MODELLING OF THE ELUTION PROCESS

GEORGE AGBEKO BANINI

A dissertation submitted to the Faculty of Engineering, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Engineering.

August, 1993.

To My Parents and My Best Half Lawrencia

To God Be The Glory, Amen!

To My Parents and My Best Half Lawrencia

To God Be The Glory, Amen!

DECLARATION

I declare that this dissertation is my own unaided work, except where specifically acknowledged. It is being submitted for the degree of Master of Science in Engineering to the Faculty of Engineering, University of the Witwatersrand, Johannesburg. It has never been submitted before for any degree or examination in any other University.

GEORGE A. BANINI

2nd day of August 1993.

ABSTRACT.

The influence of temperature on the equilibrium adsorption of gold and hydroxide ion at elution conditions was examined. Experiments were conducted for both single and multiple solute adsorption of gold and OH^- ion at the temperatures between 80 and 120°C. For gold concentration levels of between 0 and 600ppm were treated while the hydroxide ion concentration level was between 0 and 0.6M.

Three models were employed to model the equilibrium adsorption of each solute at the single solute level. These consist of the Freundlich isotherm (FI), the Modified Freundlich isotherm (MFI) and the Linearized form of the MFI (LMFI). The Modified Freundlich isotherm allowed the estimation of the change in the heat of reaction of adsorption, ΔH, and for gold ΔH of -42.63kJ/mol was estimated while -14.86kJ/mol was estimated for OH^-. These figures obtained confirmed that the adsorption process is significantly a physical one. In the case of the multiple solute adsorption, the Freundlich-type model and a General empirical multi-solute model was used for the modelling.

Rigorous statistical methods were employed to discriminate between the models. It was found that for the single-solute adsorption, the Modified Freundlich isotherm is the best model while for the multiple-solute adsorption, the General empirical model was better than the Freundlich-type model.

Kinetics of elution data were also generated with models depending upon surface diffusion and film transfer also developed. A plug flow model was also developed and simplified using the method of characteristics. These models were solved simultaneously coupled to the Modified Freundlich isotherm to simulate the experimental data obtained. It was observed that the model was less sensitive to the diffusion coefficient hence surface diffusion was eliminated. This modification implies that only film transfer affects the process. The film transfer controlled model was found to represent the experimental data very well.

ACKNOWLEDGEMENTS

I wish to thank:

- Mr W Stange, my supervisor, for his help, encouragement and advice throughout this work.

- GENMIN and Anglo American Mining Houses for their financial assistance.

- Mr M. Remotsenhoa of the Chemical Engineering Department, University of the Witwatersrand, for his part in the analysis of the solutions with the AAS.

- The Workshop staff of the Metallurgy Department and Mr B Naidoo for their role in building the experimental rig.

CONTENTS

APPENDICES

LIST OF FIGURES.

LIST OF TABLES

CHAPTER 1

INTRODUCTION

CHAPTER 1
INTRODUCTION
1.1 GENERAL BACKGROUND OF THE CIP PROCESS

The absence of an efficient elution process (one which does not destroy the carbon) militated against the development of large scale use of carbon for the recovery of gold for a long time. The birth of the Carbon-in-Pulp (CIP) process is the result of the patent due to Zadra[1] on elution. This patent led to the development of a significant flowsheet for CIP which was first implemented on large scale at Homestake Mine, South Dakota, US in 1973[2].

Figure 1.1 shows a schematic diagram of the CIP process

The CIP process recovers gold and silver from slurry streams by contacting the pulp with activated carbon. As can be seen from the flowsheet in Figure 1.1, a conventional cyanide leach precedes the CIP circuit. The circuit consists of three unit processes namely; adsorption, elution and regeneration.

The operation of the adsorption process consists of a number of well mixed continuous stirred tank reactors (CSTR) in series. Leached pulp gravitates through this series of reactors. Carbon is retained in each tank by means of a mechanical screening device while the pulp flows through the tank. The gold and other species in the solution are adsorbed from the pulp onto the activated carbon as the pulp passes through the train of contactors.

The flow of carbon in the adsorption circuit is periodic and counter current to the flow of the pulp. This intermittent manner in which the carbon is transferred causes the adsorption process to be a dynamic system in which steady-state does not exist.

Loaded carbon from the adsorption stage is conveyed to a stripping vessel, where the gold and silver are stripped from the carbon into a concentrated pregnant solution. This stage constitutes the elution process within the CIP process. Three techniques of stripping have been developed which are the Zadra, the AARL and the Organic solvent processes. (These processes will be discussed in detail in the text). All these methods use caustic cyanide solution to strip gold and silver in the form of $Au(CN)_2^-$ and $Ag(CN)_2^-$ respectively from the carbon at high temperatures. Recently

success has been achieved in the AARL and Zadra elution processes where stripping is done without cyanide. Gold and silver are recovered from the pregnant solution by either electrowinning or zinc precipitation.

The third unit process in the CIP is the thermal regeneration of the carbon. This is necessary in order to remove the inorganic and organic impurities that are adsorbed during the adsorption stage and are not removed by elution or acid washing. This process involves the heating of the carbon to about 650°C for up to 30 minutes in the absence of air. The reactivated carbon is screened at about 0.8mm to remove the fines before being recycled to the adsorption circuit.

Zinc precipitation prior to filtration has been the main recovery route for gold before the development of CIP and it's related processes such as Carbon-in-leach (CIL), Resin-in-pulp (RIP) et al. But CIP has now become the most preferred route. This is because the CIP process has demonstrated better efficiency in terms of capital expenditure, operating cost, gold recovery, throughput rate and ore constituents as compared to the zinc precipitation process[1,10].

1.2 ELUTION : A HISTORICAL PERSPECTIVE

As far back as 1927, Gross and Scot[1] made presentations indicating the use of wide range of inorganic compounds for eluting gold-cyanide complex adsorbed onto carbon. Zadra in 1950 made a breakthrough by effectively eluting gold from carbon with alkaline sodium sulphide at the temperature of 93°C. In 1952 Homestake Mines operated a modified Zadra process which utilised caustic cyanide (NaOH\NaCN) solution at atmospheric pressure and temperature of between 90 and 93°C to elute both gold and silver.

After a series of laboratory investigations, the AARL process was also developed by the Anglo American Research Laboratory in 1979. The process makes use of pretreatment of the loaded carbon with hot NaCN/NaOH solution and elution of gold and silver with softened or deionized water.

It is remarkable to note that the use of ethanol and certain other water miscible organic solvents in elution has been achieved. It has been shown that when a small portion of acetonitrile for

instance is added to aqueous cyanide solution significant desorption can be effected at temperatures such as 60°C[1,7]. The use of these organic solvents has been found to be more economical than the Zadra and the AARL methods of stripping. But the necessity for recovery of the solution and its attendant fire hazards have militated against its large scale use.

1.3 PROCESS DESCRIPTIONS

1.3.1 AARL PROCESS

After freeing the carbon from slime, wood fibre and plastic material, which will affect the elution efficiency, the carbon is loaded into the elution column for acid washing. Acid washing by 3% HCl at the elution temperature of 110 to 120°C (recently 90°C) therefore precedes the process. In fact, currently plants have been designed to acid wash at ambient temperatures and this may be done after the elution process. The [illegible]t acid is discharged into the adsorption circuit while the acid washed carbon is preheated with strong caustic cyanide solution (2 to 3% NaCN & 2% NaOH) and the carbon is allowed to "soak" in the reagent for about 30 minutes. Gold is then stripped from the carbon by the use of high quality softened or deionized water, having low ionic strength (<300g/t of Na) for 8 hours. Gold in the column eluate is recovered by electrowinning or by zinc precipitation. Figure 1.2 shows the flow diagram of the process.

1.3.2 ZADRA PROCESS

The Zadra Process makes use of continuous circulation of the eluant through the elution column and an electrowinning cell in series. The eluant made up of 0.2 to 0.5% NaCN and 1.0 to 2.0% NaOH is pumped to the elution column and this is preheated by the solution leaving the column. The temperature is then raised to 120°C by the use of steam heat-exchangers[1]. After stripping the gold from the carbon, the solution is cooled in the incoming heat-exchanger and further cooled to below its ambient boiling point in a cooler heat-exchanger. The solution then flows to the electrowinning cells normally by gravity where gold is won from the solution and finally returns to the elution column feed pumps (see Fig 1.3).

The process exhibits slow kinetics[1] taking up to 50 hours for satisfactory elution. This does not only necessitate large stripping plants but also result in a significant lock-up of gold values in the plant.

Also despite its simplicity the Zadra system requires understanding and close control to obtain consistently good result. Other problem[6] areas include:

1. contaminant build up in the eluant which may severely restrict the elution unless a high bleed off rate is maintained,
2. water balance in the circuit has often been a problem since electrowinning is conducted near 100°C.

High silver to gold ratios on carbon may also cause problems in the Zadra process. Silver is more easily eluted from carbon than gold and hence it is the first metal to report to the electrowinning cell. Since the silver is also reduced electrolytically (in cyanide solution) before gold, there is the tendency in the process to recycle solution relatively high in gold concentration. This eventually reduces the effectiveness of the eluant to desorb gold. To achieve satisfactory result it may be necessary to precipitate the silver with a sulphide (eg Na_2S) before electrowinning.

1.3.3 ORGANIC SOLVENT PROCESS

This is actually a variation of the Zadra and the AARL processes in which the eluant contains large amount of organic solvents like methanol, ethanol or acetonitrile.

A typical organic solvent process consists of the use of a mixture of 40% v/v acetonitrile-water containing 1% NaCN and 0.2% NaOH at a flow rate of 0.25 bed volume per hour at 25-70°C to elute a column of loaded carbon. The carbon is normally pre-washed with acetonitrile-water without cyanide to saturate the carbon with acetonitrile prior to elution. The procedure produces greater than 90% desorption of gold in 8-10 hours at 70°C with approximately 85% of the gold recoverable in the first bad volume of solvent.

1.4 OBJECTIVES OF THE PROJECT

Stange and King[2] indicated that as it becomes more expensive, in terms of capital, labour and energy, to design and operate mineral processing plants the need for optimum utilization of resources becomes more pronounced. The situation is intensified by the falling ore grades. Plants are therefore complex, making it difficult to ensure that design and/or operation of a plant is

optimum, especially when using manual process analysis and design techniques. Computer-based techniques called simulation allow many more scenarios to be examined and assessed during plant design or operation, hence increasing the probability of locating the optimum situation on the plant.

Computer simulations can only be done on a process when appropriate mathematical models are available to describe the process. Modelling is therefore the activity of developing a mathematical process equation that provides an adequate quantitative description of that process. Simulation is the act of applying the model to predict what happens to the real situation when changes are made in its design and/or if changes occur in the operating condition. The purpose of the model will therefore be to predict numerical values of dependent process variables on the basis of values of relevant independent variables and model parameters.

The present work is a modelling study that focuses on the cyanide-free AARL elution process through fundamental study of the factors affecting the process. Engineers and scientists have attempted to develop mathematical models describing the Zadra[3,4,5,6] and the AARL[2,9] elution processes but because of limited data used they have been considered to be inadequate.

Previous work on the modelling of the AARL elution process[2,9] has shown that variation of factors such as ionic strength, cyanide and hydroxide ion concentrations and temperature down the elution column have a very strong influence on both equilibrium isotherm and kinetic parameters. The specific objectives of the study were:

* To quantify the effects of the presence of hydroxide ion and temperature on the gold equilibrium adsorption isotherm under typical elution conditions.

* To develop an equilibrium model for gold adsorption onto carbon taking into consideration these factors.

* To generate kinetic of elution data by performing experiments under different conditions so as to get mass transfer parameters under these conditions.

* To use the laboratory data obtained from the equilibrium and kinetic experiments to

develop a comprehensive elution model for the cyanide-free AARL elution process.

Attention is focused on cyanide-free elution because of its obvious economic advantages. Apart from the fact that about 37% of the total operation cost[11] would be saved as a result of elimination of cyanide from the process, it is expected that safety would also be enhanced in the absence of cyanide. It is therefore hoped that such a kinetic model could form the basis of a general design and simulation procedure for the cyanide-free AARL elution process.

1.5 ORGANISATION OF THE THESIS

Chapter one gives a broad overview of the CIP process and the historical development of the elution process. It further discusses the various elution processes and the objective of the study. Chapter two discusses the chemistry of the elution process and the factors affecting the process. This chapter also reviews the previous work done on the modelling of the elution process and analyses the shortcomings and limitations of the models developed. Chapter three describes the experimental equipment used and the choice of experimental technique for the equilibrium work. Chapter four describes the modelling of the equilibrium data generated at both single and multi-component levels. A rigorous statistical method for discrimination between the models is also included. Chapter five describes how the kinetic model was derived and sensitivity analysis of the model with respect to some of the parameters. Chapter six presents the modelling of the kinetic data. The last chapter summarises the important findings and conclusions of the study.

