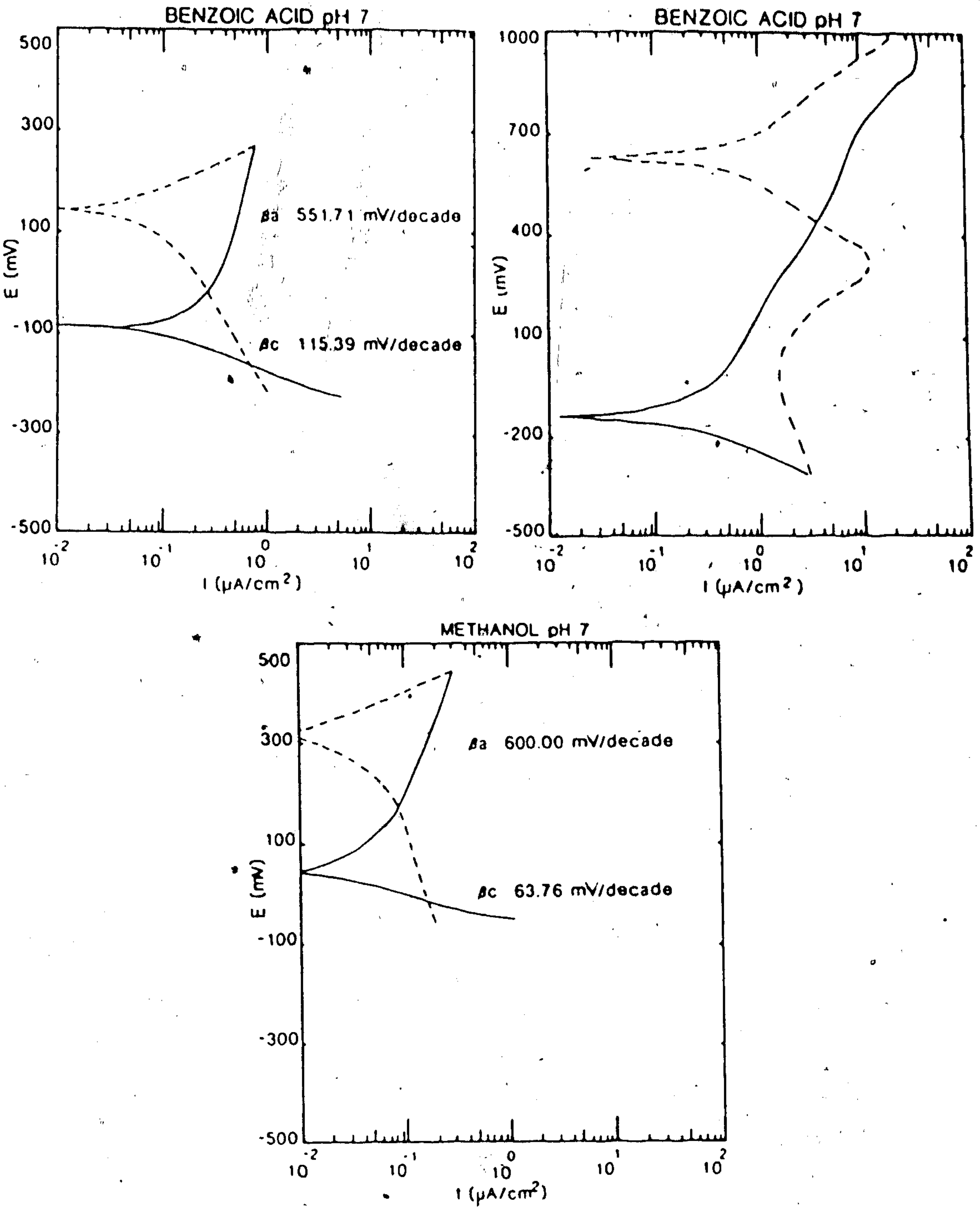


Figure III.27 Results of experiments with gold in benzoic acid and methanol.

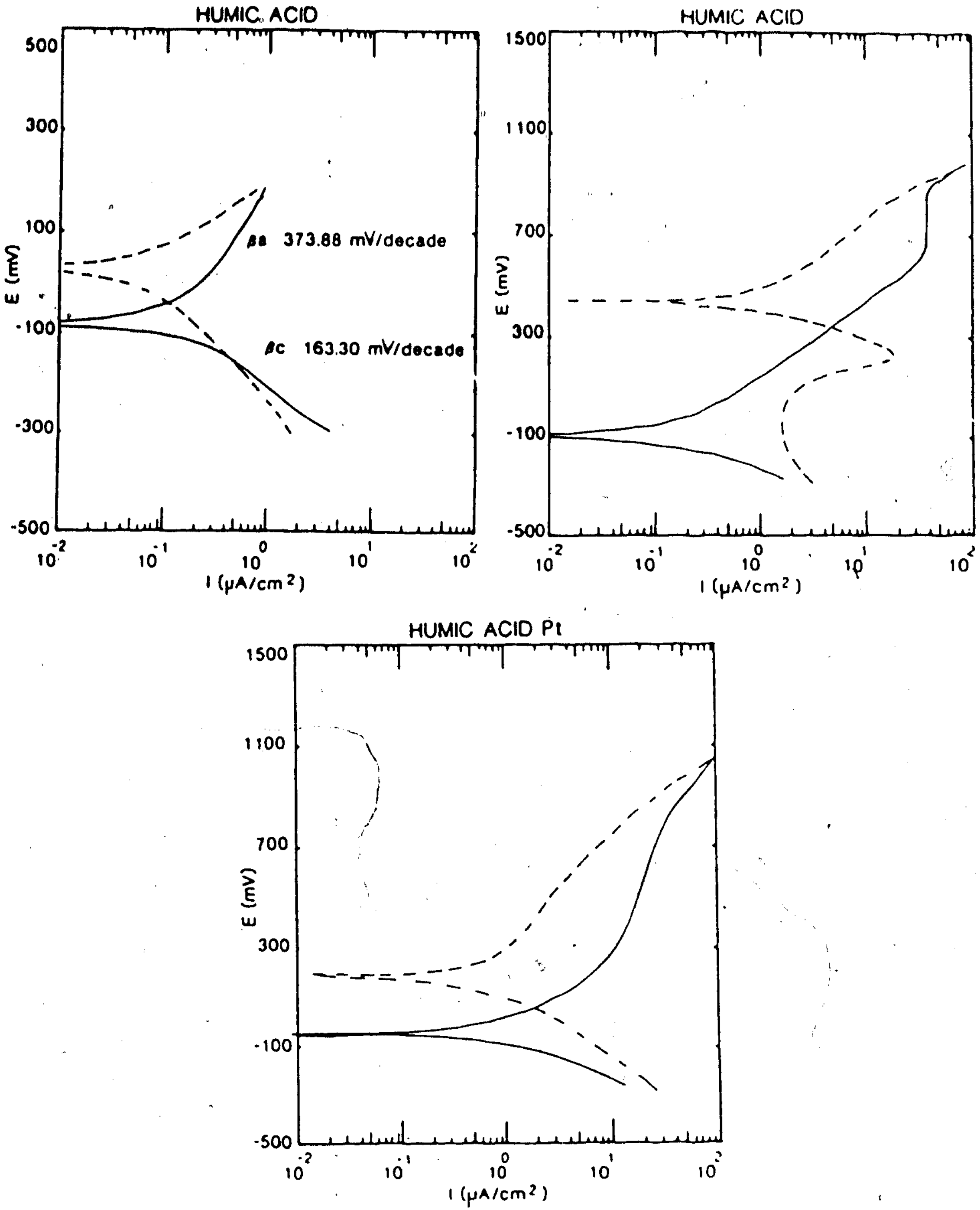


Figure III.28 Tafel and Cyclic Polarisation results with gold in humic acid and Cyclic Polarisation result in humic acid with a platinum working electrode.

oxidising species is unknown. A sweep experiment with a platinum working electrode displays similar behaviour to the experiment with a gold working electrode (Figure 28). Although the gold and platinum sweep experiments are not exactly the same, they are similar enough to conclude that both are showing solution oxidation.

From the results of the organic experiments with gold, it would appear that there is no evidence that significant gold complexation occurs in any of the solutions. Examination of the gold electrode from the humic acid solution reveals no evidence of etching or reaction of any kind. This is in strong contradiction to the results of Baker (1978) who proved through polarography that humic complexes are formed with gold. It is unknown what the cause of this discrepancy is. It is possible that the concentration of the humic acid in this study was much less than 0.10M because most of the humic material was in colloidal form. For this reason it is not possible to determine exactly to what extent humic acids complex with or if they complex with gold. From the results of the other organic ligands, though, it is possible to say that the individual functional groups are not responsible for gold transport. If there is any transport, it is due to properties of the organic molecule as a whole.

D. Results of Experiments With Silver in Inorganic Solutions

To compare oxidation of siver with oxidation of gold, the experimental techniques applied with gold were also applied with a silver working electrode. With the exception of the cyanide species and polysulphide, all the same ligands were studied as well. From the overall E°'s of silver reactions, (deBethune and Swendeman-Loud, 1964), it is apparent that silver is generally much more readily oxidised in all solutions than gold. In each experiment the current peak seen is accompanied by formation of a black film. Usually the best curves to display these peaks are the high sweeps.

Oxides

The film formed in the SO_4^{2-} solution is presumed to be a silver oxide (Figure 29). The reason for this assumption is that the E° for Ag_2SO_4 is 654 mV (NHE) or 898 mV (SCE)

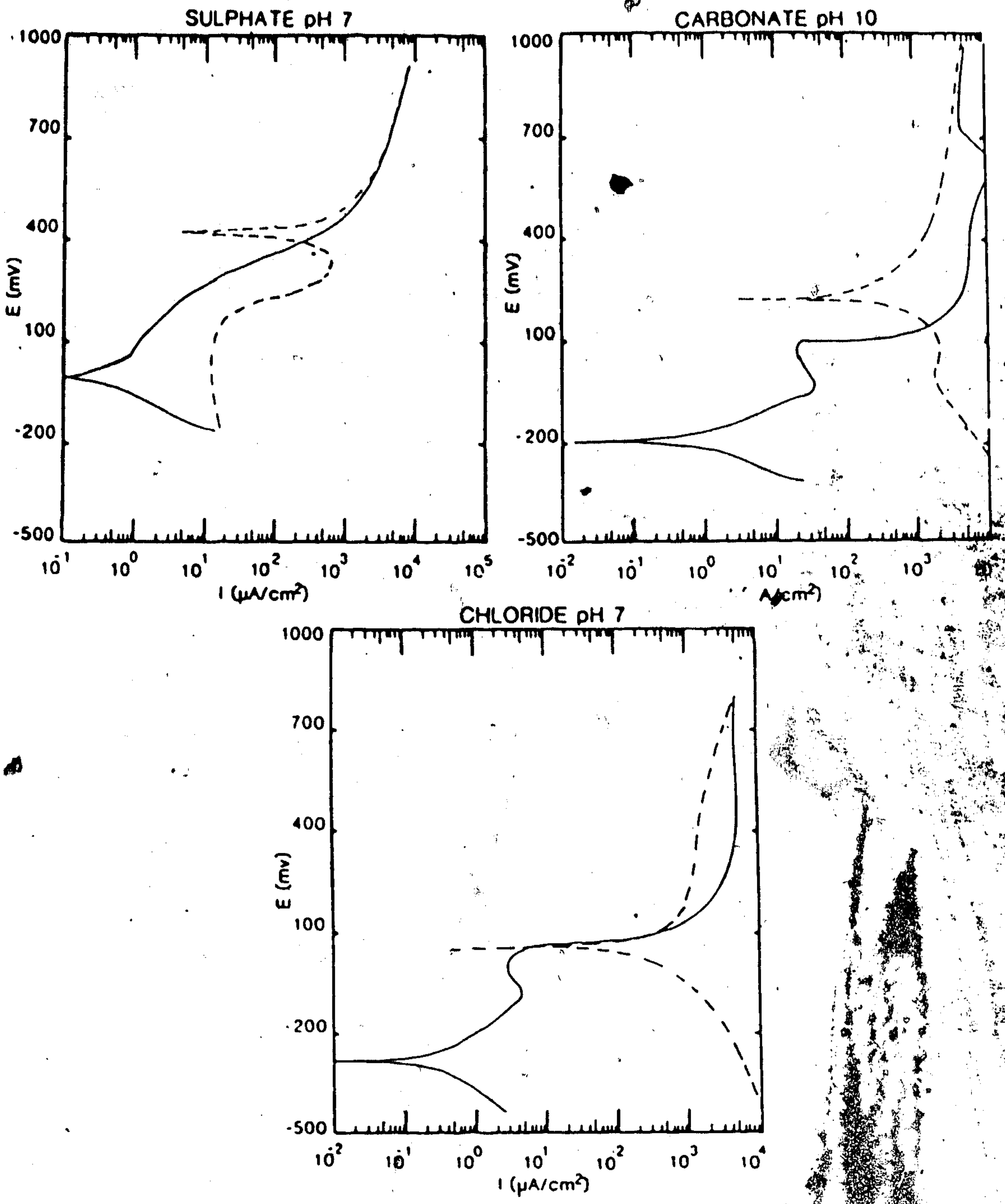


Figure III.29 Cyclic Polarisation results with silver in sulphate, carbonate, and chloride solutions.

(deBethune and Swendeman-Loud (1964)), which is much higher than the current peak shown by the experimental results. From the same data source Ag_2O formation is at 373 mV (NHE) or 617 mV (SCE) which is about 500 mV higher than the observed potential of 100 mV (SCE). As was found with the gold experiments, this is a reasonable difference in potential between the experimental peak and E°.

The silver oxidation peak in the carbonate solution, (Figure 29), seems to be at a lower potential than the peak in the sulphate solution but, from deBethune and Swendeman-Loud,'s data of 470 mV (NHE), 714 mV (SCE) for Ag_2CO_3 formation the oxide is again most likely because it has a lower E°. The oxidation peak in the carbonate solution is probably lower than that in the sulphate solution because the carbonate solution had a pH of 10 whereas the sulphate solution had a pH of 7. As was discussed in the gold chloride results, an increase in pH causes Ecorr to be reduced. Because reduction of Ecorr is due to water stability the water stability may cause oxide peaks to reduce as well.

Chloride Solution

Silver in Cl^- solution (Figure 29) readily oxidises to form a film as well as a complex. The latter is inferred by the presence of a precipitate which forms on the counter electrode. The potential for AgCl formation is 224 mV (NHE), or 468 mV (SCE). The experimental potential where the current starts to accelerate is about 50 mV (SCE), so it can be assumed that the film formed is AgCl. The morphology of this film will be described in a later section.

Sulphide Solutions

As in the chloride solution, a film and complex are formed in the sulphide solution, although passivation is not observed. The film is thought to be Ag_2S (Figure 30). This is because E° of Ag_2S formation is at -660 mV (NHE), or -416 mV (SCE). Ecorr in the HS^- experiment is about -800 mV (SCE) followed by extreme oxidation. Also like the chloride solution the Ag_2S film has a distinct morphology which will be shown in a later section.

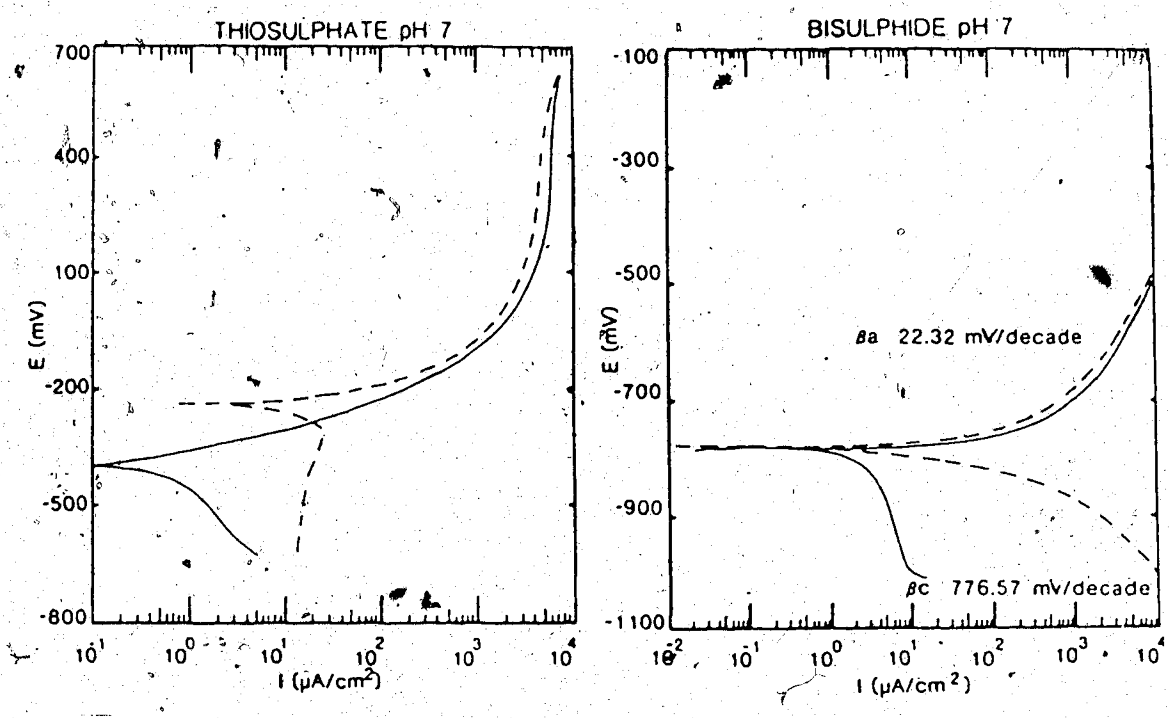


Figure III.30 Results of experiments with silver in bisulphide and thiosulphate solutions.

In the thiosulphate solution it is not clear what the oxidati[illegible]on is (Figure 30). Formation of $Ag(S_2O_3)_2^{3-}$ is at -227 mV (SCE) (deBethune and Swendeman-Loud, 1964), but the Ecorr of the reaction is at about -350 mV (SCE). Obviously this potential is too high for Ag_2S formation and only about 100 mV below the Ag-thiosulphate reaction. Considering that all the other experimental reactions in this study start at 400-600 mV lower than E°, it is doubtful that Ag-thiosulphate reaction is occurring in the observed potential range. It is possible that another unknown Ag-thiosulphate reaction is occurring, because again a black precipitate forms on the counter electrode indicating that a mobile complex has formed.

Unlike gold, all the silver experiments can undergo Tafel analysis in the region of Ecorr. The corrosion rates of these experiments are compiled in Table 2. From the results of these experiments it can be said that silver will oxidise significantly faster in most cases than gold. This does not, however, mean that complexes are forming to a far greater extent. As was found with gold in the Cl^- solution the current was produced by, a combination of complex formation and oxide formation. In the silver experiments some type of solid is formed in all solutions. This means that the effective amount of Ag complex is not as high as the current may indicate.