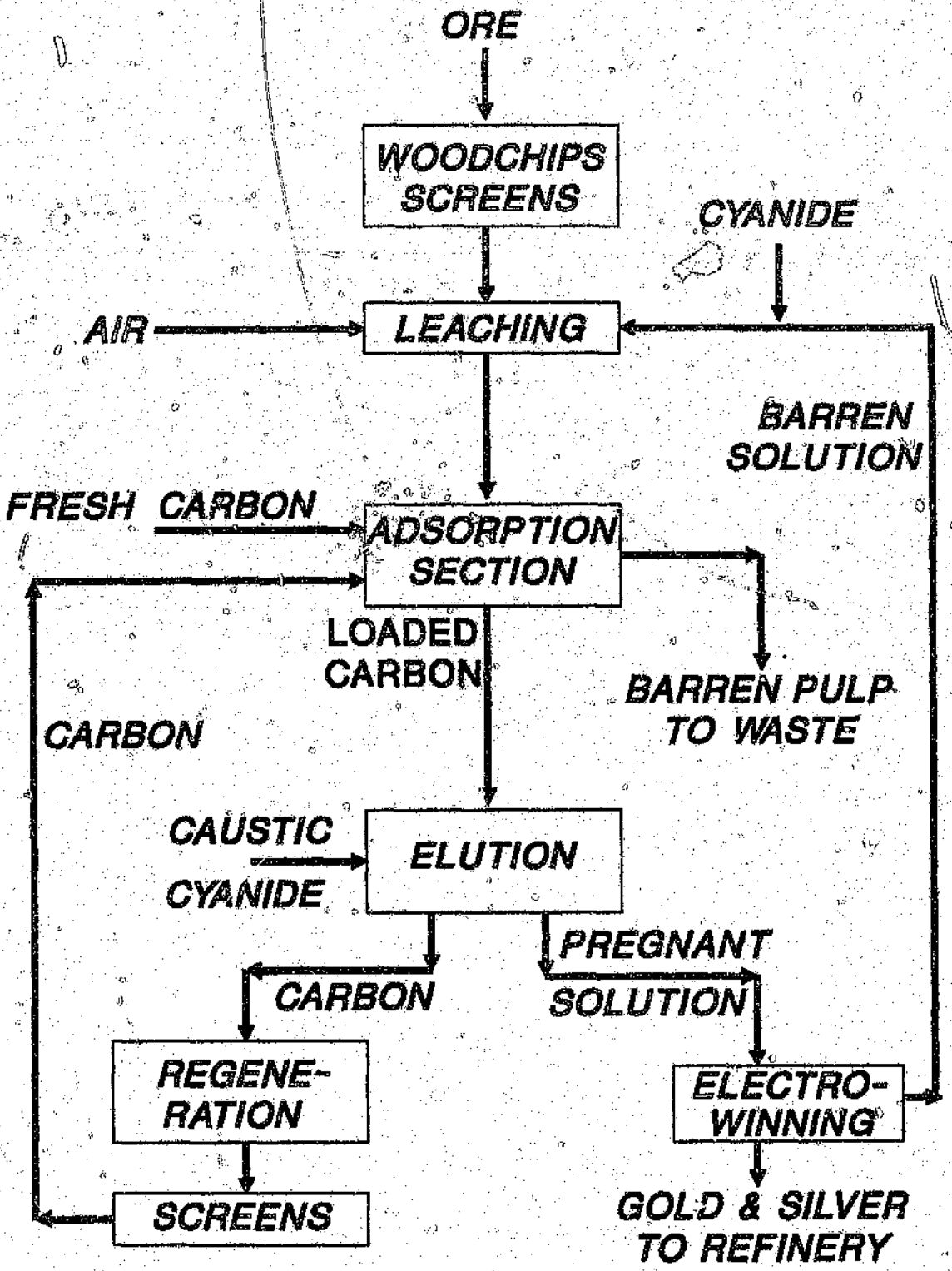


Figure 1.1: Flowsheet of the CIP process

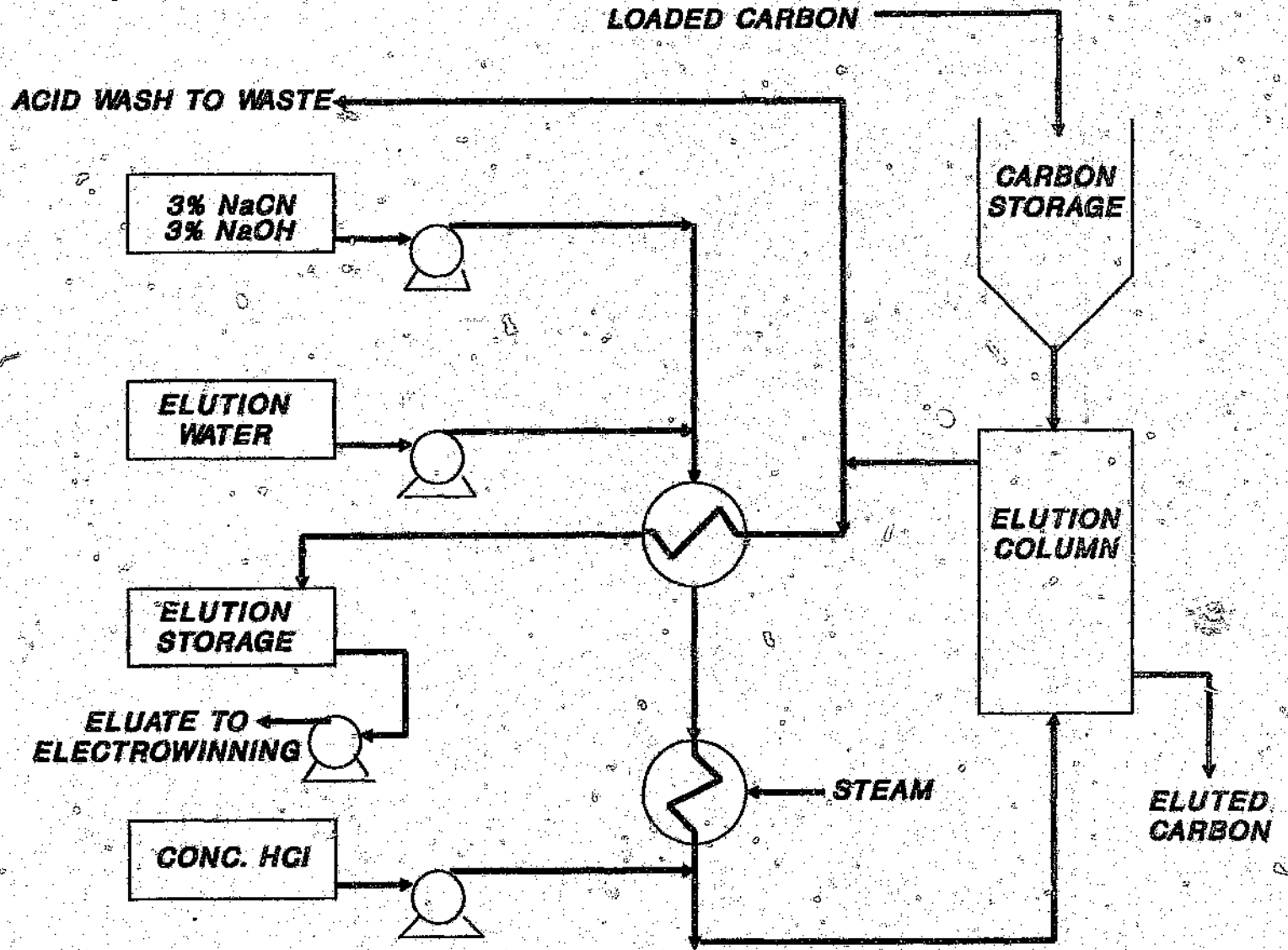


Figure 1.2: Flowsheet of the AARL elution process

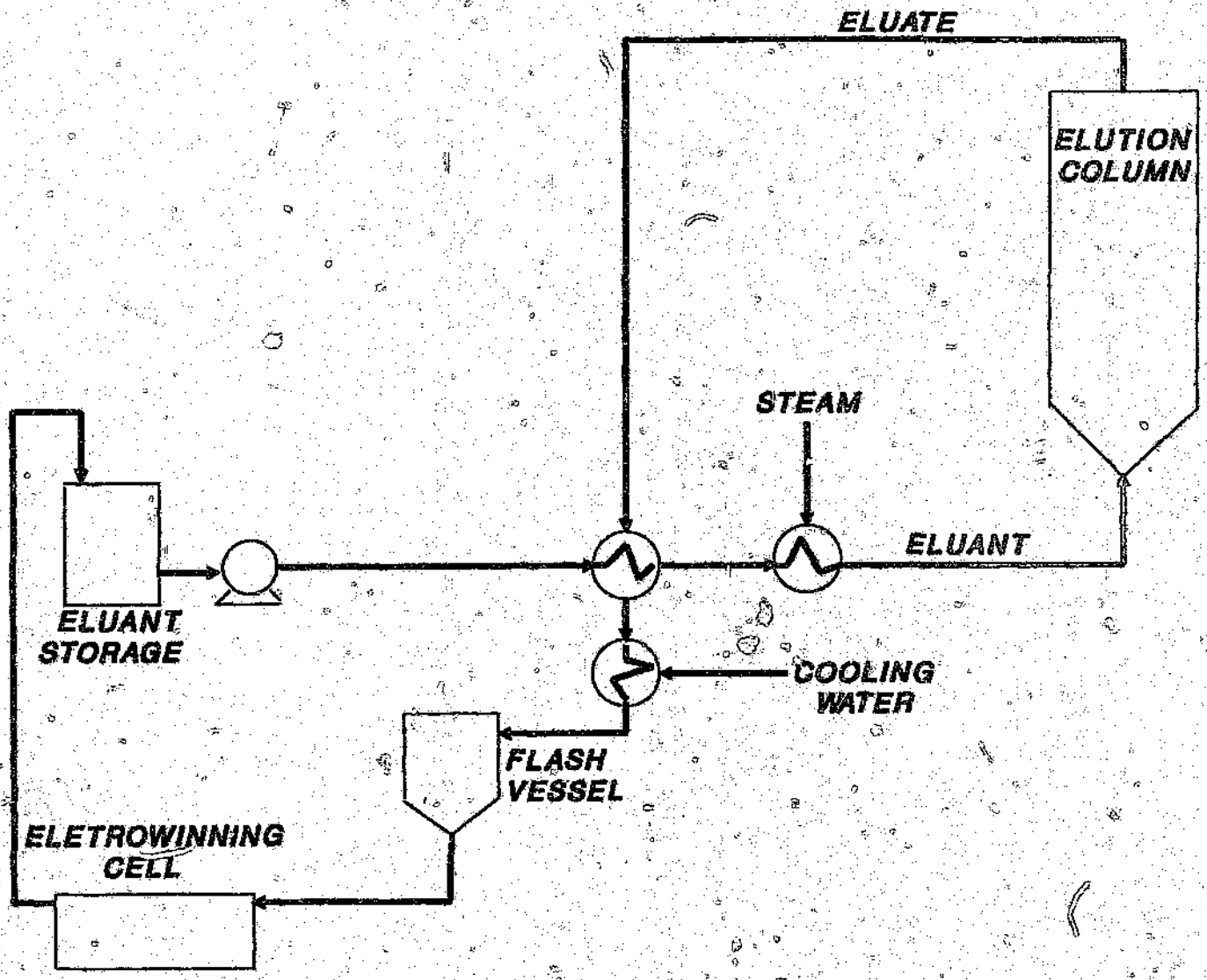


Figure 1.3: Flow diagram of the Zadra elution process

CHAPTER 2

LITERATURE REVIEW

CHAPTER 2

LITERATURE REVIEW

2.1 ACTIVATED CARBON - PHYSICAL STRUCTURE & MECHANISM OF ADSORPTION/ELUTION

Figure 2.1 shows a physical picture of the carbon structure under adsorption. Physically, the carbon particle contains a complex network of pores which may be classified in terms of nominal diameter as macropores, mesopores and micropores:

Macropores	50 - 2000nm
Mesopores	5 - 50nm
Micropores	0.8 - 5nm.

This classification is however arbitrary and usually depends upon the instrument or method used. Since the surface bounding cylindrical or irregular shaped pores increases considerably with decreasing diameter, it is the walls of the micropores which contribute the major part of the internal surface area of the carbon. The macropores essentially serve as liquid filled ducts within which adsorbate molecules are transported by diffusion to the mesopores and micropores where most of the adsorption occurs. The micro-structure of the activated carbon can therefore be seen as a large number of micro-crystallites interlinked by micropores, mesopores and macropores.

From modelling point of view, many investigators have used a single rate expression to describe the adsorption of gold onto activated carbon[1]. Van Deventer[18] has also proposed a branched pore model in which the mechanism of adsorption is assumed to be multi-step with different diffusion mechanisms for the macropores and the micropores respectively. This approach was used by Van [illegible]we[19] in his work on elution.

From Figure 2.1 four transport processes that take place in the system are distinguished. These are film diffusion, pore diffusion, surface diffusion and adsorption. Since elution/desorption is merely the reverse of adsorption, the transport mechanism would be as follows: desorption, surface diffusion, pore diffusion and film diffusion. These mechanisms are defined as follows[31]:

Film diffusion is the diffusion from the bulk liquid phase through a hypothetical

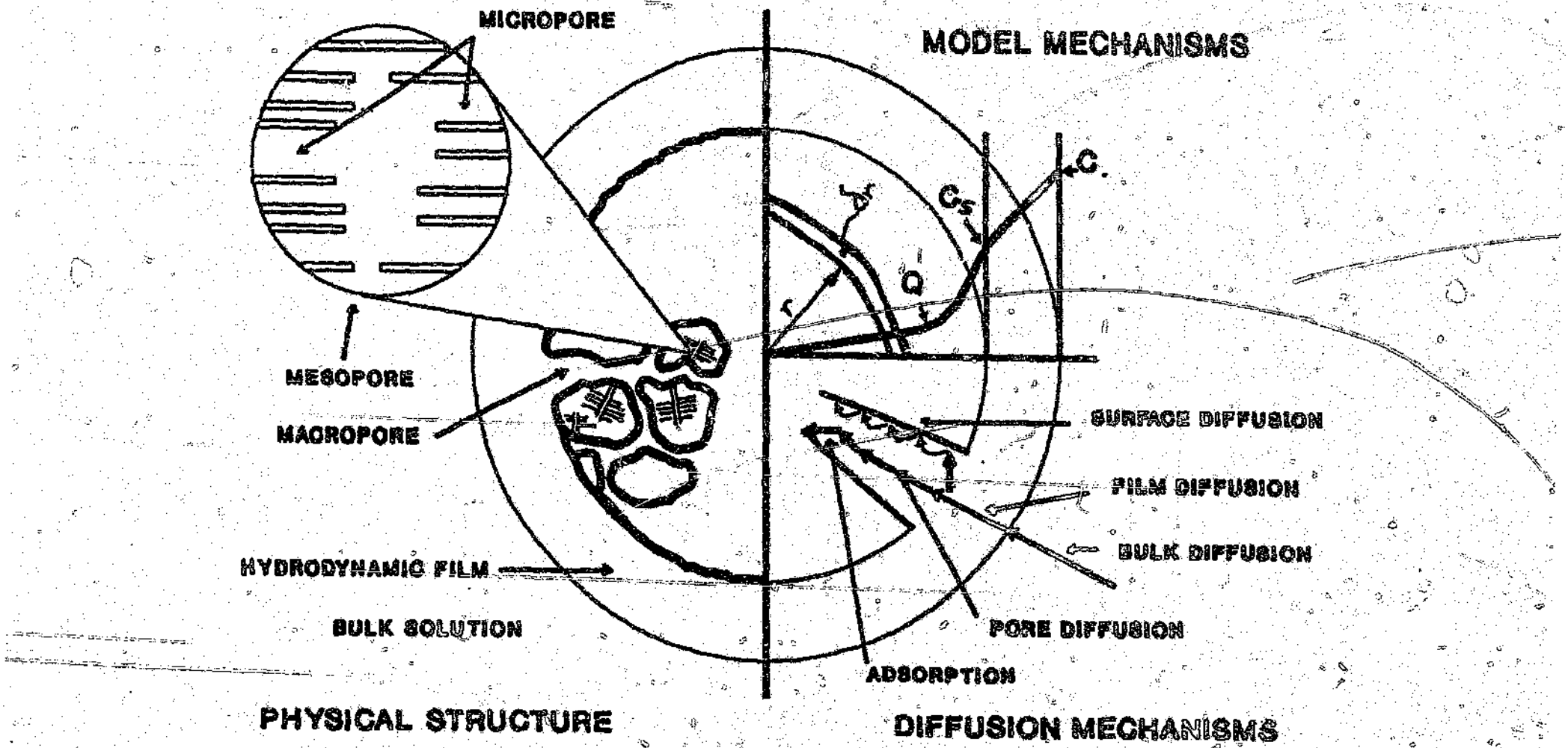


Figure 2.1: Schematic representation of Intraparticle Adsorption and Diffusion Mechanism after Le Roux[20]

hydrodynamic boundary layer or film surrounding the particle.

Pore diffusion is the transfer that involves diffusion of solute through the pore liquid of the particle.

Surface diffusion is the migration of the adsorbed molecules along the internal pore wall. **Adsorption** onto the internal carbon surface. Desorption therefore is stripping from the internal carbon surface.

As shown in Figure 2.1 the pore and surface diffusion mechanisms act in parallel. Levenspiel[34] has shown that when mass transfer takes place through a number of steps in parallel or in series, the rate of the parallel steps are additive. He stated further that the overall reaction rate is determined by the slowest or rate determining step in a series of mass transfer and reaction steps. From this the effects of pore and surface diffusion on mass transfer are therefore additive.