The purpose of examining silver was to understand the processes that cause changes in gold fineness with transport in supergene and fluvial environments. There is no problem explaining the commonly reported phenomenon of increase in fineness with distance from source (i.e: Boyle, 1979). This is because silver is much more readily oxidised than gold, to form a silver oxide and complex. There are examples reported however, where gold is not enriched, but gold and silver move together, that are more difficult to explain. Perhaps in a solution where gold is very mobile such as in Cl^- or HS^-, but where a silver solid is formed, there is enough reduction in the mobility of silver through precipitation that both metals will move at the same rate.

E. Results of Experiments with Silver in Organic Solutions

The experiments with silver in organic solutions were conducted in a similar manner to the gold experiments. All the same organic ligands were studied with the exception of methanol.

The behaviour of silver is very similar in all the organic solutions. In most cases the best curves to illustrate the oxidation behaviour are the high sweep results. These are shown in Figure 31. All the anodic sweeps show an acceleration at 200-400 mV (SCE) except the humic extract. The experiments were also all accompanied by film formation. Data given by deBethune and Swendeman-Loud (1964), for $AgC_2H_3O_2$ (acetic acid) oxidation is 643 mV (NHE) or 887 mV (SCE). This is too high for the reaction seen in the acetic acid results. There are no data for the other organic ligands but it is likely that the potential for the reaction of silver with the other organic ligands would be similar to that for acetic acid. The potential for Ag_2O formation is 345 mV (NHE) or 589 mV (SCE). This is much closer to the experimental results. Also, because it is at a lower potential it is likely to happen at a lower potential. As a result it is interpreted that in all these experiments Ag_2O is forming.

Behaviour of silver in the humic extract is very unusual (Figure 32). In the Tafel region, the Tafel constants are quite normal but when the experiment is reversed a significantly lower rest potential results. This behaviour was not observed previously in this study. The film formed on the silver surface is similar to any other silver oxide seen so it should cause the reverse rest potential to be higher than the original rest potential, as it does in the other solutions. From the gold experiment with humic extract it was assumed that the results were those of solution oxidation. In the gold experiment the rest potential was about -100 mV (SCE). In the silver experiment the reverse rest potential is approximarely -200 mV or lower, so it cannot be assumed that the unusual behaviour is a result of solution behaviour. One possibility to explain the lower rest potential is that silver reacts with the solution to form a Ag-organic solid or complex which has a lower rest potential than Ag_2O and lower than the humic extract. Because the humic compounds are composed of C, H, and O it would be impossible to verify this hypothesis with the EDXA on the SEM.

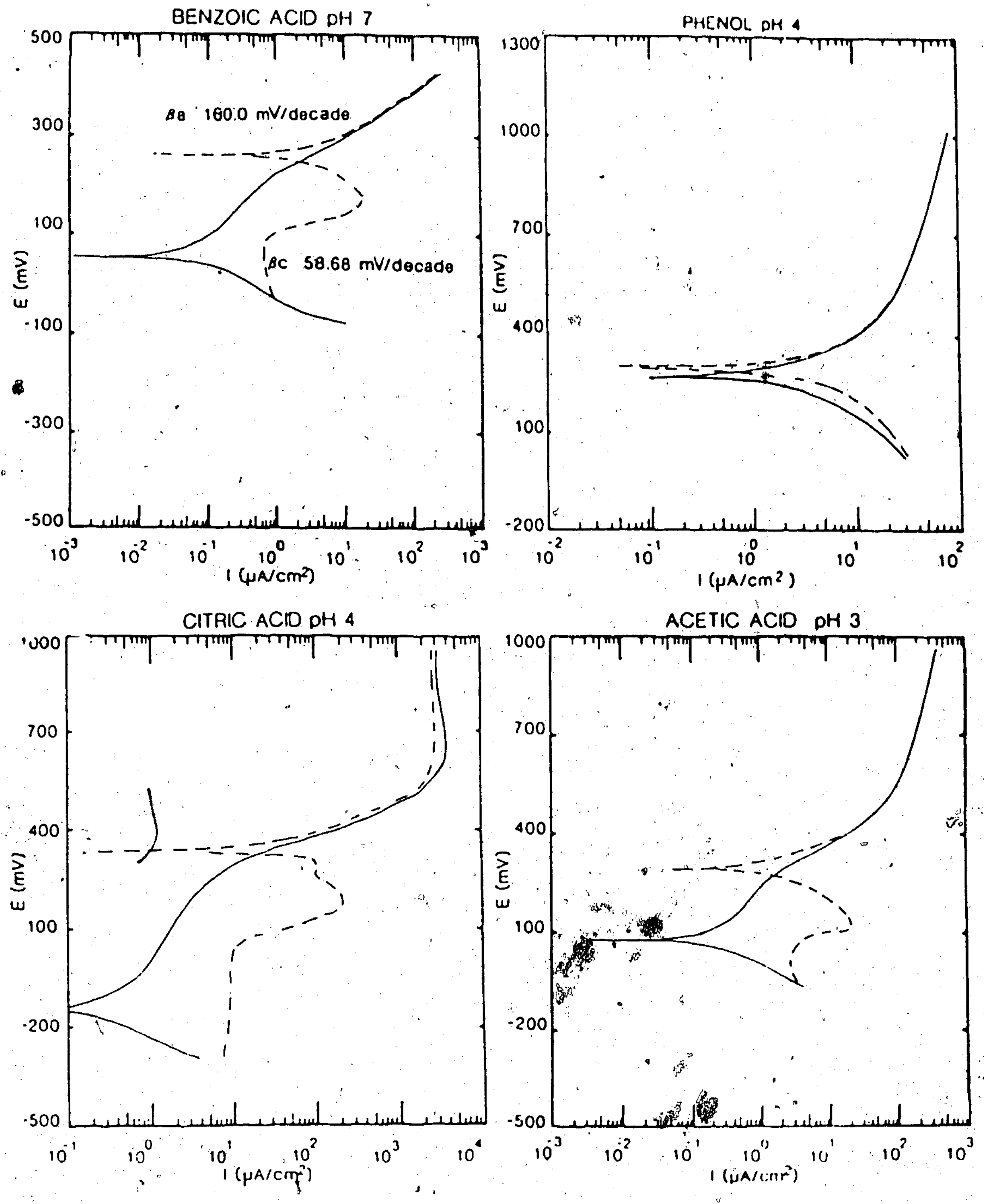


Figure III.31 Results of experiments with silver in benzoic acid, phenol, citric acid and acetic acid.

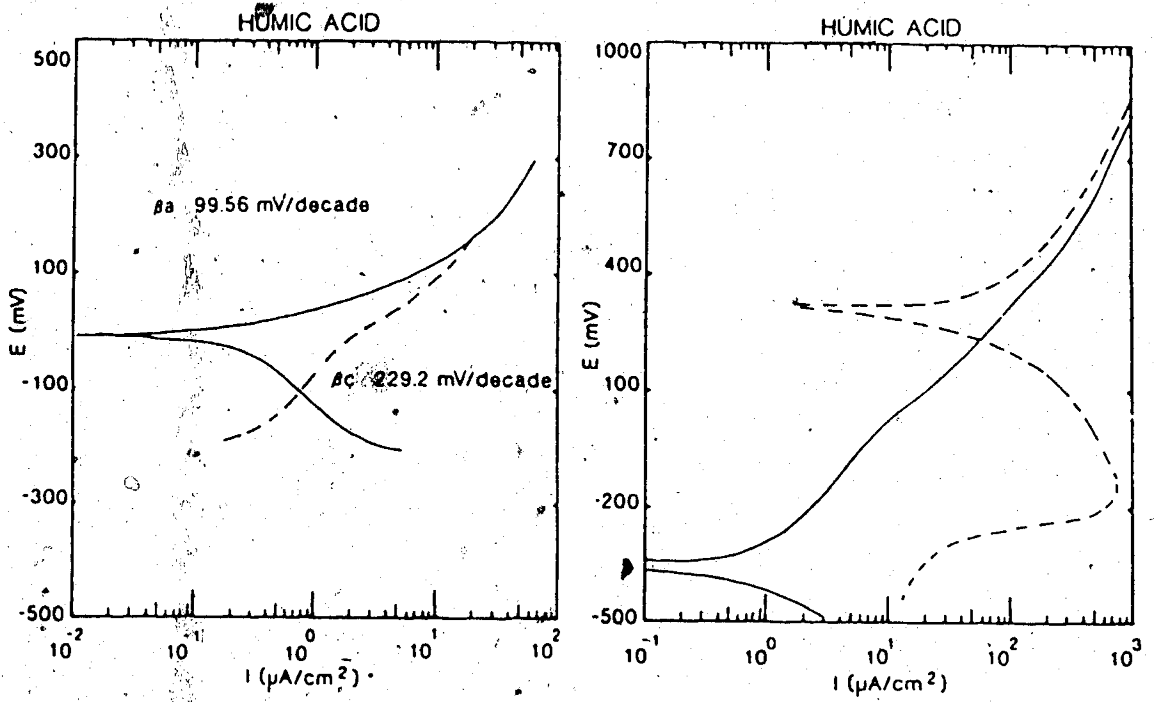


Figure III.32 Tafel and sweep results with silver in humic acid.