From the Figure, film mass transfer mechanism acts in series with the intraparticle (pore and surface) diffusion mechanisms and the adsorption reaction. Therefore the slowest of these three mechanisms would constitute the rate-controlling mechanism. In reality, the rate controlling mechanism changes with time. For adsorption it is suggested that the overall rate is often determined at the initial stages by film mass transfer mechanism and then by internal diffusion[35]. The reverse will be true for elution.

It is a well founded assumption that surface diffusion controls intraparticle diffusion and that pore diffusion can often be neglected under the following conditions:

a. when the adsorbent has a high affinity for the adsorbate,
b. when the adsorbate is reversibly adsorbed, and
c. when the adsorbate has a favourable isotherm[31].

Young[42] has defined that the adsorbate will have a favourable isotherm if n, the exponent in the Freundlich isotherm is less than 1. For an activated carbon-aurocyanide system all three conditions above are true. It is stated that pore diffusion will only be dominant under conditions of high pore fluid concentration. Van Deventer[18] and Van der Merwe[19] in their modelling work eliminated pore diffusion based upon these assumptions.

2.2 THE CHEMISTRY OF ELUTION

The best understanding of the adsorption/elution mechanism is summarised in Equation 2.1 from Adams[3] work;

$$M^{n+}_{(aq)} + nAu(CN)^-_{(aq)} \Leftrightarrow M^{(n+)}[Au(CN)^-_2]_{n(ads)} \qquad 2.1$$

(where M^{n+} could be ions like K^+, Na^+, Ca^{2+} et al). Adams has shown that this adsorption equation is thermodynamically reversible. Thus chemical and physical effects which enhance elution will therefore inhibit adsorption and vice versa. These factors therefore form the basis of the elution process and they are as follows:

1. temperature,
2. ionic strength,
3. cyanide and hydroxide concentrations and
4. organic solvent.

The effect of these factors on elution will be discussed later in the chapter.

As seen from the chemical equation above, gold adsorbs as an $Au(CN)^-_2$ ion pair. For elution to be favoured it demands that the solution must have low concentration of such spectator ions like Ca^{2+}, Na^+ et al, hence low ionic strength. By so doing the equilibrium reaction above will tend to shift to the left favouring elution. Under low pH conditions the $Au(CN)^-_2$ complex tends to form AuCN which is difficult to elute. There is therefore the need for the solution involved in the elution process to have a high pH which connotes a basic environment. This will mean that the ionic strength of the solution will invariably be high. Further the presence of CN^- and OH^- ions have a modifying effect on the surface of the carbon structure. This results in enhancement of elution. However, high CN^- and OH^- ion concentration results in high ionic strength which will in turn favour adsorption. Elution is therefore an attempt at arranging these factors so that gold is successfully desorbed.

2.3 FACTORS AFFECTING THE ELUTION PROCESS

Davidson[11] suggested that the AARL procedure is essentially a chromatographic mechanism whereby metal cyanocomplexes are sequentially desorbed from the preheated carbon using an

ionic strength gradient as a means of effecting elution. Because of this mechanism, both the plug flow of eluate through the system and the geometry of the column play an important role. But from Van der Merwe's[19] work the above assertion has been put in doubt. The above conclusion might have been drawn as result of by-passing of solution through the column. While temperature plays perhaps the most significant role in gold elution (Zadra & AARL processes), the parameters affecting elution are interrelated to some extent thus making their evaluation and definition somewhat complex.

2.3.1 TEMPERATURE

This is probably the most important variable. An increase in temperature results in a significant decrease in the adsorptive power of carbon. The exothermic nature of the loading of gold is typical of most heterogeneous adsorptive processes. Thus all operating elution procedures are carried out at elevated temperatures. Both the Zadra and the AARL processes operate above 90°C and 83% of the AARL elution systems in South Africa, for instance, operate at 110°C or above. Because of the high temperatures under which the AARL elution process has to operate it thus has to be a pressure process.

2.3.2 IONIC STRENGTH

As indicated by the chemical equation above, gold is normally adsorbed onto carbon as an ion pair of the type $M^{n+}[Au(CN)_2^-]_n$. The presence of ionic species like Ca^{2+}, Na^+ et al in the adsorption medium generally results in an increase in the loading capacity of carbon and this effect is found to depend on the type of cation and it's concentration[3].

Hence, desorption is favoured by conditions of low ionic strength and the absence of ions like Ca^{2+} and Mg^{2+} ,which enhance gold adsorption. Low ionic strengths tend to shift the equilibrium reaction to the left favouring desorption. This forms the basis of the AARL elution process in which the pretreatment with hot caustic cyanide converts the calcium ion pair into the less strongly adsorbed $Na^+[Au(CN)_2^-]$, which is then eluted under the conditions of low ionic strength produced by the use of deionized water. An increase in ionic strength therefore results in a decrease in elution rate.

2.3.3 CYANIDE AND HYDROXIDE CONCENTRATION

The capacity of carbon for gold adsorption decreases with increasing cyanide, and to a lesser

extent, hydroxide concentration. Adams[3] has postulated that the presence of these ions has surface charge effect on the carbon. This results in the reduction of the adsorptive capacity of the carbon. This effect forms the basis of the Zadra process in which caustic cyanide at high pH is used to shift the adsorption equilibrium to favour elution.

The eluant composition has an effect on the rate of elution; with the opposing influences of cyanide and hydroxide concentration on one hand and ionic strength on the other hand. Adams[3] has shown that as the ionic strength increases, the rate of elution decreases and that it is possible to perform elution by using only hydroxide or cyanide solution alone. Also the rate of elution increases with increasing concentration of either cyanide or hydroxide at constant ionic strength.

2.3.4 ORGANIC SOLVENT

Attempts have been made in which various organic solvents were added to aqueous solution to promote more efficient desorption of gold. The studies proved that even at low temperatures, gold can be eluted in the presence of high concentration of certain solvents. Adams[3] suggested that the action of organic solvents in elution is due to preferential adsorption of the organics on the surface of carbon, displacing the adsorbed $M^{m+}[Au(CN)_2^-]_n$ species.

2.3.5 WATER QUALITY AND ACID TREATMENT

It is shown that to maintain overall efficiency, hot acid washing of the carbon with dilute HCl prior to gold elution is essential for the AARL elution procedure[11]. Investigations have shown that cold dilute acid will effectively remove calcium and zinc from carbon. Hot acid, at about 95°C, will remove calcium, zinc and nickel together with a large proportion of iron and silica. Gold, silver and copper are not eluted from carbon using cold or hot acid.

It is reported[6] that cold acid washing results in the limited formation of an AuCN type species, the reaction being considerably more marked when hot washing is employed. From a gold elution point of view, the AuCN formed is very difficult to elute. Adams[3] has shown that after the acid washing step only 50% of the loaded gold on the carbon can be desorbed by regional water. To convert the AuCN formed into a state that is amenable to elution, presoaking is employed. Presoaking converts the AuCN to $Au(CN)_2^-$ which is easily eluted with good regional water.

Apart from the removal of calcium, zinc, nickel et al which influence gold elution kinetics, acid washing has an effect on the adsorption process. Without acid washing poor adsorption may be encountered in the adsorption circuit. This is due to the passivation of the carbon surface with calcium carbonate. Acid washing destroys the calcium carbonate hence liberating the carbon for adsorption. Because of the difficulties of eluting AuCN formed after the acid washing stage, some newly built plants employ acid washing after elution.

2.4 MODELLING OF THE ELUTION PROCESS

Adams and Nicol[4] made the first attempt at the modelling of the elution process and this was based on the Zadra process. The authors assumed that the adsorption and desorption of gold from activated carbon in the presence of cyanide does not involve any slow chemical reactions and that the slow steps in these processes can be associated with mass transport in the solution and solid phases. They considered the carbon as a homogeneous phase through which the aurocyanide diffuses to an interface where equilibrium with the aurocyanide in the solution is assumed to be rapid. A linear model was used to describe this equilibrium. It was supposed that the conditions during the Zadra process remain constant and that the process could therefore be modelled with a single, fixed equilibrium isotherm. The model was kept very simple by describing intraparticle diffusion with a single mass transfer coefficient. All the experiments were performed in a CSTR.

A phenomenological mathematical model of the rate, of adsorption, hence desorption, of a compound onto/from activated carbon must incorporate or at least consider the rate of adsorption/desorption reactions, and of the mass transfer mechanisms within the adsorbent particle. These are then related to the reactor or contacting model employed. Therefore lumping the mass transfer and the rate constant of the reaction together is erroneous and unjustifiable. In fact the model mixes kinetic and equilibrium parameters together and this is unrealistic. Further it has been shown that the adsorption/desorption equilibrium is non-linear even at low solution concentration[18]. Hence the use of a linear model to describe the equilibrium of gold desorption is not consistent with what is known. Also the model has no means of predicting changes in parameters under different conditions of cyanide ion, hydroxide ion, temperature et al.

Van der Merwe[19] has shown that the conditions during elution in the Zadra process do not remain constant hence the use of a single, fixed equilibrium isotherm can not be accepted. Adams and

Nicol[4] provided an extension of their model to describe elution in a column but did not provide any experimental evidence for it's applicability thereof and it is therefore unlikely that the model will be of any industrial relevance.

Adams[6] in another publication attempted to apply the model developed for an elution column to fit experimental data. In this work he employed a column with a 5ml carbon bed and the flow rate of the eluant was 14.9 bed volumes per hour. Though the fit obtained was good it could be said that such a system resembles a CSTR. A further attempt was made to describe the elution of gold from a 25ml carbon bed at a flow rate of 2.3 bed volumes per hour. The inability of the model to fit this system was attributed to the fact that not enough time was allowed for the eluant to diffuse into the carbon. The experimental technique was therefore changed by first equilibrating (pretreating) the carbon in cyanide solution before the experiment. The theoretical curves obtained after this process were found to correspond more closely to the experimental data. In practice, however, the Zadra process is not performed with cyanide pretreatment. The effectiveness of the model is therefore questioned.

So far only three published reports have been presented on the modelling of the AARL elution procedure. The main reasons for this are probably the following:

1. The lack of the understanding of the pretreatment process,
2. The change in chemical composition of the eluate during the elution, and
3. The apparent complexity of the opposing effects of high ionic strength and high cyanide concentration.

The first published report on the modelling of the AARL process was presented by Van der Merwe and Van Deventer[9]. The model was such that factors such as potassium concentration, cyanide concentration and gold concentration at any time and height in the column were modelled separately.

The model was essentially the same as the branched-pore model used by Van Deventer[18] for the simulation of the adsorption of aurocyanide onto carbon. The authors showed that an intraparticle-film diffusion model with a shifting equilibrium could be used to simulate the AARL elution curves.

The equilibrium adsorption expression was found to be a function of mainly the pretreatment conditions, concentration of spectator cations, temperature, pH and the deactivation of the carbon surface caused by the degradation of cyanide. The isotherm is therefore used to account for the changes in cation, cyanide and hydroxide ion concentrations during the elution process. An attempt was made to model gold elution from the Zadra and the AARL processes using the same fundamental model.

In further work, Van der Merwe[19] showed that an equilibrium approach to modelling could be used in the case of "weak adsorption", that is where severe pretreatment conditions were used. He observed that under such conditions kinetic influences were irrelevant, so that the velocity of flow through the column did not affect the elution behaviour. When the influence of pretreatment was less profound, so that the equilibrium of adsorption was higher, a kinetic approach was required to model elution data.

The model of Van der Merwe[19] provided good fits to experimental data. But the number of parameters to be estimated are too many and the model is also too complex mathematically. Further it is unrealistic that film diffusion mechanism should be applied to gold elution while potassium was not treated using the same approach. More work therefore needs to be done to substantiate the validity of the model.

Stange and King[2] in 1990 presented another paper on the modelling of the AARL process. The model is based on the fact that at the end of the soaking period a certain chemical environment has been established which facilitates desorption. Although the chemical environment is appropriate for desorption very little gold on the carbon diffuse into the bulk of the solution in the column since mass transfer is hindered by the stagnant solution condition. This step, called the pretreatment step, is regarded as the initial condition for the model. When the deionized water is passed through the column, mass transfer from the carbon to the bulk of the solution is greatly enhanced. In addition the ionic strength decreases in the column, facilitating desorption.

The column is modelled as a plug-flow packed-bed reactor during the washing period with a hyperbolic partial differential equation. It was assumed in the rate expression that mass transfer is limited by film diffusion and that the equilibrium isotherm is linear for the elution of Na^+ and

aurocyanide complex. An exponential relationship between the sodium ion and the aurocyanide ion equilibrium was also assumed.

The model is found to give good fit to an experimental data generated from a large industrial plant. But at this stage the model is found to inadequate because of the following:

1. It can not describe the pretreatment stage of elution.
2. The use of a linear isotherm to describe the equilibrium of gold and sodium ion elution is unjustified because the equilibrium isotherm has been found to be non linear always[16].
3. The assumption of exponential relationship between gold and sodium ion equilibrium was not proved by any experimental evidence.

Stange[13] tested the predictive nature of the model by assessing the effect of increased ionic strength of the wash water on elution performance. This was done by running the simulator with different sodium ion concentrations in the wash water. The result obtained has shown that the model is not sensitive to ionic strength. This is contradictory since the elution process has been known to be sensitive to the ionic strength of the eluant[3,16]. This further strengthens the inadequacy of the model at the moment.

The above observations emphasize the fact that the elution process can not be modelled without considering the effect that the various factors have on the equilibrium and the kinetic isotherm parameters. Further the nature of the desorption reactor and the mechanism of intraparticle transport must be carefully taken into consideration as discussed above. Chapter five discusses the way these factors were taken into consideration in the derivation of the models.

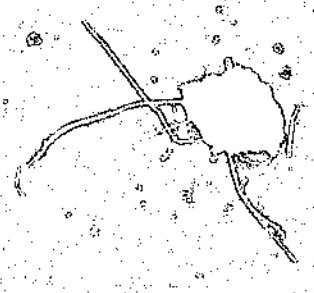
2.5 CONCLUSION.

The factors affecting the elution process have been discussed in this Chapter and it has been shown that these factors are intertwined such that isolation of anyone of them would be a very difficult task. Further, previous attempts to model the elution process have been discussed and the limitations of the models mentioned.

The next Chapter will discuss the experimental set-up used in this study and the search for an experimental technique.

CHAPTER 3

EXPERIMENTAL SET-UP AND CHOICE OF EXPERIMENTAL TECHINIQUE



CHAPTER 3

EXPERIMENTAL SET-UP AND CHOICE OF EXPERIMENTAL TECHNIQUE

One of the objectives of the project is to study the influence of temperature and hydroxide ion on the equilibrium adsorption of gold under typical elution conditions. This will facilitate the development of an equilibrium model that takes into effect these influences. At the plant level the elution process is a multi-solute system. Thus, the work is extended to examine the simultaneous adsorption of gold cyanide and hydroxide ion under elution conditions.

A lot of publications have emerged on the equilibrium adsorption of gold cyanide onto activated carbon[12,17,18,19,20]. Generally, these experiments were conducted at ambient temperatures. Hence in general terms the equilibrium measurement in this work could have been below 80°C as other workers have done. But this would have defeated the aim of the project since such a condition will not be representative of the elution condition as practised under industrial situations.