IV. Surface Features

Another result of electrochemical experiments is that the surfaces of the electrodes often record evidence of reactions which have occurred. This evidence may be in the form of films or etching on the electrode. The purpose of examining these features is that it is likely that metals in a natural environment will show similar features. Therefore, if they are observed, it will be possible to determine the conditions under which the natural metal was leached or deposited. These features were examined optically and by semiqualitative analysis with a Cambridge Stereoscan 250 Scanning Electron Microscope with a Kevex 7000 EDXA capacity. Images were taken of an unreacted electrode for comparisons (Plate 1).

A. Films

Cyanide Species

Both CN^- and SCN^- solutions produce a film on the gold electrode during Cyclic Polarisation experiments. In the case of the CN^- solution, the film is dark and very thin. This is probably a gold oxide as discussed in the results. An SEM image was not obtained because the film disappeared with continued oxidation. The film produced in the SCN^- solution was thicker with a reddish colour. This film persisted after it was formed. The SCN^- film is shown in Plate 2. Semiquantitative analysis of this film shows only gold to be present, although C or N, which are undetected by the EDXA, may be giving the film its reddish colour.

Chloride

In the Cl^- solutions a thin dark film also formed during the Cyclic Polarisation experiments. At pH 4 this film grew quickly and evenly but at pH 7 and 10 it was more sluggish to form (Plates 3,4 and 5). The reasons for this are not clear [illegible] at pH 4 the formation of substantial amounts of $AuCl_4^-$ allows a thicker oxide layer [illegible] up. This is a possibility because electrochemical researchers (Gaur and Schmid, 1970; Gallego et al., 1975)

Plate IV.1 Surface of a gold electrode before any experiments.

Plate IV.2 Film formed on gold in SCN$^-$ solution.

Plate IV.3 Film formed on gold in chloride solution at pH 4.

Plate IV.4 Film formed on gold in chloride solution at pH 7.

suggest that formation of a gold oxide film is caused by competition between Cl^- and OH^- ligands for adsorption sites on the gold surface. This idea originated with observation of iron which oxidises much more rapidly in the presence of Cl^- ion. It is suggested here that Cl^- may prevent passivation of the iron surface by Fe-oxide by blocking access to some of the adsorption sites.

A question which arises is whether the $AuCl_4^-$ is forming by further oxidation of the Au-oxide (Angerstein-Kozlowska 1984) or by direct contact with fresh gold (Gallego et al. 1975). Either case is possible as can be seen by the SEM images of the Au-oxide. It is apparent that although oxide evenly coats the gold surface it is porous and allows access to the fresh gold as well. It was found by Gaur and Schmid (1970) that if the gold is oxidised past 1100 mV (SCE) the oxide film completely covers the gold resulting in extreme passivation. This means that, at 1100 mV neither Au-oxide or $AuCl_4^-$ can form. It would seem then that the $AuCl_4^-$ must be forming at the fresh gold surface otherwise there would still be a high current from further oxidation of the oxide.

Silver

In all the silver experiments except for Cl^- and HS^-, the films formed were probably oxides, (i.e. Plate 6). The films from the Cl^- and HS^- experiments are shown in Plates 7 and 8. It can be seen that both AgCl and Ag_2S have very distinct morphologies. These films are important because Cl^- and HS^- are the two most important complexing agents of gold as determined in this study. Therefore, if they are seen in natural systems they may give valuable clues as to the complex responsible for gold mobility.

B. Etching

Gold in the presence of 0.10M Cl with Fe^{3+} shows very little oxide formation compared to the other Cl^- solutions, but it shows extreme etching, (Plate 9). This does not seem to be a pH effect since the electrode from the Cl^- solution at pH 2 was indistinguishable from the one at pH 4. As can be seen in Plate 9, the surface is obviously etched to the point

Plate IV.5 Film formed on gold in chloride solution at pH 10.

Plate IV.6 Oxide film formed on a silver electrode.

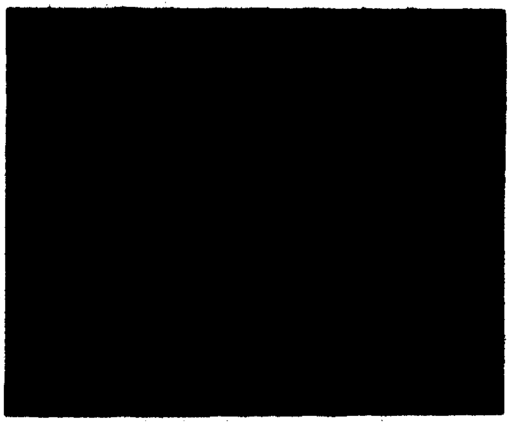


Plate IV.7 Ag-Cl film formed on a silver electrode.

Plate IV.8 Ag-S film formed on a silver electrode.

Plate IV.9 Etching of a gold electrode from the ferric chloride solution.

Plate IV.10 Surface of the gold electrode from the bisulphide solution.

that the polishing scratches are being eliminated. It would appear that the presence of Fe^{3+} in the solution enhances oxidation through processes already discussed in the results, but the EDXA indicated that there was no iron on the surface of the gold.

The surface of the gold from the HS^- solution is suspected to have been etched to some extent, (Plate 10) particularly when compared to the control electrode. More than etching, however, there appears to be flakiness on the surface. Semiquantitative analysis with the EDXA shows that sulphur is not present so the flakes are not deposits of sulphur bearing compounds.

Films Formed by Reduction of the Solution

As a natural corollary to gold oxidation and complexation in solution, there are also environments where the gold is deposited. This phenomenon is illustrated beautifully in the $FeCl_4^-$ solution. It has previously been shown that the working electrode is strongly etched which means that there is a significant amount of $AuCl_4^-$ in the solution. In the $FeCl_3$ experiment, a smooth unscratched gold disk was used as the counter electrode. Plate 11 illustrates how the gold is deposited on the counter electrode as small spheres. More interestingly, though, there seems to be a crystallographic preference for deposition. Before the experiment was conducted the polycrystalline nature of the gold electrode was not visible but afterward it was outlined distinctly by the precipitated gold. Jean and Bancroft (1985) noted a similar sphere shape for gold that was reduced onto sulphide minerals from $AuCl_4^-$ solution. Preferential deposition was noted by Hammelin and Bellier, (1973), and was determined to be in the 111, 332, 221 and 110 crystal directions.

To study deposition of gold from $AuCl_4^-$ solution to the irregular scratched surface, a 0.01M solution of $AuCl_4^-$ was prepared by dissolving 1.97g of gold in aqua regia. The HNO_3 was boiled off while HCl was periodically added to the solution. The addition of HCl was repeated 3 or 4 times then the acid was completely boiled off. Finally the resulting solid was redissolved in 1 litre of deionised water. The pH of the solution was then adjusted to 4. Reduction of the gold in solution onto the gold working electrode occurs readily if the

Plate IV.11 Deposition of gold from ferric chloride solution onto the gold counter electrode.

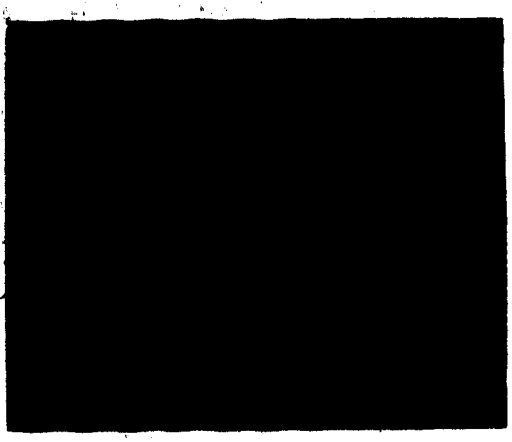


Plate IV.12 Deposition of gold from $AuCl_4^-$ solution onto the gold working electrode.

potential is brought below 800 mV (SCE). Initially the gold forms spheres as described before (Plate 12) but with continued reduction the gold acquires a crystalline shape, (Plate 13).

Plate IV.13 Continued reduction of gold from $AuCl_4^-$ solution onto a gold working electrode.

V. Geological Implications

The results of this study have improved the understanding of the properties of gold transport in low temperature settings. Such settings include supergene environments, soils, placers, and low temperature reducing scenarios such as bogs or euxenic marine environments. The results of this study outline conditions which are favourable for certain ligands to transport gold. Also these results can yield actual rates of oxidation of the metal. The morphological features of gold surfaces observed also provide information on the dissolution and precipitation of gold. Through the following examination of the experimental results and comparisons with natural environments, it will be possible to better assess the conditions under which gold transport has occurred.

Throughout this study, data have been presented in the form of current densities, but in order to make these data more meaningful with respect to natural environments, they must be converted to corrosion rates and the corrosion rates applied to a geologic scenario. The corrosion rates are cal[illegible]ted through the equation found in the experimental section.

$$W/t = 0.13\ IM/nd$$

Table 2 lists the ligands which show evidence of gold oxidation along with potential and current data, and the calculated corrosion rates for each ligand. Also listed, are the minumum lengths of time for each ligand to transport gold in the following hypothetical geologic scenario. It should be pointed out that these would be absolute minimum times because, with the exception of in the CN^- experiments, a significant film was formed on the electrodes.

It is apparent that, although corrosion rates are a useful tool for comparing gold oxidation rates between various ligands, the rates are not always the rates of complex formation, particularly when oxide films are formed. In such cases calculations of solubility using thermodynamic data can be useful in establishing boundary conditions for maximum gold solubility. Because E^0 for $AuCl_4^-$ is well known, it is possible to calculate the equilibrium concentrations of $AuCl_4^-$ at various Eh's and decide on a cut off value below which the

Table V.2 Corrosion rates for gold and silver in various solutions.