Further a choice of a reproducible and meaningful experimental technique will affect the model developed. This will either substantiate the essence of the model or not. From the above discussion the following potential difficulties emerged:

1. The need for an experimental set-up that could be used to perform experiments above 80°C. This demands the set-up to be well controlled to curtail fluctuations in temperature. It must also be properly lagged to reduce heat loss.

2. The ability for the experimenter to separate kinetic and equilibrium effects by the use of such a set-up.

3. The need for establishing a meaningful equilibrium time for each species at such high temperatures. This is further aggravated as isotherms have to be performed at both single and multi-component levels.

The chapter therefore describes the experimental set-up used and how the problems related to such a set-up were solved. It further discusses how equilibrium time was established and the choice of experimental technique used to obtain the data.

3.1 EXPERIMENTAL SET-UP

The experimental rig consists of a reservoir in which the experimental solution is stored, a pump, a heating element, an elution column, a pressure gauge and regulating valve and a cooling coil. (See Figure 3.1).

The reservoir is made up of a stainless steel tank of 10 litres volume. During all the experiments, the solution in the tank is continuously stirred by a magnetic stirrer to effect thorough mixing. This is to ensure homogeneity of the solution that is been pumped through the column during the experiments and at the time of sampling. The solution is circulated through the rig by a high-pressure pump at the flow rate of 3l/hr. The volume of the mini-column is 0.75 litre hence this flow rate is 4 bed-volumes/hour. This figure is very comparable to the industrial situation since a typical AARL process is conducted at the flow rate of 2 bed volumes/hour.

The solution that is pumped from the reservoir is first heated by a heating element before going through the mini-column. The temperature of the column is monitored by a thermocouple, and controlled using a PID controller. The heating column is fully lagged by fibre-glass wool so as to reduce loss of heat.

The mini-column is a stainless steel column with an enclosing jacket. Hot oil is circulated in the jacket to raise the temperature of the column to the desired one and to maintain it at that level throughout the experiment. The carbon is placed in a wire-mesh basket before being placed into the column. The basket has been designed such that it fits tightly the inner diameter of the column so as to reduce by-pass of the solution and to enhance plug-flow.

The pressure is also monitored by a pressure gauge. In all experiments the pressure was above 260kPa which is high enough to keep steam in the form of liquid at temperatures at and above 100°C[14]. This situation ensures that the experimental condition of the solution that is being used at all temperatures is relatively the same. Before the solution flows back into the tank, it is cooled by the use of a water heat-exchanger. Water therefore flows in and out the cooling unit so as to effect the cooling.

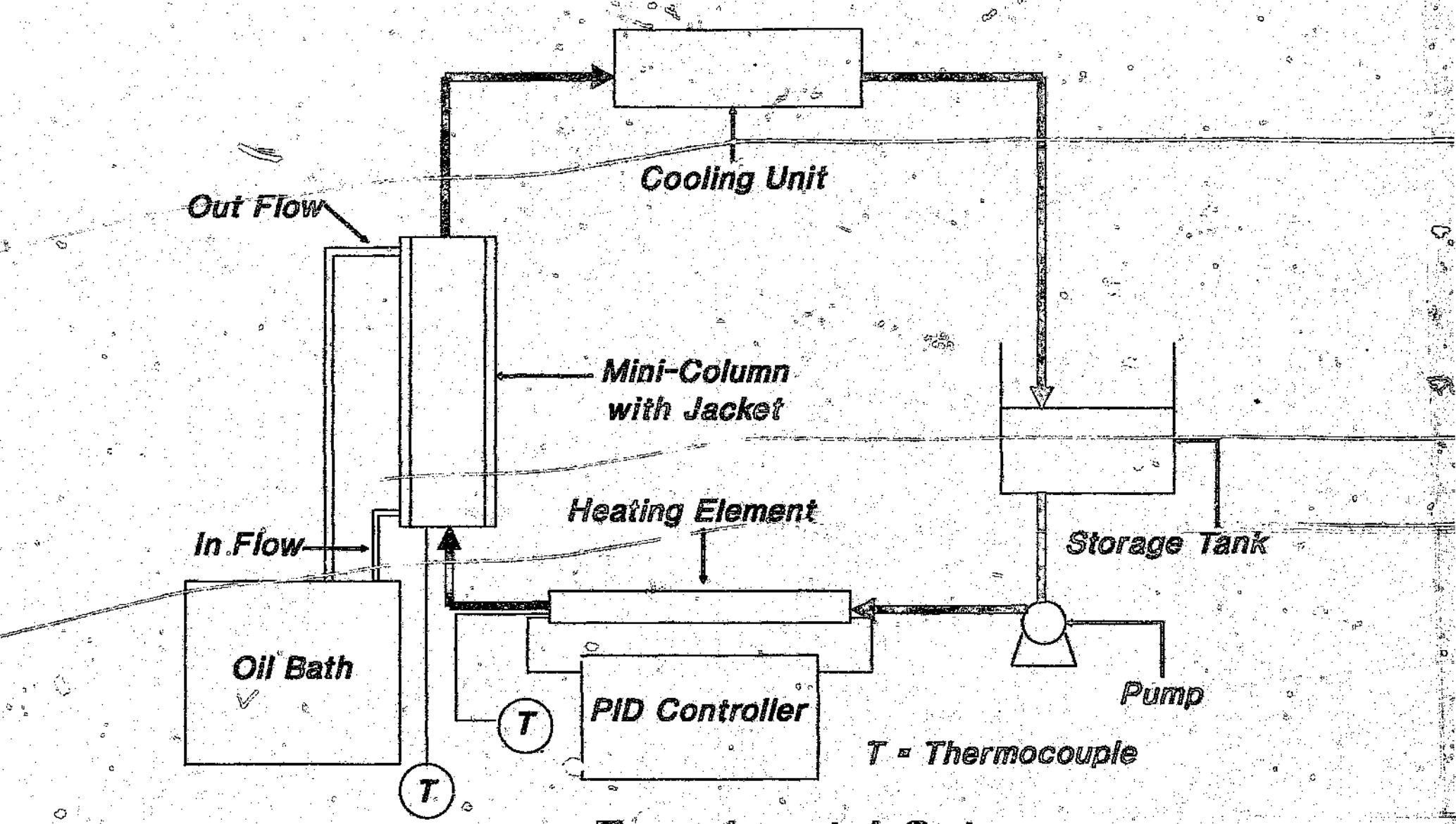


Figure 3.1: Experimental Set-up.

3.2 CHEMICALS AND CARBON PREPARATION

All the chemicals used, such as NaOH, HCl et al, were of the analytical grade and were procured from LABCHEM. Analysis for OH^- ion was done by titrating the solution against standard HCl with phenolphthalein as an indicator. The gold potassium cyanide used was obtained from Johnson Matthey and this has a gold content of 68.00% by mass.

The carbon used for all the experiments was Mitsubishi virgin carbon obtained from Grootviel Mines. Before being used for the experiments the carbon was conditioned by continuously stirring in water for at least two hours and later thoroughly washed with water. Washing with water removes the fines from the carbon. After this process the carbon was oven dried and then sieved to sizes between +1.00mm to -2.36mm. Before any experimental work was performed the sieved carbon was oven dried again at 90°C for at least three days to remove any water adsorbed on the carbon.

OH^- ion alone has been considered in this study because of the focus on cyanide-free elution. The presence of the OH^- ion is to determine its influence on the adsorption of gold as would be used in elution but not its ability to compete with gold.

3.3 CHOICE OF EXPERIMENTAL TECHNIQUE

A better interpretation is given of equilibrium data if the time of equilibrium establishment between the adsorbent and the adsorbate is known. This demands that the kinetics of adsorption of the various species at the temperatures between 80 and 120°C must be studied. This is to help establish the time at which equilibrium is established. Several approaches have been tested and discussed below for each solute.

3.3.1 HYDROXIDE ION

3.3.1.1 EXPERIMENTAL TECHNIQUE 1

In this case 3 litres of 0.1M hydroxide ion solution was contacted with 50g of carbon at various temperatures for 5 hours. Samples were taken at 30 minutes intervals. From Figure 3.2 it was assumed that equilibrium has been established after 3 hours. Sampling in the equilibrium experiment was then done after every 3 hours. 50g of carbon was contacted with 0.1M OH^- solution for 24 hours. After each time of sampling the solution was altered in the step of 0.05M. Figure 3.3 shows the result obtained.

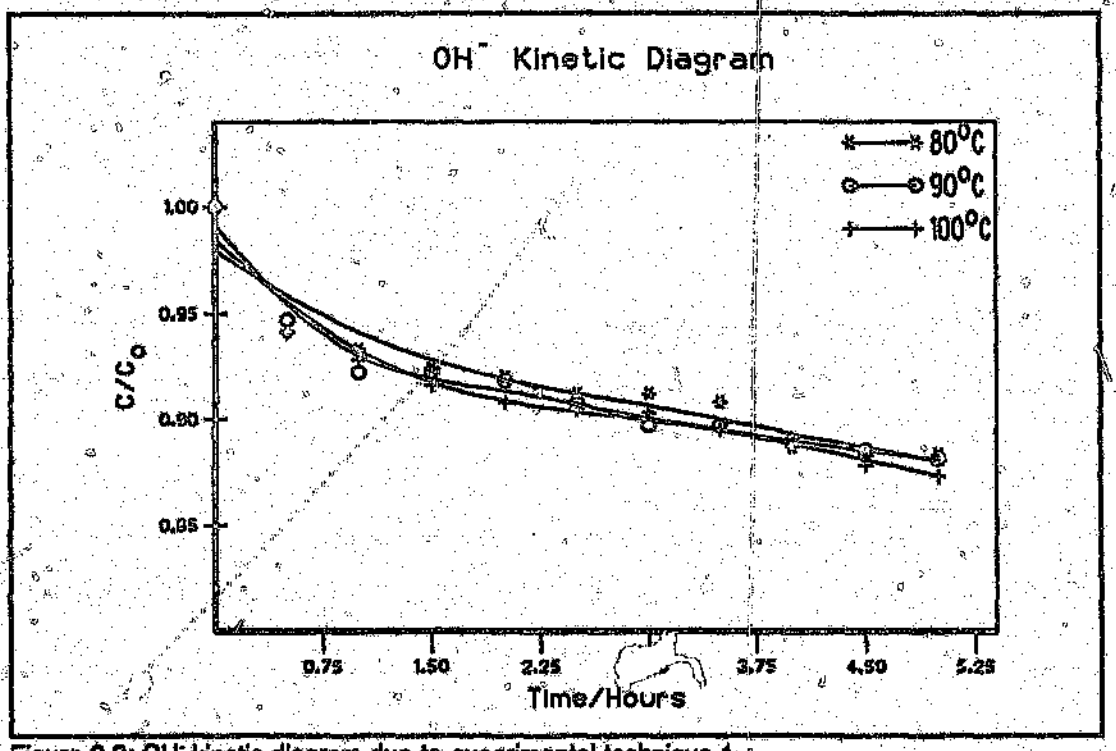


Figure 3.2: OH^- kinetic diagram due to experimental technique 1.

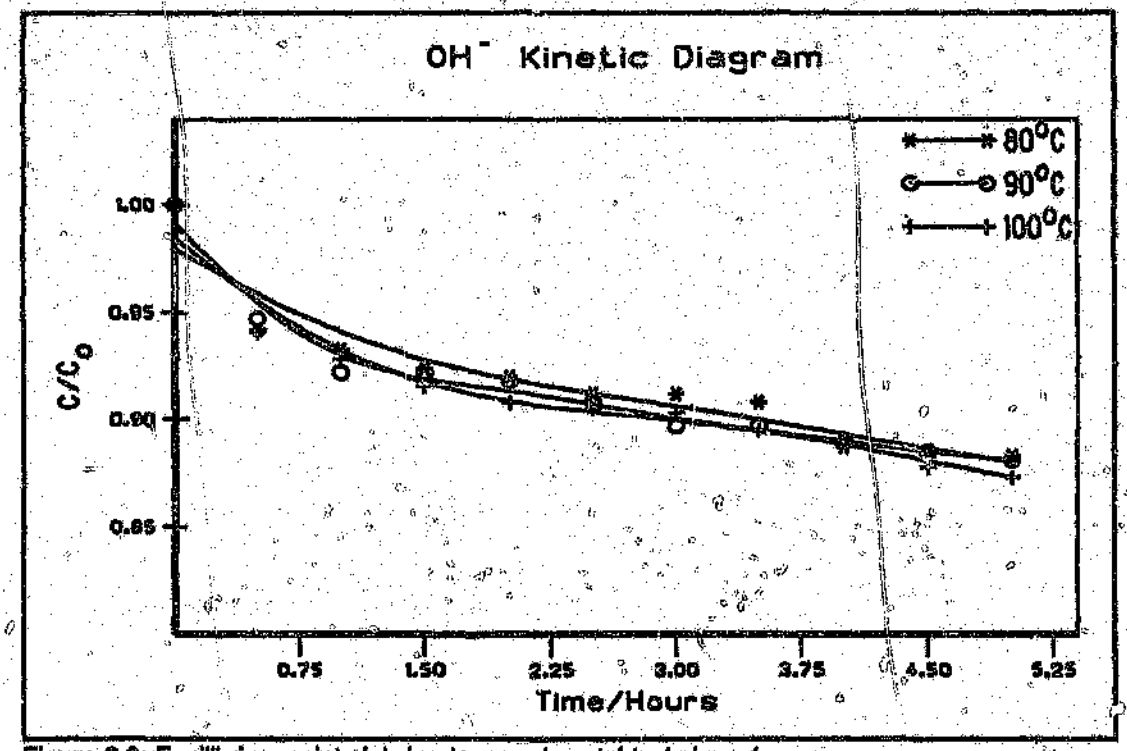


Figure 3.3: Equilibrium point plot due to experimental technique 1.

The Figure indicates that equilibrium adsorption of OH^- onto carbon is not affected by temperature. This is doubtful considering the exothermic nature of the adsorption process. This led to the development of the second technique.

3.3.1.2 EXPERIMENTAL TECHNIQUE 2

The equilibrium time of 3 hours obtained from the first technique was maintained. But to get an isotherm six portions of 3 litres 0.2M of OH^- solution was contacted with six different weights of carbon ranging between 25 and 70g. Figure 3.4 shows what was obtained.

The curves show an inverse relationship between the equilibrium loading and the concentration. This relationship does not conform to any known adsorption process[15]. A third technique was thus developed.