Ligand	Potential mV (NHE)	Current Density $\mu A/cm^2$	pH	Corrosion Rate (mpy)	Corrosion Rate $g/y/cm^2$	Time to move 30,000 g gold
GOLD						
CN^-	-1124	14	10	6.070	0.0490	9.80 days
SCN^-	744	500	7	216.7	1.75	6.58 hrs
Cl^-	800	6000	4	2600	20.3	0.568 hrs
	771	2000	4	866.7	6.99	1.65 hrs
	750	600	[illegible]	260.0	2.03	5.49 hrs
$S_2O_3^{2-}$	256	60	7	26.00	0.210	2.29 days
HS^-	-464	100	7	43.22	0.356	1.35 days
SILVER						
SO_4^{2-}	156	30	7	40.08	0.172	1.48 days
CO_3^{2-}	-44	2000	10	2672	11.5	0.533 hrs
Cl^-	-44	2000	7	2672	11.5	0.533 hrs
HS^-	-994	200	7	267.2	1.15	5.33 hrs
$S_2O_3^{2-}$	-444	200	7	267.2	1.15	5.33 hrs
Citric	156	160	10	213.7	0.883	6.93 hrs
Humic	-144	16	10	21.4	0.088	2.88 days

amount of $AuCl_4^-$ in solution is too small to concentrate gold in a geologically reasonable length of time. This is shown by calculating how much water is available to mobilise gold in an oxidising environment. Consider as an example: the average rainfall in the Colorado River basin is 37.7 cm/year of which 3.58 cm/year actually infiltrates into the ground (Holland, 1978). The Colorado River basin was chosen for this example because there are a number of supergene enriched deposits in the southwestern United States (i.e. Boyle, 1979). This rain falls over a gold body 1km^2, of 300,000 tons grading 1.0 g/ton, with an average grain size of 40um. [illegible] body has been supergene enriched to produce a zone of 1000 tons grading 30 g/ton. The total amount of water going through the deposit per year is 3.58 X 10^7 litres. Assuming that initially the enriched zone had no gold in it, 30,000 g of gold has been transported to, and deposited in this area. The rate of water flow under equilibrium conditions with concentration of Cl^- of 0.1M, and a Eh of 771 mV, will move 2.88 X 10^{-6} g/year of $AuCl_4^-$. It therefofe takes 1.04 X 10^{10} years to move 30,000 grams of gold. This is not a reasonable length of time for supergene processes to occur. It is found that the concentration of $AuCl_4^-$ drops off very quickly with a decrease in Eh. If the concentration of Cl^- is 1.0M then it takes 1.04 X 10^8 years to move 30,000 g of gold.

Considering the variability in rainfall, runoff, permiability, Cl^- concentration, and degree of gold enrichment of various deposits, it is felt that the thermodynamics of the $AuCl_4^-$ complex show that the minimum Eh that is reasonable for economic transport is probably 700 mV with Cl^- of 2.0M. The kinetic data gathered from the experiments in this study indicate that at 800 mV, the corrosion rate of gold in the chloride solution at pH 4 is 20.3 g/cm^2 per year. To calculate the length of time it would take a complexing ligand to transport 30,000 g of gold, the total surface area in the gold occurrence must be calculated. This is necessary because the current data is per cm^2. The calculation is presented in Appendix 2. If the total surface area of the initial deposit is 2.28 X 10^7 cm^2, then with the above corrosion rate there, will be 4.62 X 10^8 g of gold transpoted in one year. Since only 30,000 g of gold has to be transported it takes 0.57 hours.

There are a number of factors that make this supergene scenario unrealistic such as: it assumes that every grain of gold has complete access to the solution, it does not account for the distance the gold has to move to get to the area of enrichment, and it assumes 100% efficiency in gold redeposition and continuous flow of unsaturated water. As a means of comparing relative rates of oxidation however, this type of scenario is useful. Considering that the corrosion rate is 0.57 hours this means that even if a very small fraction of the current is due to $AuCl_4^-$ formation, it would not take long for the solution to be saturated with respect to $AuCl_4^-$ so therefore the equilibrium solubility of gold is the controlling factor in gold chloride transport.

Although E° for Au-sulphide com[illegible] known, it can be seen that the maximum current densities in the HS^- and S_2O_3 experiments, in the suspected region of gold co[illegible] formation, are about 60 μA/cm² and 100 μA/cm² respectively. In the HS^- case the time it takes to transport 30,000 g of gold is 1.35 days. Again even if most of the current is due to oxidation of the sulphide species, it should not be difficult to reach gold saturation in a sulphide solution. Like the chloride solution, it is equilibrium solubilities which dictate how much gold is transported in the sulphide solutions.

A. Environments of Deposition

Garrels and Christ (1965) present an Eh-pH diagram showing the Eh-pH conditions of a variety of natural solutions. Superimposed on this diagram are the conditions, as determined in this study, for transporting complexes, (Figure 33). The dashed lines represent the threshhold for $AuCl_4^-$ transport of significant quantities of gold, and the regions of the current peaks for the reduced sulphur solutions.

It can be seen in Figure 33 that there are a variety of environments where gold complexing can take place. The most obvious environment is in the region of low to neutral pH, high Eh mine waters where $AuCl_4^-$ is dominant. Other areas where gold transport may occur include the transitional environments where thiosulphate complexes may dominate, and euxenic marine environments where bisulphide complexes may dominate.

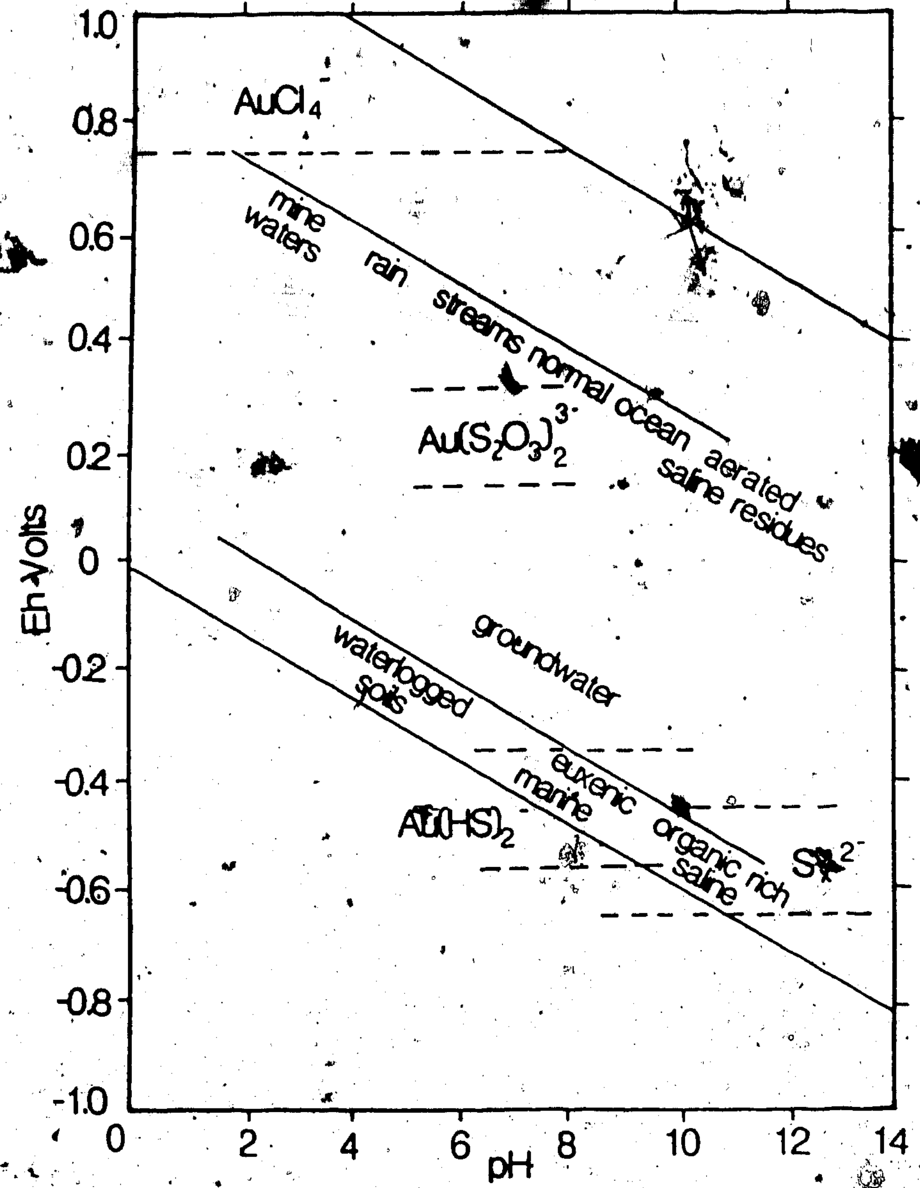


Figure V.33 Eh-pH diagram outlining the conditions of natural waters and conditions of gold transport as determined in this study. Adapted from Garrels and Christ (1965).

B. Supergene Transport of Gold

Although supergene enrichment of gold has been reported for numerous localities (Boyle, 1979), detailed accounts of the processes of gold enrichment are sparse. Anderson (1982) gives a general review of conditions produced by supergene processes. He concludes that oxidation of abundant sulphides above a relatively deep water table in fairly unreactive rocks produces the best environment for leaching of metals. This is due to the low pH induced by H_2SO_4 production through oxidation of the sulphides.