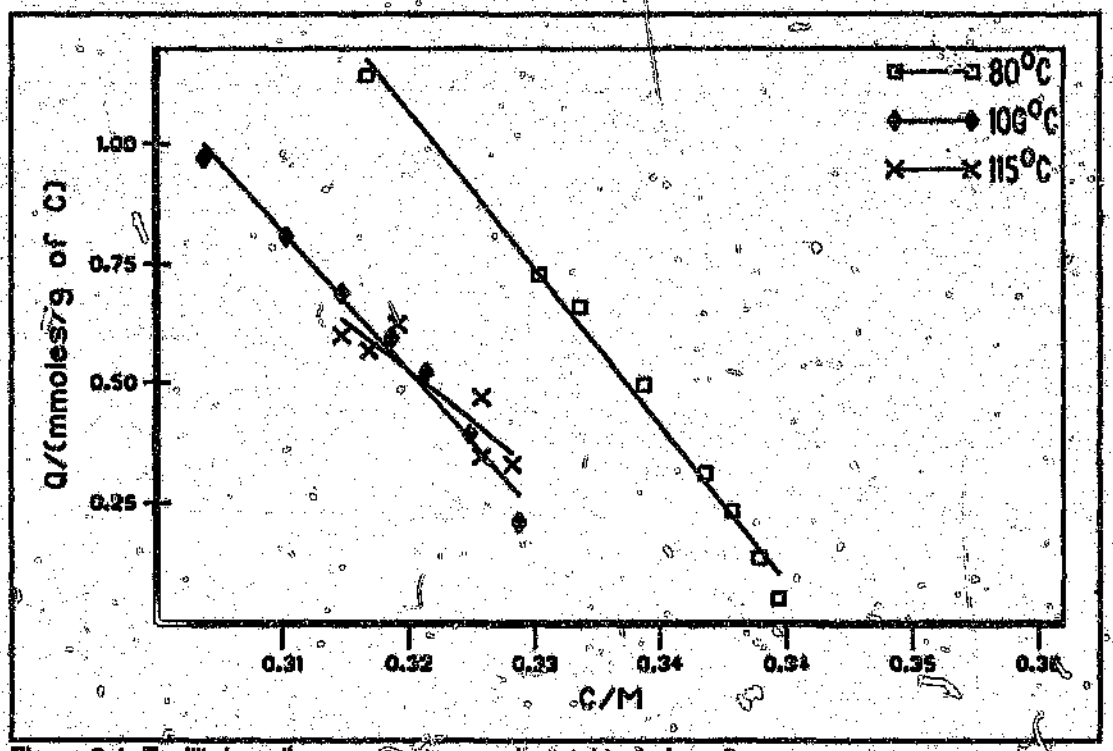


Figure 3.4: Equilibrium diagram due to experimental technique 2.

3.3.1.3 EXPERIMENTAL TECHNIQUE 3

From the results of the first two techniques the following were identified as possible shortcomings:

1. The equilibrium time is too short.
2. The volume of solution being circulated is too large.

Kinetic runs were therefore performed again at different levels of OH^- ion concentration (between 0.1 and 0.4M). 1.5 litres of each solution was contacted with 15g of carbon at 80°C for 10 hours. Samples were taken after every 2 hours. Figures 3.5 and 3.6 illustrate the results obtained.

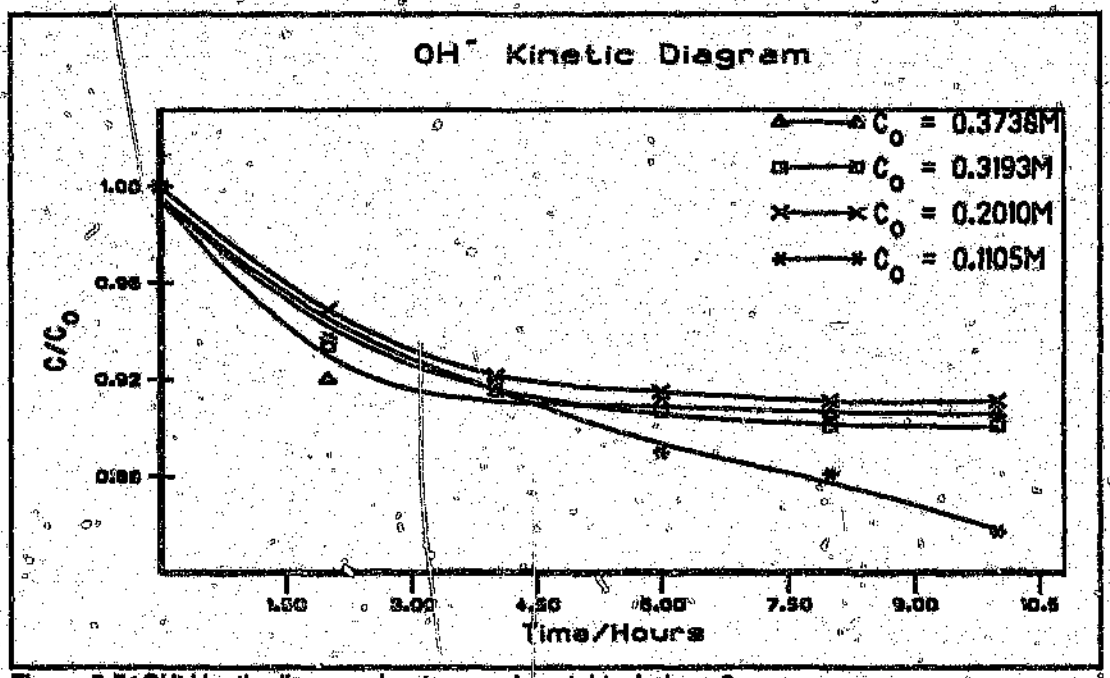


Figure 3.5: OH^- kinetic diagram due to experimental technique 3.

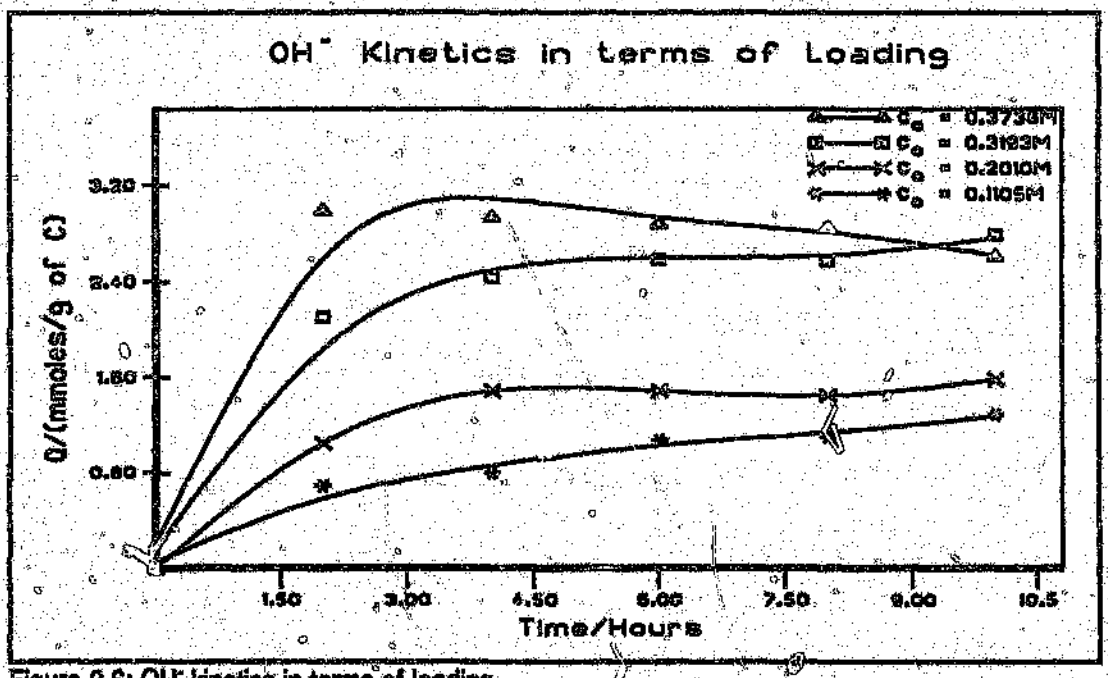


Figure 3.6: OH^- kinetics in terms of loading.

The result as shown indicates that the rate of equilibrium establishment is dependant on the initial concentration of the OH^- in the solution. The higher the initial concentration, the faster the equilibrium attainment. This is not unexpected because the more concentrated the solution the greater the probability of collision between the OH^- and the surface of the activated carbon, assuming that the collision theory is to be used to explain the adsorption. In fact any equilibrium limited diffusion type system will be expected to behave as such. Hence since equal mass of carbon is being used for the different concentrations the more concentrated solutions will cause the adsorption sites on the carbon particles to get filled up quickly resulting in faster equilibrium attainment. Therefore when the equilibrium experiment was being performed at 100 and 115°C the following equilibrium times were used for each initial OH^- concentration.

Table 3.1: Equilibrium times obtained at the various initial concentrations of OH^- ion.

C_o/M	Time/hrs
0.4 and above	4
0.3	6
0.2	8
0.1	10
0.05	12

A typical isotherm obtained using this technique is shown in Figure 3.7. It shows the non linear nature of the adsorption system and the result is more satisfactory than the results from the first two techniques. This technique was therefore used for further work and the result obtained will be discussed in Chapter 4.

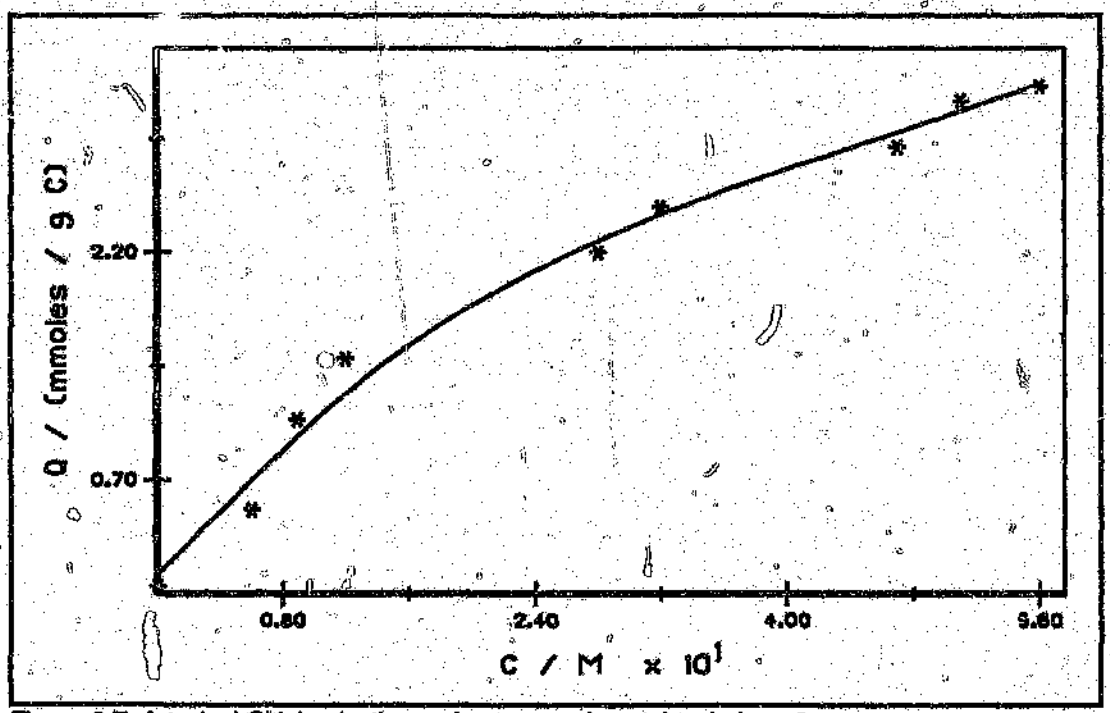


Figure 3.7: A typical OH^- ion isotherm due to experimental technique 3.

3.3.2 GOLD

3.3.2.1 EXPERIMENTAL TECHNIQUE 1

This is similar to the technique described for OH^- ion in Section 3.3.1.1. Three litres of 50ppm aurocyanide solution was contacted with 50g of carbon for five hours at the temperatures of 80, 100 and 115°C. Samples were taken in the interval of 30 minutes. Figure 3.8 shows the results obtained.

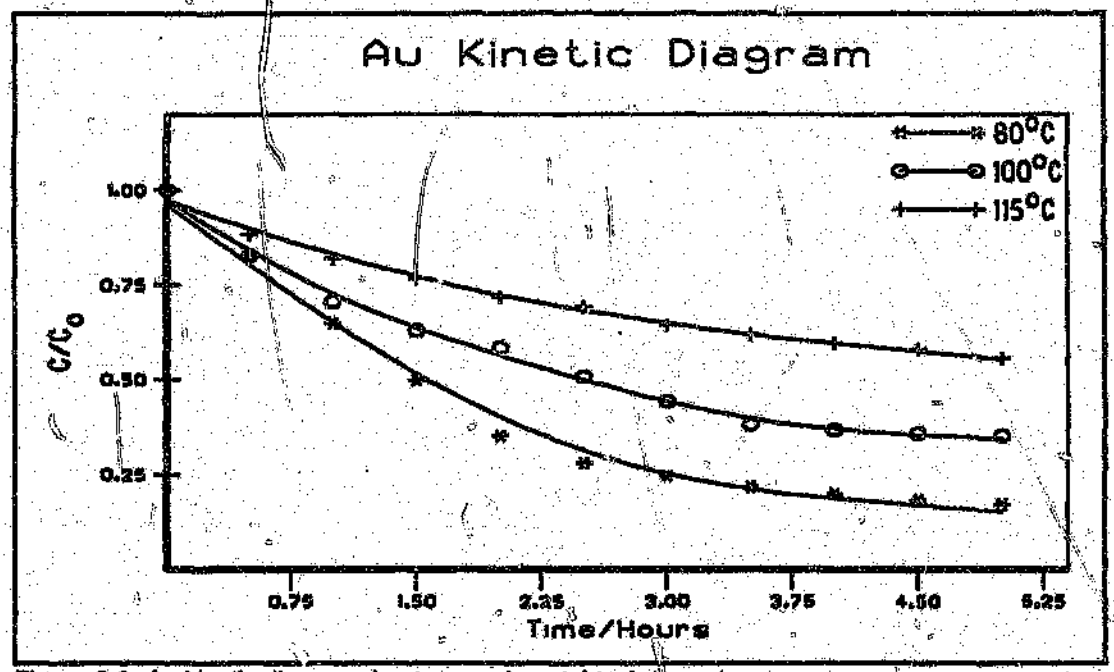


Figure 3.8: Au kinetic diagram due to experimental technique 1.

An equilibrium time of 4 hours was assumed. In the equilibrium experiment different weights of carbon were equilibrated with 50ppm of aurocyanide solution for the equilibrium time. This produced Figure 3.9.

The curves obtained have shown the exothermic nature of the adsorption process. Increase in temperature results in reduction in the amount of gold adsorbed. The curves also show a linear dependence of the equilibrium loading on the concentration. However it is known that the adsorption process (and therefore the elution process) is non-linear even at low equilibrium concentrations[16]. An attempt to fit the data with a linear model: $Q_e = AC_e$ produced intercepts for each temperature. This intercepts were difficult to account for resulting in the need for a more meaningful technique.

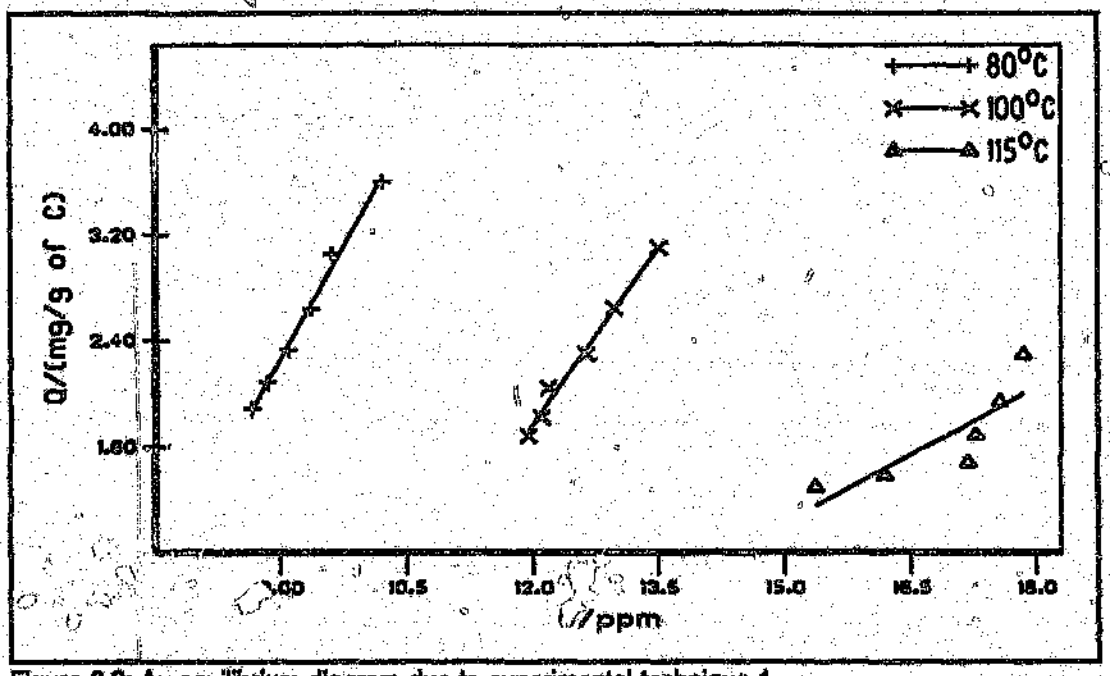


Figure 3.9: Au equilibrium diagram due to experimental technique 1.

3.3.2.2 EXPERIMENTAL TECHNIQUE 2

Kinetic runs similar to the ones performed in Section 3.3.1.3 were done at 80°C. 1.5 litres of aurocyanide solution ranging between 20 and 600ppm was contacted with 15g of carbon each for 10 hours. Samples were taken at regular intervals of 2 hours. Figures 3.10 and 3.11 show the result.

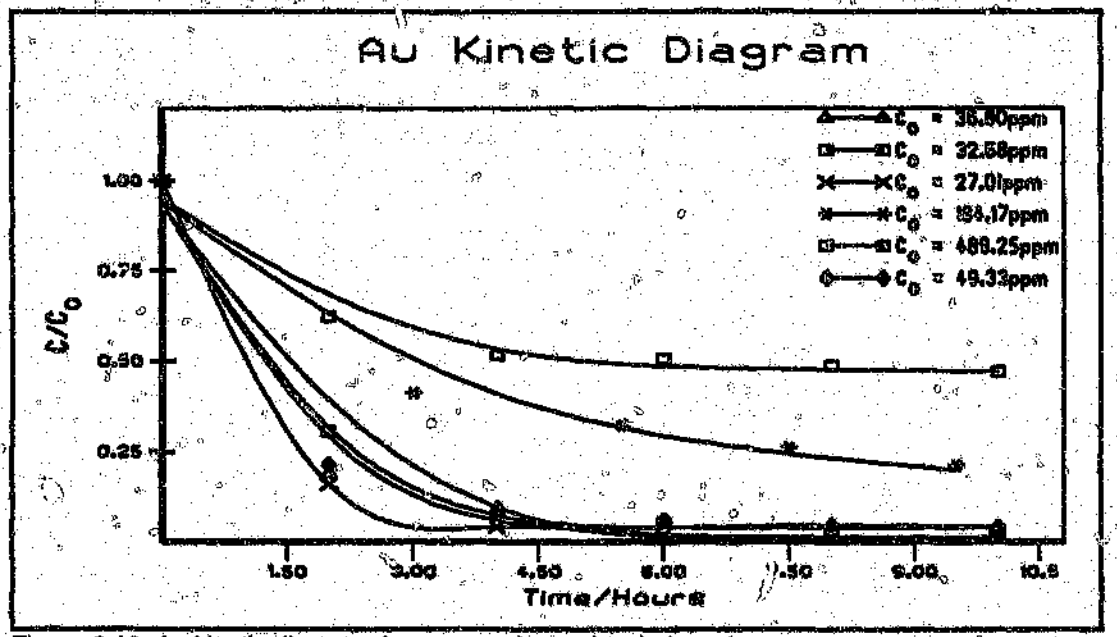


Figure 3.10: Au kinetic diagram due to experimental technique 2.

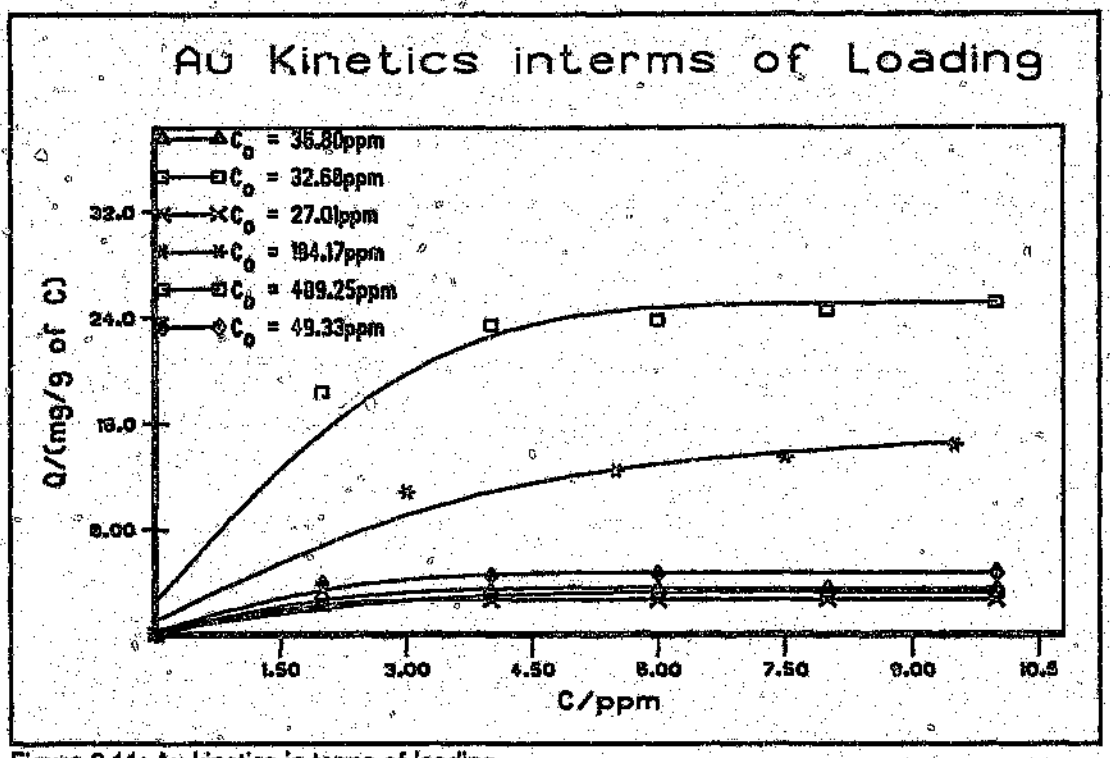


Figure 3.11: Au kinetics in terms of loading.

Unlike the OH^- experiment in Section 3.3.1.3, the rate of adsorption, hence the time for equilibrium, was not sensitive to the initial concentration of the solution. Virtually all the curves seem to have tapered off after 5 hours. There is therefore very little adsorption after 5 hours. Hence in the equilibrium experiment, 5 hours was used as the contact time. The result from the equilibrium work will be discussed in the next chapter.

In the case of multi-solute adsorption of OH^- and Au 5 hours was taken as the equilibrium time. For each experimental run specific concentration levels of OH^- and Au ion in the same solution was used to contact 15g of carbon. The result is discussed in chapter 4.

The choice of equilibrium time has been a "bone of contention" since no consensus has been reached by previous workers on it. Critical analysis of the time of equilibrium used by previous workers revealed that the equilibrium time depends largely on the experimental set-up and the experimental conditions prevailing in the system. For instance Cho et al[17] have assumed equilibrium establishment to be after 3 hours when working at temperatures between 25 and 70°C in a CSTR experimental set-up. Nicol et al[12] have shown that equilibrium is not established between gold on

carbon and that in solution after several weeks of contact time when they isolated the carbon in a basket on a plant. Van Deventer[16] working on synthetic solution in a CSTR has shown that a kind of pseudo-equilibrium is established after 3 weeks. He further showed that the adsorption isotherms obtained for equilibrium time of 3 weeks and that of 5 weeks were the same. These experiments were done at normal temperatures. Hence Van der Merwe[19] in his work on elution used 3 weeks as his equilibrium time working in a batch STR at temperatures between 25 and 70°C. Fuerstenau et al[20] assumed that for a low gold concentration in solution and high carbon dosage 2 hours could be taken as equilibrium time.

From the above discussion it could be seen that the equilibrium times selected for the experiments in this work are justified. This is because the experiments were performed at temperatures between 80 and 120°C as compared to the works done previously and it has been known that temperature greatly inhibits adsorption, (which implies that temperature tends to accelerate equilibrium). In effect keeping the experiment running for times longer than the one selected would not have yielded any better result than what was obtained.

3.4 CONCLUSION

A search for an appropriate experimental technique has been made and this yielded the fact that:

1. the equilibrium attainment of OH^- depends on the initial concentration of the solution, the higher the concentration the faster the establishment of equilibrium, vice versa,
2. initial concentration does not affect the equilibrium attainment of gold such that there is an appreciable equilibrium attainment after 5 hours.

Based on these facts, equilibrium experiments were performed for the single and multi solute adsorption of OH^- and Au. The outcome of these experiments will be discussed in the next Chapter.

CHAPTER 4

MODELLING OF THE SINGLE AND MULTI-SOLUTE EQUILIBRIUM DATA

CHAPTER 4

MODELLING OF SINGLE AND MULTI-SOLUTE EQUILIBRIUM DATA

This chapter deals with modelling of the single and the multi-solute equilibrium adsorption data of OH^- and Au respectively.

There are two main models that can be used to describe an experimental data, these are:

1. Theoretical, Conceptual or Mechanistic Model and
2. Empirical Model.

Theoretical models are generally used when the phenomenon under study is well understood such that it is possible to write it down in a plausible functional form. The required physical laws are often expressed by differential equations and the parameters are non-linear. When the mechanism underlying a process is not understood sufficiently well or it is too complicated to allow an exact model to be postulated from the theory, empirical models are useful.

Theoretical models are more favoured in their applicability than empirical models as they are supported by basic principles. They can therefore be used to predict a response over a wider region than is possible with purely empirical functions. Empirical models are therefore limited in the immediate region of study, hence they provide shaky basis of extrapolation. Despite this disadvantage, empirical models can provide basis for understanding the basic factors affecting the system. Hence they could be used as a springboard to the development of a significant theoretical model.

4.1 EQUILIBRIUM ISOTHERMS - EXAMINATION OF THE MODELS

An equilibrium isotherm is a mathematical expression relating the concentration of the adsorbate in the liquid phase with the concentration of the adsorbate on the adsorbent at constant temperature.

Care must be taken regarding the interpretation given to the ability for a particular isotherm to fit experimental data. The various isotherms have been developed based on fundamental assumptions

regarding the nature of the adsorption system so as to give the equation a theoretical basis. But these assumptions may not hold for a complex, heterogeneous system like the activated carbon-aurocyanide system. Hence, the equations listed below must be treated as empirical or "fitting" models with the various parameters determined from regression on data sets rather than by independent measurements of fundamental parameters. Therefore if a particular equation fits a set of data well, it should not be concluded that the theoretical basis on which the model has been developed applies to the system in question, but rather the equation is a good empirical model for that data set.

4.1.1 Single-component equilibrium isotherms

The most commonly used isotherms for single component solutes are as follows:

1. Linear Isotherm,

$$Q_e = A C_e$$

2. Langmuir Isotherm,

$$Q_e = \{A C_e\} / \{B + C_e\}$$

3. Freundlich Isotherm,

$$Q_e = A C_e^N$$

OR $$C_e = a Q_e^n$$

Note: $a = (1/A)^{1/N}$ and $n = 1/N$

Q_e = Equilibrium Loading (g / t of C)

C_e = Equilibrium Concentration (ppm)

The linear isotherm has been used by Nicol et al[12] to describe the adsorption of gold onto activated carbon and it was based on the assumption that the isotherm can be used at low concentrations. But as indicated earlier, experimental measurements have shown that gold adsorption is non-linear at low concentrations[10].

The Langmuir isotherm is based on the assumption of mono-layer adsorption on a fixed number of equivalent sites and no interaction between adsorbed molecules. At low concentrations therefore, the Langmuir isotherm reduces to a linear form. A few workers have however used it to describe the adsorption of gold and silver onto activated carbon[21,22].

The Freundlich isotherm is based on the assumption that the adsorption energy obeys an exponential distribution. Though the Freundlich isotherm often represents experimental data better than the Langmuir isotherm it does not reduce to Henry's law at concentrations approaching zero. Despite this disadvantage several workers have however used the isotherm to describe experimental data for adsorption[18,19,23,24].

The popular Freundlich isotherm, $Q = A C^{n}$, has been applied to experimental data obtained for the single component adsorption of both gold and hydroxide. But, as will be discussed later, the application of the Freundlich isotherm results in the estimation of as much as six different parameters for the three temperatures studied. To reduce the number of parameters the Freundlich isotherm was modified to include the temperature dependency of the pre-exponent parameter A. This modification therefore reduced the number of parameters to be estimated for the three temperatures to only three. Below is the discussion of the theoretical basis upon which the modification has been done.

The relationship between the change in the free energy of a reaction, ΔG, and the equilibrium constant K is given as:

$$\ln K = \frac{-\Delta G}{R*T} \qquad 4.1$$

Hence the variation of ln K with temperature T is:

$$\frac{\partial \ln K}{\partial T} = \frac{-1}{R} * \frac{\partial \left(\frac{\Delta G}{T}\right)}{\partial T} \qquad 4.2$$

where R = Gas constant.

Assuming that ΔH is the change in the enthalpy of the reaction, then the relationship between ΔG and ΔH is

$$\frac{\partial \left(\frac{\Delta G}{T}\right)}{\partial T} = -\frac{\Delta H}{T^2} \qquad 4.3$$

Substituting Equation 4.3 into 4.2 yields the *Van't Hoff Isochore*:

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{R * T^2}$$

The above equation implies that

$$\partial \ln K = \frac{\Delta H}{R * T^2} \partial T \qquad 4.4$$

Therefore integrating equation 4.4 yields:

$$\ln K = \frac{-\Delta H}{R * T} + \beta$$

where β is a constant of integration.

Assuming further that the equilibrium constant K is given as

$$K = \frac{Q}{C^n}$$

where,

Q = Equilibrium loading of the solute on the adsorbent,

C = Equilibrium concentration of the solute in solution and

n = Parameter to be estimated by non linear regression.