Highly Oxidising Environments

From the results of this study it is apparent that $AuCl_4^-$ will form to sufficient concentration for enrichment of gold at a minimum potential of 700 mV or higher. The gold is reduced from the $AuCl_4^-$ state by passing into deeper zones where the oxidation potential is lower, or by passing near fresh surfaces of sulphide minerals. Jean and Bancroft (1985) have shown experimentally that sulphide ions on the surface of sulphide minerals will reduce gold from $AuCl_4^-$ solutions. Because of these mechanisms of deposition it is not likely that the $AuCl_4^-$ could be transported all the way to the water table like other metals such as copper (Anderson, 1982). For this reason it is probably unlikely that gold will form a distinct blanket of enrichment. The more likely scenario in most cases for supergene enrichment of gold, is that gold will migrate down through an oxidising gold deposit and precipitate as rims or crystalline gold on fresh gold nucleii, or become incorporated onto the surfaces of sulphide minerals. These sulphides may later oxidise to limonite thus providing one explanation of the common association of gold with limonite (i.e. Mann, 1984). In this way the increase in grade of the deposit may be very gradual and perhaps not recognised as a supergene phenomenon.

The presence of Fe^{2+} and Fe^{3+} will probably not play a role in the transport of gold in the supergene environment. As can be seen by the results of the experiments with ferric chloride it is obvious that the presence of Fe^{3+} in the solution caused gold complexes to form much faster than in Cl^- solution alone, but this occurred because Fe^{3+} was reducing to Fe^{2+} which forced the oxidation of gold. In natural solutions, other metal cations such as Cu or Ag will oxidise far more readily than gold. It is more likely in a natural environment, that $AuCl_4^-$ will act as an oxidising agent by causing Fe^{2+}, from pyrite or other iron bearing minerals, to oxidise, therefore causing the gold to reduce. Again this may explain the common association of gold with limonite.

An example of $AuCl_4^-$ transport is presented in a study of gold enrichment by Mann (1984). Mann found that lateritic weathering in the Yilgarn block of Australia had oxidised large areas containing epigenetic gold and sulphide bearing veins. Oxidation of these sulphides in a semi-arid environment produced the necessary Eh-pH conditions for Au-chloride transport. The prevailing onshore winds provided the required source of chloride. According to Mann's studies, the groundwater has a pH of 3 to 4 with Eh's up to 500 mV (NHE). The data from the equilibrium calculations, however, show that the Eh for gold transport has to be at least 700 mV. It is possible that in the past the Eh was much higher than it is now, or that Mann had problems with accurate measurement of Eh in the soils. In addition, the chloride content of the waters may have been far greater than those examined in this study. The higher Cl^- content would allow greater gold transport at the same or lower potentials.

Mann reports that the supergene gold from his study area is crystalline or wiry, and that the gold sometimes forms large nuggets. It would seem from this evidence that the gold was deposited by reduction of $AuCl_4^-$ onto gold nucleii. This deposition was probably due to lowering of the oxidation potentials as the solutions descend.

Another example where $AuCl_4^-$ is responsible for gold deposition is at a deposit at Sierra Gorda, Chile (Pohl, 1985). Here the presence of boleite, paratacamite, hematite and gold indicate that the environment of supergene alteration was indeed under oxidising conditions with abundant chloride available. In the Sierra Gorda case the pH is between 6 and 7 and transport is considered to be at 800 mV (NHE) or 1044 mV (SCE), and the chloride concentration was on the order of 2.0M. From the chloride results at pH 7 the current density at 1044 mV (SCE) is about 6000 $\mu A/cm^2$. In this case the corrosion rate is 6.0 X 10^8 g/year. Referring back to the hypothetical example of gold enrichment, it would take a matter of minutes for 30,000 g of gold to be oxidisd under these conditions. It is probably not likely that the solution at Sierra Gorda was oversaturated with respect to $AuCl_4^-$, nor would it be necessary for it to be oversaturated to explain the gold transport. From equilibrium calculations with Cl^- concentration of 2.0M, it would take 2,214 years to move 30,000 g of gold which is a reasonable length of time. Again gold is probably redeposited as a result of Eh decrease as the solution decsends into the ground.

According to the results of the gold-chloride experiments, there should be gold-oxide on the gold in the leached zone of both these deposits. Pohl (1985) did not report any such coatings but Mann (1981) stated that gold in his study was commonly coated with Fe-oxides. As was found with the $FeCl_3$ results any Fe^{3+} cations in the solution seem to inhibit formation of Au-oxide. Because iron is so common in natural environments it might explain the lack of Au-oxide seen. Also in the above cases the pH is too high for soluble Fe^{3+} to exist. For this reason Fe^{3+} will be precipitated as Fe-hydroxide so the presence of Fe-hydroxides on the gold is not surprising.

Mann (1984) discusses an increase in gold fineness with depth in the supergene zone as well as the presence of high fineness rims on nuggets. This is consistent with the results of this study which show silver to be rapidly oxidised in chloride solution especially at such high Eh conditions. This would indicate that once dissolved, the silver is more likely to stay in the solution and be transported all the way to the water table

Transitional Environments

Between the oxidising environment and the water table the Eh-pH conditions are probably those of the transitional environment in Figure 33, where $S_2O_3^{2-}$ may complex with gold.

At a deposit near Wau in Papua New Guinea, it was suggested by Webster and Mann (1984) that $S_2O_3^{2-}$ was responsible for gold transport. In this example it was noted that gold was not particularly enriched with respect to silver. According to the results of this study, silver is much more readily oxidised in the presence of $S_2O_3^{2-}$ than gold is. At 500 mV (SCE) Ag-$S_2O_3^{2-}$ has a current density of 6000 $\mu A/cm^2$ whereas the peak at 500 mV (SCE) in the

$Au(S_2O_3)_2^{3-}$ results is only $100\ \mu A/cm^2$. It would seem that thiosulphate transport cannot in this case explain the parallel transport of gold and silver. It is possible that at the initiation of sulphide mineral oxidation some HS^- could be released. This HS^- could persist long enough to pick up gold and move it a short distance (Pitul'ko, 1976). If this happened repeatedly over a long time span, it may be possible to transport a significant amount of gold. Also the rate of silver transport could be reduced if a large amount of the silver was precipitated as a Ag-Sulphide before it could be transported very far.

Soil Environment

Soils can display a variety of chemical characteristics depending on rainfall, rock type, vegetation, etc. (Rose et al., 1979). If there are no carbonate species [illegible] the organic compounds tend to make the soils more acidic whereas, the presence of carbonate will neutralise this effect. Oxidation potential can be variable as well, depending on whether there is enough oxygen available to decompose the organic matter present. If there is, then conditions will be fairly oxidising but if there is not then anoxic reducing conditions such as that found in bogs will prevail (Rose et al., 1979).

Lakin et al. (1974) discuss a number of types of plants which produce cyanide compounds and release them into the soil where they may complex with gold. Here the complex may be picked up again by the same plants or by other ones which will concentrate the gold in their tissues. As seen by the results of this study, more oxidised soils with a lower pH will probably sustain SCN^- complexes, whereas CN^- complexes would be more abundant in anoxic alkaline soils. It is possible that in these environments gold could easily be transported by cyanide species, and redeposited when the cyanide species decompose or move into environments with different Eh-pH regimes.

Pitul'ko et al. (1976) discuss the possibility that reduced or partially oxidised sulphide species may be concentrated in the soil at the water permafrost interface. This process would cause gold complexes to form readily. From the soil they could be washed into the streams or be redeposited by oxidation of the sulphides.

Although the results of the experiments of this study show no complexing of golds with organic ligands, the possibility of the existence of gold-humic acid complexes cannot be ruled out. Particularly because there were problems in this study in getting the humic acid to dissolve so the results are inconclusive. Severson et al. (in press), present a good case for organic transport in the Livengood region of Alaska. By a similar method as that proposed by Pitul'ko et al. (1976), they propose that it is organic compounds that concentrate at the water permafrost interface. Here the high concentration of organic material picks up gold. The compound is then washed into the streams during spring runoff. In this environment it may be difficult to distinguish between concentration due to CN^- species, sulphide species, or due to organic compounds.

C. Placer Environment

A selection of natural gold nuggets was examined to determine if there were any features on the surfaces which might indicate that processes of chemical transport or deposition of gold have occurred. Five nuggets from Hunker Creek in the Klondike, Yukon and three from Burwash Creek, Yukon were examined. In all cases the surfaces are irregular and flaky, i.e. (Plate 14). It is not possible from these images to determine whether the flakiness is due to depositional processes or leaching of the surface, but it can be distinguished from the processes of abrasion as seen in Plate 15.

One nugget from the Klondike has an unusually high silver content as determined by the EDXA, (Plate 16). This nugget has small sphere-like structures on its surface which are probably silver oxides. According to the EDXA analysis the nuggets from Burwash Creek all have Fe-oxide on the surface (Plate 17), suggesting that there is a local abundance of Fe^{3+} in the water or in the sediment. The Burwash nuggets are otherwise very similar in surface features and morphology to those from the Klondike.

When trying to understand the processes of placer transport of gold, there are a few questions which stand out as being particularly important. Firstly, what is the origin of uncommonly large nuggets? More specifically, are they formed in the placer streams or were

Plate V.14 Surface of a gold nugget from Hunker Creek, Yukon.

Plate V.15 Abraded surface of a gold nugget from Burwash Creek, Yukon.