Then it could be written that

$$\frac{Q}{C^n} = EXP\left(\frac{-\Delta H}{R*T} + \beta\right)$$

Such that

$$Q = A_0 EXP\frac{-\Delta H}{R*T} C^n \qquad 4.5$$

The above equation is therefore the Modified Freundlich Isotherm (called MFI in this work). With this modification the parameters ΔH, A_o and n can be determined by non-linear regression using experimental data generated for all the three temperatures considered. The estimation of the enthalpy change of the reaction gives an idea of whether the adsorption reaction is physisorption or chemisorption since the enthalpy change is a measure of the bond strength established during the reaction.

The third model used is the linearized form of the modified Freundlich isotherm (LMFI) which is given below:

$$\ln Q = B_0 + \frac{B_1}{R*T} + B_2 \ln C \qquad 4.6$$

4.1.2 Multi-component Isotherms

Single solute isotherm parameters are often used in multi-solute isotherms. The general idea is to first measure and model single solute isotherms. The parameters obtained are then used to model the multi-solute case.

a. Freundlich-type isotherm.

Sheindorf et al[28] have modified the Freundlich isotherm to describe a multi-component system such that for an N-component system,

$$Q_i = A_i C_i \left(C_i + \sum_{k=1 \neq i}^{N} a_{i,k} C_k\right)^{n_i - 1} \qquad 4.7$$

where,

Q_i = Equilibrium loading of component i,

C_i = Equilibrium solution concentration of component i,

A_i = Single soluto pre-exponent parameter of component i,

n_i = Single solute exponent parameter of component i,

C_k = Equilibrium concentration of component k, and

$a_{i,k}$ = An interactive parameter of component k on component i adsorption or a competition coefficient of component k in the multi-component system.

The above equation has been used by Van Deventer[16] to model the simultaneous adsorption of gold and silver cyanide complexes.

Applying the modification made to account for the temperature dependency of the pre-exponent parameter of the Freundlich isotherm in the previous section and considering a two component system for gold and hydroxide ion we have the following two equations:

$$Q_{Au} = A_{Au} EXP\left[\frac{-\Delta H_{Au}}{R*T}\right] C_{Au} \left(C_{Au} + a_{Au,OH} C_{OH}\right)^{n_{Au}-1} \qquad 4.8$$

and

$$Q_{OH} = A_{OH} EXP\left[\frac{-\Delta H_{OH}}{R*T}\right] C_{OH} \left(C_{OH} + a_{OH,Au} C_{Au}\right)^{n_{OH}-1} \qquad 4.9$$

From these two equations it implies that only the multi-component system competition coefficients $a_{Au,OH}$ and $a_{OH,Au}$ respectively need to be estimated using non-linear regression multi-solute data.

b. General empirical multi-solute isotherm.

Fritz et al[29] also developed a general empirical multi-component isotherm such that for an N-component system,

$$Q_i = \frac{A_i C_i^{n_i}}{D_i + \sum_{j=1}^{N} a_{ij} C_j^{b_{ij}}} \qquad 4.10$$

where,

Q_i, C_i, A_i and n_i have the same meaning as defined above in Equation 4.7, and

D_i, a_{ij} and b_{ij} are parameters to be determined using non-linear regression.

Several modifications of the model could be derived by appropriate adjustment of the model parameters. For instance, if $n_i=b_{ij}=D_i=1$, the relationship above in Equation 4.10 becomes the Langmuir equation

$$Q_i = \frac{A_i C_i}{1 + \sum_{j=1}^{N} a_j C_j}$$

which has been used by many workers. Le Roux[30] and Young et al[31] used another modified form of the above equation to fit data obtained for the simultaneous adsorption of aurocyanide and xanthate onto carbon. While Glover[32] and Young et al[33] in another publication used another modified version to fit data obtained for the simultaneous adsorption of aurocyanide and zinc cyanide complexes onto strong base anion exchange resin. For a two-component system like the one being considered we have the following two equations to be fitted:

$$Q_{Au} = \frac{A_{Au} C_{Au}^{b_{Au}}}{D_{Au} + a_{Au,Au} C_{Au}^{b_{Au,Au}} + a_{Au,OH} C_{OH}^{b_{Au,OH}}} \qquad 4.11$$

and

$$Q_{OH} = \frac{A_{OH}\, C_{OH}^{n_{OH}}}{D_{OH} + a_{OH,OH} C_{OH}^{b_{OH,OH}} + a_{OH,Au} C_{Au}^{b_{OH,Au}}} \qquad 4.12$$

The following parameters are then to be determined for Au and OH^- data respectively: $a_{Au,Au}$, $a_{OH,OH}$, $b_{Au,Au}$, $b_{OH,OH}$, D_{Au}, D_{OH}, $a_{OH,Au}$, $a_{Au,OH}$, $b_{Au,OH}$, and $b_{OH,Au}$. The modification made in the section above for the parameter A was then substituted into the equation to account for the temperature effect.

4.2 APPLICATION OF THE MODELS

4.2.1. Single component system.

The experimental data obtained for the single solute adsorption of Au and OH^- respectively have conformed to the exothermic nature of the adsorption process. As temperature increases the amount of solute adsorbed decreases as seen in Figures 4.1 and 4.2. The data is presented in Appendix 2.

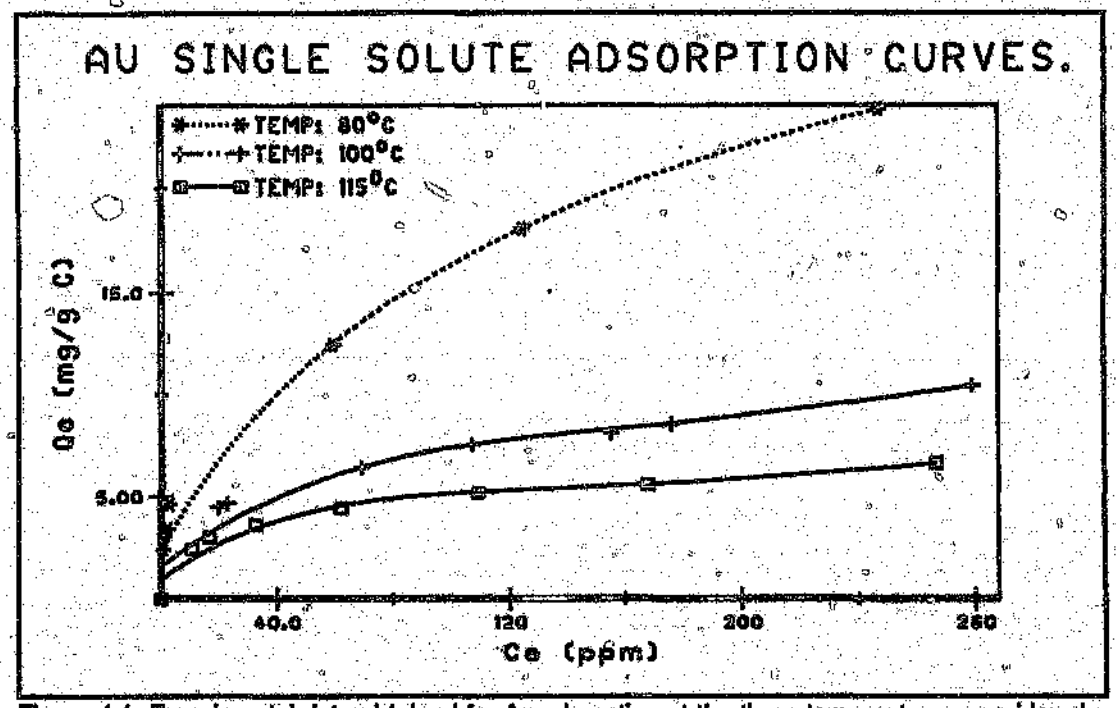


Figure 4.1: Experimental data obtained for Au adsorption at the three temperatures considered.

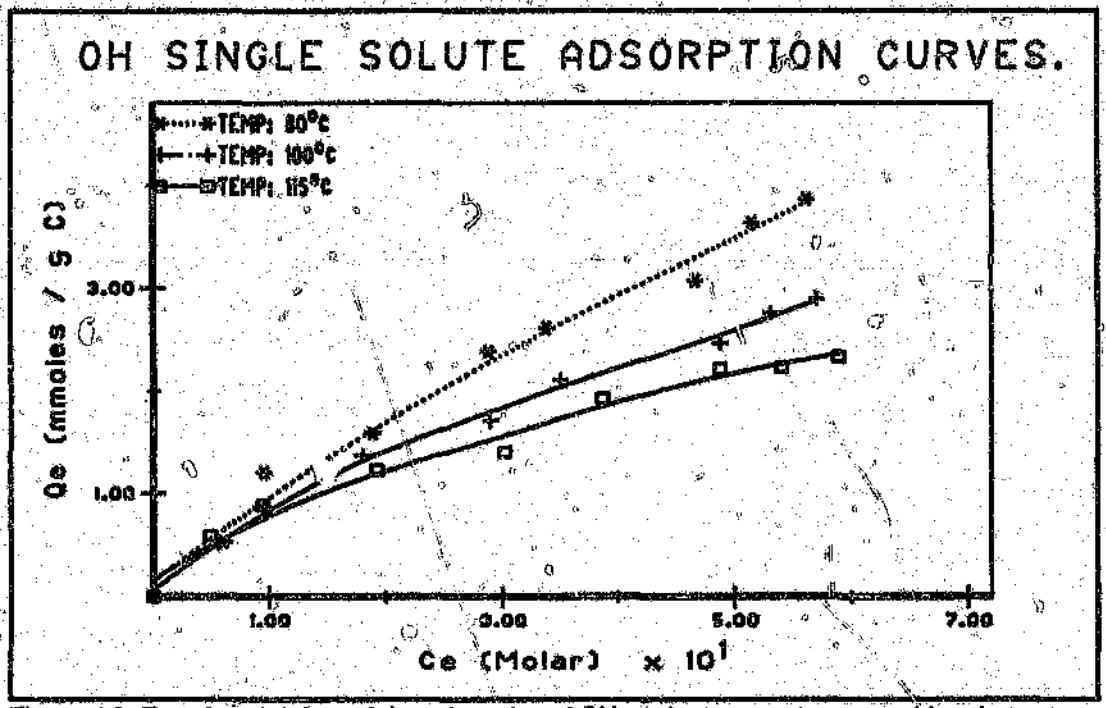


Figure 4.2: Experimental data of the adsorption of OH^- at the temperatures considered.

The experimental data was fitted to the Freundlich Isotherm, the Modified Freundlich Isotherm MFI and the Linearized form of the MFI using the SAS Non-Linear Regression Subroutine[34]. The Freundlich Isotherm yields the following parameters as shown in Table 2.

Table 4.1: Parameters obtained using the Freundlich Isotherm and their Correlation Coefficients (R).

AU				OH^-		
T/°C	A/[(mg/g C)/ppm]$^{1/n}$	n	R	A/[(mmoles/g C)/ M]$^{1/n}$	n	R
80	2.9866	0.3675	0.9959	6.2363	0.8114	0.9712
100	1.7383	0.3108	0.9951	4.3319	0.7145	0.9934
115	1.2520	0.2920	0.9929	3.1267	0.5604	0.9897

Tables 4.2 and 4.3 give the parameters obtained for the MFI and LMFI respectively.

Table 4.2: Parameters obtained for the MFI and their Correlation Coefficients (R).

PARAMETERS	Au	OH^-
A_J/[(mg/g C)/(mg/l)]$^{1/n}$ * [mole/Joules]	1.4239E-6	3.5305E-2
-ΔH/(Joules/mole)	4.2627E4	1.4855E4
n	0.3770	0.6984
R	0.9888	0.9833

From Tables 4.1 and 4.2 it can be seen that the parameter *n* from both isotherms (is FI and MFI) is less than one for each solute. It could therefore be concluded that the equilibrium isotherm for each solute is favourable.

Table 4.3: Parameters obtained for the LMFI and their Correlation Coefficients (R).

PARAMETERS	Au	OH^-
B_0	-12.6245	-2.1634
B_1	-4.0125E4	-1.1188E4
B_2	0.3749	0.3174
R	0.9664	0.9708

Below are the figures obtained.

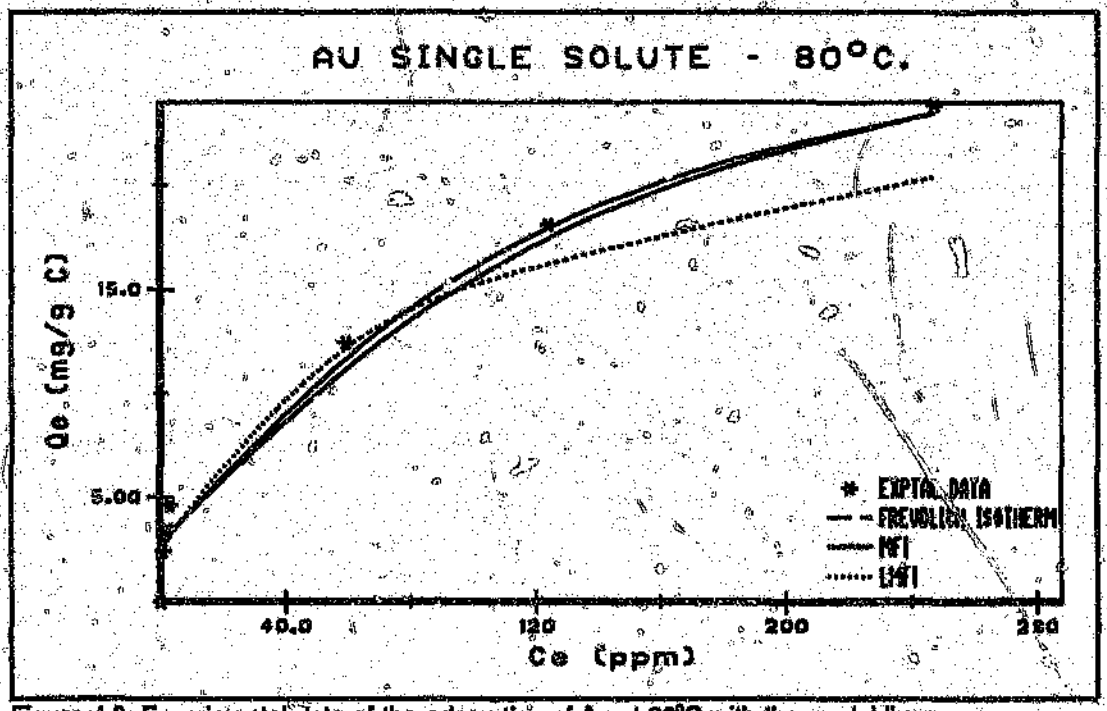


Figure 4.3: Experimental data of the adsorption of Au at 80°C with the model lines.