Plate V.16 Siver oxides on the surface of a silver rich nugget from Hunker Creek, Yukon.

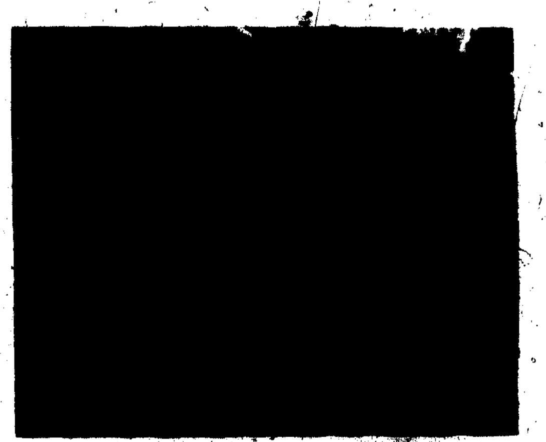


Plate V.17 Fe-oxides on the surface of a gold nugget from Burwash Creek, Yukon.

they already large when they were weathered from the lode gold source? Secondly, what is the origin of high fineness gold rims on placer nuggets? In this case the question revolves around whether or not silver has been leached or diffused from the rim of the gold nugget, or whether very pure gold has been deposited on the nugget. Finally, as a corollary to the first two questions, is rim formation related to the formation of large nuggets?

In an effort to better answer the above questions, there are a few related facts which must be pointed out. According to the compilation by Boyle (1979), the fineness of placer gold is invariably greater than the fineness of gold from the presumed lode source, and the rims on the gold nuggets are of higher fineness than the nugget. From the data of Brandon (1964), the ion contents of rivers and streams are usually extremely low meaning that there are very few possible gold transporting agents available, (i.e. Cl^- on the order of 2ppm). Any theory which tries to explain gold transport in the placer environment must account for the above characteristics.

In addressing the problem of the origin of gold rich rims on nuggets, Giusti (1983) noted that in general, rims on gold grains from Alberta rivers were from 0.001 - 0.03 mm in thickness with sharp contacts with the nuggets. Knight (1985) finds similar thickness and contacts for rims found on gold from the lower Fraser River drainage area of British Columbia. In this case Knight specifies that the contact between rim and core is sometimes cuspate. Although Knight acknowledges that diffusion of silver within gold to form a rim would leave a gradation in fineness in the rim, he suggests that if the rim were full of defects from previous leaching, the silver would diffuse more rapidly through the rim than through the nugget as a whole. In this way the sharp contact between rim and core could be formed. This hypothesis seems unlikely because, firstly, the gold in the rim is more pure than that in the nugget and should therefore contain fewer structural defects. Also from the results of the experiments in this study where $AuCl_4^-$ is reduced onto gold, it can be seen that the gold quickly becomes crystalline as deposition continues.

By the process of elimination it can only be concluded from the previous discussion that gold enriched rims are formed by the deposition of gold from the stream waters. If this is the case it would be expected that rims should become thicker with distance transported. This thickening has been observed by Gorskov et al. (1971), as reported in Knight (1985). Is it possible then that succesive thickening of the rim could account for the formation of very large nuggets? If so, the large nuggets should be of very high fineness with a small core of lesser fineness. This is not the case. If the large nuggets have a rim, it is usually on the same order of thickness as rims on small nuggets. The conclusion to be drawn from this is that rim formation and nugget formation are two distinct processes.

To explain nugget formation, the paucity of transporting agents in streams should again be pointed out. An alternative to nuggets being formed in the streams may be that nuggets have already been formed before they get to the streams but, as evidenced by their higher fineness, after the lode source of gold has been weathered. This theory comes back to the concept of supergene enrichment in soils through processes already discussed. In the case of placer gold, the lode source is deeply weathered, releasing gold particles and probably solubilised gold into the soil. Here the gold is probably transported by inorganic or organic agents, depending on local conditions, until it is reduced onto the particles. By this process, the particles could grow to quite a large size before they are eroded into the streams. In this way it is also possible to explain the increase in fineness of nuggets compared to their source. As seen by the results of the silver experiments in this study, silver will oxidise and be transported away from the source much faster than gold will. Once in the streams, the gold nuggets can collect a thin rind of pure gold from stream waters which may still contain very dilute residual gold complexes or colloids washed in from the soils. It is not surprising that the rim is of much higher fineness than the nugget because by the time the nuggets have reached the stream, the bulk of the silver has been removed from the system.

This idea is supported by studies done by Severson et al. (in press) in which they examine the formation of placer gold grains within the soil in the Livengood region of Alaska. Also, the large nuggets of gold found in Australia, Mann (1984), not only are good evidence of supergene enrichment, they also illustrate the fact that supergene enrichment of gold can form large nuggets in the soil.

Perhaps some types of placer deposits are simply an extention of supergene enrichment, whereby topography or a high amount of rainfall causes slumping and soil creep which moves the gold into streams instead of remaining entirely in the soil or oxidised zone.

D. Low Temperature Reducing Environments

As shown in Figure 33, one other low temperature, non-hydrothermal scenario, which is reducing enough to sustain bisulphide complexes of gold, is the euxenic marine environment. According to Stanton (1973) this environment may also have abundant available H_2S. Obviously gold-bisulphide complexes are stable under these conditions and the gold could be concentrated from the seawater and rocks or from ocean-floor volcanic vents. Upwelling currents may move the euxenic water to higher levels where the HS^- would be oxidised and gold precipitated. Areas where euxenic waters may be upwelling such as the edges of shallow banks or continental shelves may be the locus of gold deposition.

VI. Conclusions

There are a number of conclusions to be drawn from this study. These include both conclusions regarding the experimental method itself, and those regarding the results of the experiments.

In general the Tafel experiments and Cyclic Polarographs were successful in distinguishing the most interesting ligands from a large group. It is possible that this type of study could be even more successful applied to more reactive metals, the reason being that it is less likely that oxidation properties of the solution would overpower those of the metal.

The results of this study reveal that the cyanide, chloride and sulphide species show the best evidence for complexing with gold. In a natural environment the cyanide species are probably important in soils where they are formed through biologic activity. The reduced character of the CN^- ligand allows this to be important in anoxic environments whereas the more oxidised SCN^- ligand would be important in aerated environments.

The chloride results indicate that significant transport of gold can occur at $AuCl_4^-$ concentrations of less than pptrillion. This allows the range of Eh conditions of $AuCl_4^-$ transport to extend as low as 700 mV at 2.0M Cl^- concentration, which also extends the pH conditions for transport to more neutral values. In addition it was found that the higher the concentration of chloride the more gold is oxidised.

The environments which allow $AuCl_4^-$ transport include enrichment in oxidising ore bodies, both where sulphides are present to create a low pH, and where there are reactive rocks present to neutralise the pH. Gold enrichment by $AuCl_4^-$ may not, however be very obvious in a natrual environment due to the disseminated character of its probable concentration.

The thiosulphate yields qualitative evidence for the dissolution and transport of gold. It is not possible, however, to ascertain the extent of formation of Au-thiosulphate complexes. It can be stated that transitional environments where partial oxidation of sulphides allows metastability of thiosulphate will be the areas where gold transport as a thiosulphate complex occurs.

The same evidence that indicates thiosulphate mobility of gold also indicates bisulphide mobility. In this case very reducing conditions such as those found in euxenic environments or reduced bogs or soils allow the gold bisulphide complex to form.

In the cases of NH_4^+, OH^-, and organic complexes, the electrochemical evidence does not show that significant gold complexing occurs. Work by other researchers, however, shows evidence to the contrary. In the case of NH_4^+ there is experimental evidence from this study that some species is oxidising but, it could not be determined whether it was NH_4^+ or a gold-ammine complex forming. In the case of OH^- and the organics, however, there was no evidence from this study that oxidation was occurring at all. It is probable that problems with the humic acid resulted from a lack of dissolution of the humic acid.

VII. References

Angerstein-Koslowska H. (1984) Surfaces, cells, and solutions for kinetics studies. In *Comprehensive Treatise of Electrochemistry*. vol. 9: *Electrodics: Experimental Techniques*.. (eds. Yeager E., Bockris J. O'm., Conway B.E.,Sarangipani S.) Plenum Press 15-59.

Anderson J.A. (1982) Characteristics of leached capping and techniques of appraisal in: *Advances in Geology of the Porphyry Copper Deposits of Southwestern North America:* (Titley S.R. ed.), Tuscon, Univ. of Ariz. press 275-295.

Baker W.E. (1978) The role of humic acid in the transport of gold. *Geochim. Cosmochim. Acta.* 1978, 42, 645-649.

Boyle R.W. (1979) *The Geochemistry of Gold and its Deposits*. *Geol. Surv. Canada Bull.* 280, 584p.

Brandon L.V. (1964) Groundwater hydrology and water supply in the District of Mackenzie, Yukon Territory, and adjoining parts of British Columbia. *Geol. Surv. Canada* paper 64-39.

Cloke P.L. and Kelly W.C. (1964) Solubility of gold under inorganic supergene conditions. *Econ. Geol.*, 59, 259-270.

Cronan C.S. and Aiken G.R. (1985) Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. *Geochim. Cosmochim. Acta* 49, 8, 1697-1705.

de Bethune A.J. and Swendeman-Loud N.A. (1964) *Standard aqueous electrode potentials and temperature coefficients at 25°C*. (Hampel C.A. pub.) Skokie Ill. 19p.

Garrels R.M. Christ C.L. (1965) *Solutions, Minerals, and Equilibria* Freeman Cooper and Co. San Francisco 450p,

Gallego H.J., Castellano C.E., Calandra A.J., Arvia A.J. (1975). The electrochemistry of gold in acid aqueous solutions containing chloride ions. *J. Electroanal. Chem.* 66, 207-230.

Gaur J.N. and Schmid G.M. (1970) Electrochemical behaviour of gold in acidic chloride solutions. *J. Electroanal. Chem.* 24, 279-286.

Giggenbach W.F. (1974) Equilibria involving polysulphide ions in aqueous sulphide solutions up to 240°C. *Inorg. Chem.* 13, no. 7, 1724-1733.

Giusti L. (1983) *The Distribution Grades and Mineralogical Composition of Gold Bearing Placers in Alberta.* MSc. thesis Univ. of Alberta, 397p.

Granger H.C. Warren C.G. (1969) Unstable sulfur compounds and the origin of roll-type uranium deposits. *Econ. Geol.* 64, 160-170.

Hamelin A. and Bellier J.P. (1973) Role de l'orientation crystallographique dans l'adsorption de l'ion chlorure sur l'or I-zone [110]. *J. Electrochem. Soc.* 41, 179-192.

Harrell J.B. (1975) Modern applications of potentiodynamic data in research and industry. Unpub. report. Petrolite Corp. Houston Texas, 24p.

Helgeson H.C. and Garrels R.M. (1968) Hydrothermal transport and deposition of gold. *Econ. Geol.* 63, 622-635.

Henley R.W. (1973) Solubility of gold in hydrothermal chloride solutions. *Chem. Geol.* 11, 73-87.

Hoare J.P. (1984) A cyclic voltammetric study of the gold oxygen system. *J. Electrochem Soc.* 131, 8, 1808-1815.

Holland H.D. (1978) *The Chemistry of the Atmosphere and Oceans.* John Wiley and Sons Inc. N.Y., 351p.

Jean G.E. and Bancroft G.M. (1985) An XPS and SEM study of gold deposition at low temperatures of sulphide mineral surfaces: concentration of gold by adsorption/reduction. *Geochim. Cosmochim. Acta* 49, 979-987.

Kerrich R. and Fyfe W.S. (1981) The gold-carbonate association: source of CO_2, and CO_2 fixation reactions in Archean lode deposits. *Chem. Geol.* 33, 265-294.

Kirk D.W., Foulkes F.R., Graydon W.F. (1980) Gold passivation in aqueous alkaline cyanide. *J. Electrochem. Soc.* 1962-1969.

Knight J.B. (1985) *A Microprobe Study of Placer Gold and its Origin in the Lower Fraser River Drainage Basin, B.C.* MSc. thesis Univ. of B.C., 197p.

Krauskopf K.B. (1951) The solubility of gold. *Econ. Geol.* 46, 858-870.

Lakin H.W., Curtin G.C., Hubert A.E. (1974) Geochemistry of gold in the weathering cycle. *U.S. Geol. Surv. Bull.* 1330 80p.

Latimer W.M. (1952) *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*. Prentice-Hall, Inc. N.J. 392p.

Mann A.W. (1984) Mobility of gold and [illegible]itic weathering profiles: some observations from Western Australia. *Econ. Geol.* 79, [illegible]-49.

Morel F.(1983) *Principles of Aquatic Chemistry*. John Wiley and Sons Inc. N.Y., 446p.

Mortimer C.E. (1979) *Chemistry a Conceptual Approach*. 4th ed. D. Van Nostrand Co. N.Y. 815p.

Ogryzlo S.P. (1935) Hydrothermal experiments with gold. *Econ. Geol.* 30, 400-424.

Ong H.L. and Swanson V.E. (1969) Natural organic acids in the transportation, deposition, and concentration of gold. *Quart. Colo. School of Mines* 64, 1, 395-425.

Peshchevitsky B.I., Yerenburg A.M., Belevantsev V.I., Kazakov V.P. (1970) Stability of gold complexes in aqueous solutions. *Isvest. Sib. Otd. Akad. Nauk S.S.R.,* 4, 75-83. (in Russian).

Pitul'ko V.M. (1976) The behaviour of gold in the oxidation zones of the far north. *Geochem. Int.* 13, 2, 157-163.

Pohl D.C. (1985) Supergene gold migration and enrichment, Sierra Gorda, Chile. Abstracts with Programs. (San Fran. meeting) *Trans. of American Geophys. Union.* 66, 46.

Robinson F.P.A. and Frost F.A. (1963) Anodic polarisation characteristics of gold and silver in chloride and sulphate media. *Corrosion.* 19, 4, 115-119.

Rose A.W., Hawkes H.E., Webb J.S. (1979) *Geochemistry in Mineral Exploration*, 2nd ed. Academic Press Inc. N.Y. 657p.

Schnitzer M. (1982) Organic matter characterisation. in: *Methods of Soil Analysis Part 2., Chemical and Microbiological Properties 2nd ed.* (Page A.L., Miller R.H., Keeney D.R. eds.) *Soil Science Soc. of America Inc.* Madison Wisconson., 581-594.

Severson R.C., Crock J.G., McConnell B.M. (1985) Processes in the formation of crystalline gold in placers (in press).

Seward T.M. (1973) Thio complexes of gold in hydrothermal ore solutions. *Geochim. Cosmochim. Acta* 37, 379-399.

Skibsted L.H. and Bjerrum J. (1974) Studies on gold complexes II. The equilibrium between gold (I) and gold (III) in the ammonia system and the standard potentials of the couples involving gold, diamminegold (I), and tetramminegold (III). *Acta Scandinavica.* 28, 764-770.

Smith F.G. (1943) The alkali sulphide theory of gold deposition. *Econ. Geol.* 38, 561-590.

Stanton R.L. (1972) *Ore Petrology* McGraw Hill Inc. 713p.

Stern M. and Geary A.L. (1957) Electrochemical polarisation I. A theoretical analysis of the shape of polarisation curves. *J. Electrochem. Soc.* 104, 1, 56-63.

Varshal G.M., Velyukhanova T.K., Baranova N.N. (1984) The geochemical role of gold (III) fulvate complexes. *Geochem. Int.* 21, 3, 139-146.

Webster J.G. and Mann A.W. (1984) The influence of climate geomorphology and primary geology on the supergene migration of gold and silver. *J. Geochem. Expl.* 22, 21-42.

Wranglen G. (1985) *An Introduction to Corrosion and Protection of Metals.* Chapman and Hall Ltd. N.Y. 288p.

VIII. Appendix 1 Nernst Equation Calculations.

E° for Au = $AuCl_4^-$ = 1.00 V in 1.0M Cl^-

Nernst Equation:

$$E = E^\circ - RT/nF \ln(K)$$

$$K = aAuCl_4^-/a^4Cl_4^-$$

F = 96,487 coulombs.mol^{-1}

n = # of electrons in the reaction

So how much $AuCl_4^-$ will there be at 771 mV in a chloride solution of ~~0.1M~~?

$$0.771 = 1.00 - 0.0197(\log a^4Cl^- - \log aAuCl_4^-)$$

Note: K is inverted because the reaction is at a lower potential than E°, therefore the reaction is favoured in the opposite direction.

$$15.62 = -\log aAuCl_4^-$$

$$aAuCl_4^- = 2.37 \times 10^{-16} M$$

Which is equivalent to:

$$2.37 \times 10^{-16}\ mol/1000g\ H_2O$$

$$1mol\ AuCl_4^- = 339\ g$$

$$= 8.05 \times 10^{-5}\ ppt$$

IX. Appendix 2. Calculation of time for the geological scenario.

For this problem the surface area of the metal in a deposit has to be known. In the cases of gold and silver the surface area will be different for both. To calculate corrosion rates the formula derived in the experimental section will be used.

Necessary information:

Area and volume of a sphere, $4\pi r^2$, $4/3\pi r^3$

Density of gold and silver, 19.7 g/cm^3, 10.5 g/cm^3

Atomic weight of gold and silver, 197.0 g, 107.9 g

Surface area calculations:

Gold: 300,000 g of 40μm spheres with $r = 0.002$ cm

Area of 1 sphere = 5.024×10^{-5} cm^2

Volume of 1 sphere = 3.35×10^{-8} cm^3

Weight of 1 sphere = 6.60×10^{-7} g/grain

Total number of grains = 4.54×10^{11}

Therefore the total surface area = 2.28×10^{7} cm^2

Silver:

Weight of 1 sphere = 3.516×10^{-7} g/grain

Total number of grains = 8.53×10^{11} grains

Therefore the total surface area = 4.29×10^{7} cm^2

Example calculation of corrosion rate and time to transport 30,000 g of metal in a supergene environment:

$$W/t(\text{mpy}) = 0.13\ IM/nd$$

Corrosion rate for gold in a Cl$^-$ solution of 0.1M at 800 mV (NHE) or 1044 mV (SCE).

$$0.13 \times 6000\mu A/cm^2(197.0)/3(19.7)$$

$$\text{corrosion rate} = 2600 \text{ (mpy)}$$

This value is converted to grams / year / cm by dividing by 2.54 (conversion from inches to cm) and dividing by 1000 (converting from milli-inches), then multiplying by the density of the metal (to convert from volume of metal corroded to the weight of metal corroded).

$$2600/2.54/1000 \times 19.7 = 20.2 \text{ g/y/cm}^2$$

This value is then multiplied by the total surface area.

$$20.2 \times 2.28 \times 10^7 = 0.568 \text{ hrs.}$$