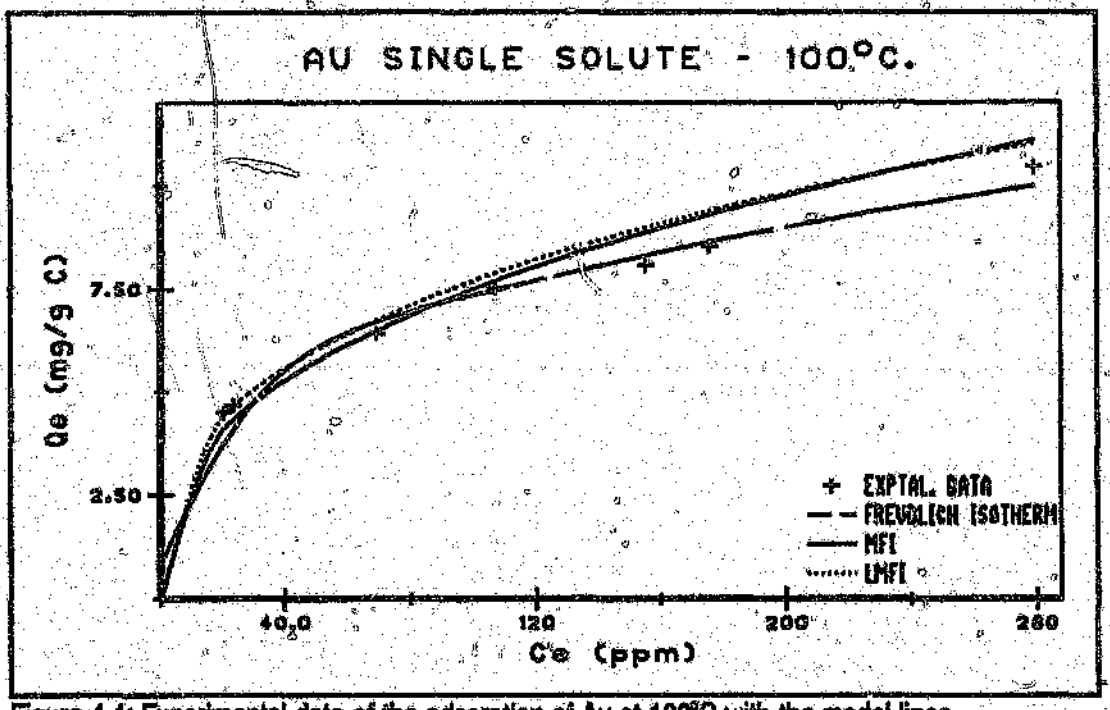


Figure 4.4: Experimental data of the adsorption of Au at 100°C with the model lines.

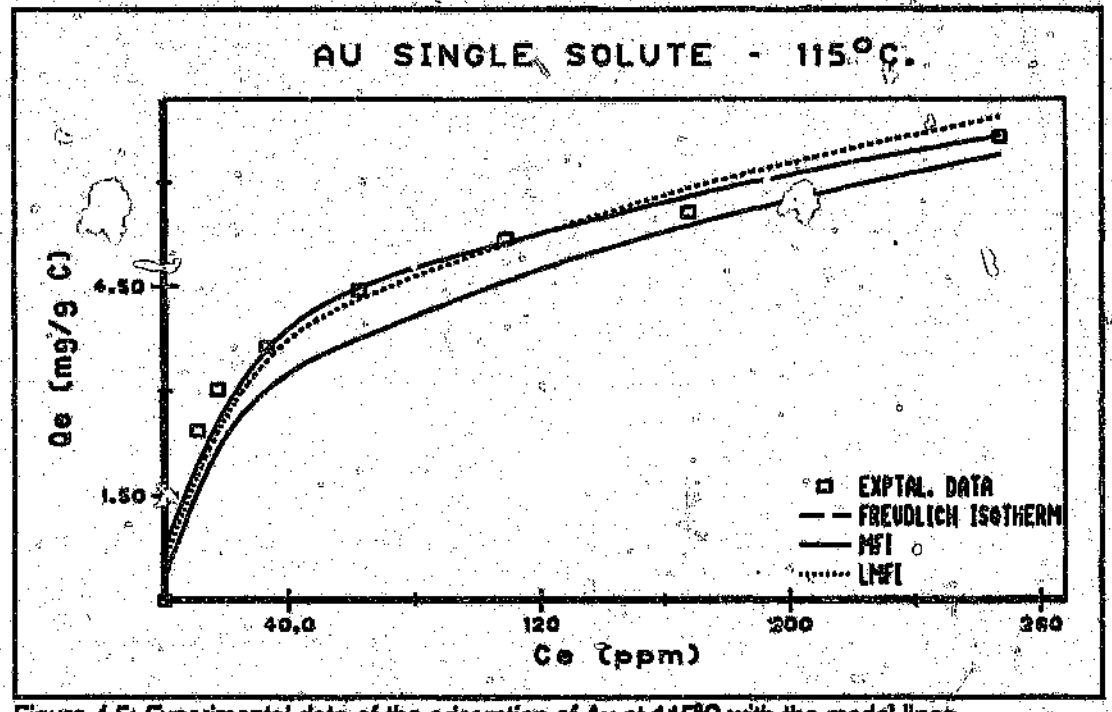


Figure 4.5: Experimental data of the adsorption of Au at 115°C with the model lines.

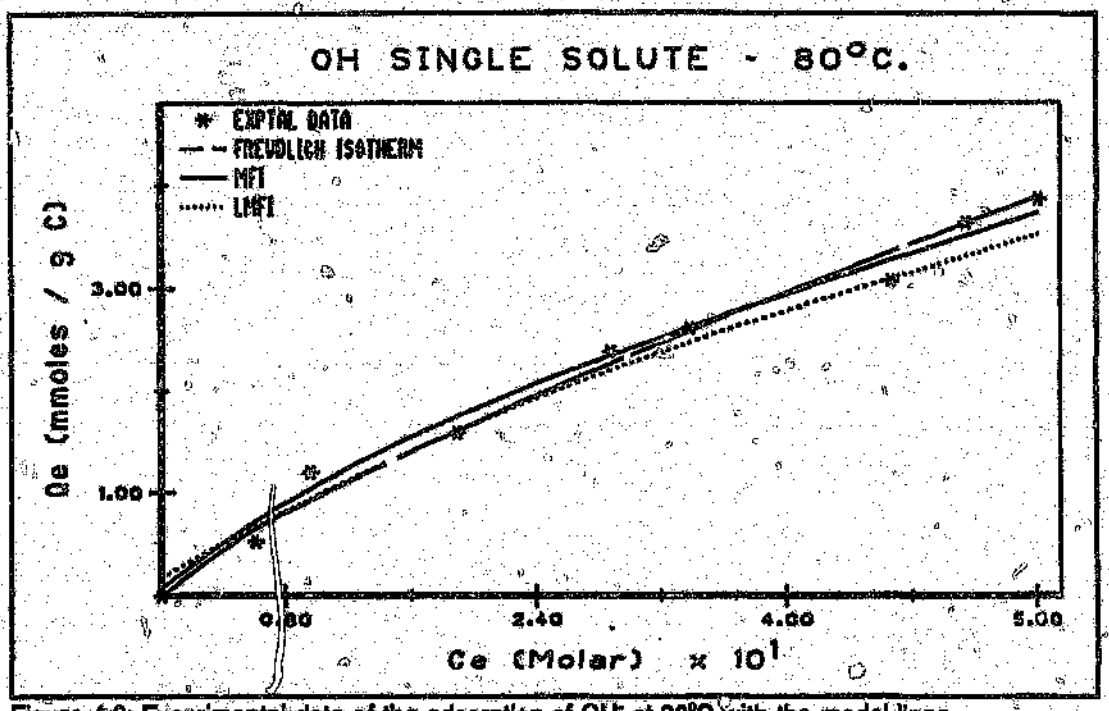


Figure 4.6: Experimental data of the adsorption of OH^- at 80°C with the model lines.

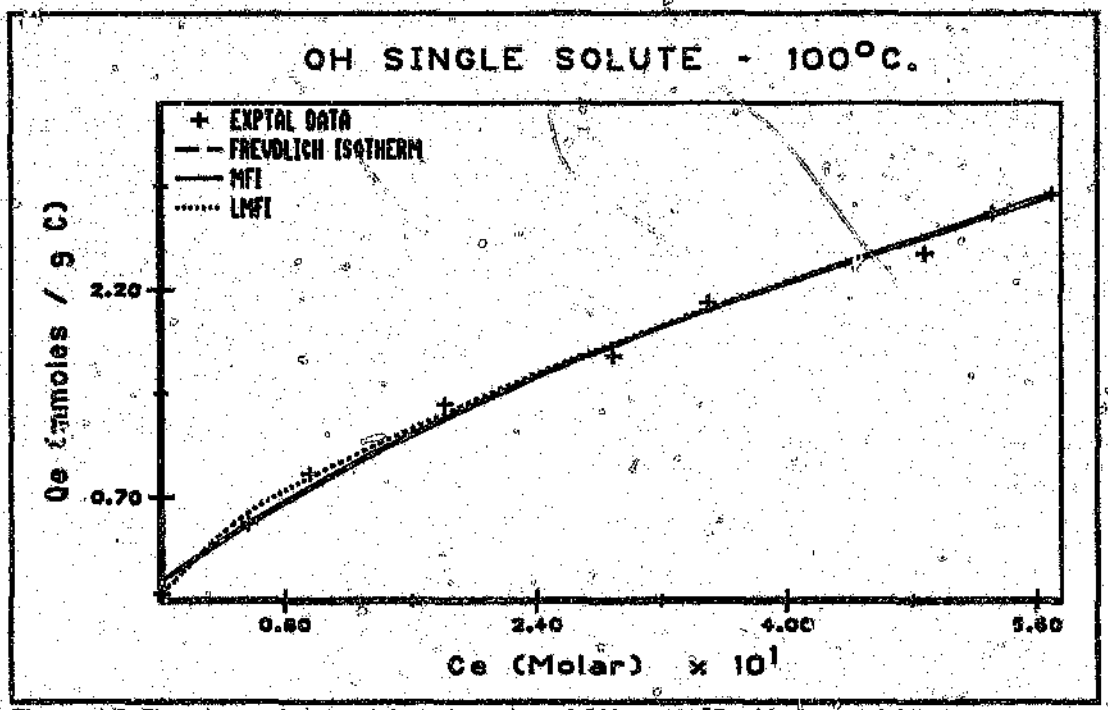


Figure 4.7: Experimental data of the adsorption of OH^- at 100°C with the model lines.

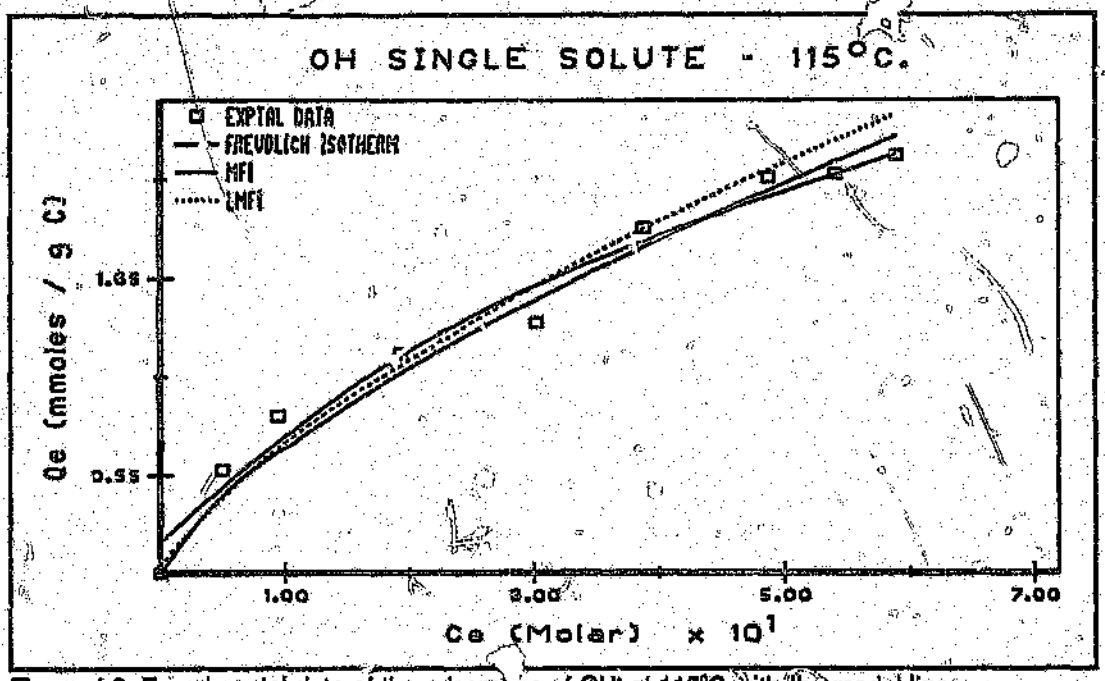


Figure 4.8: Experimental data of the adsorption of OH⁻ at 115°C with the model lines.

4.2.2 Multi-component system modelling.

The result obtained is shown below in Figures 4.9 and 4.10 and the data appears in Appendix 2.

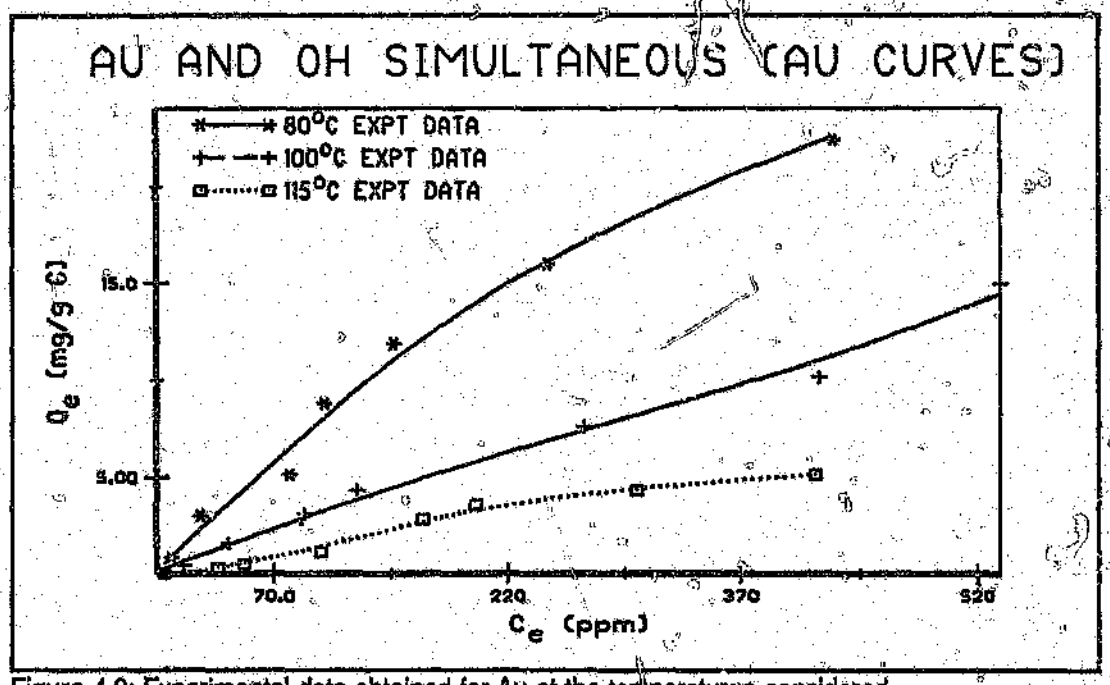


Figure 4.9: Experimental data obtained for Au at the temperatures considered.

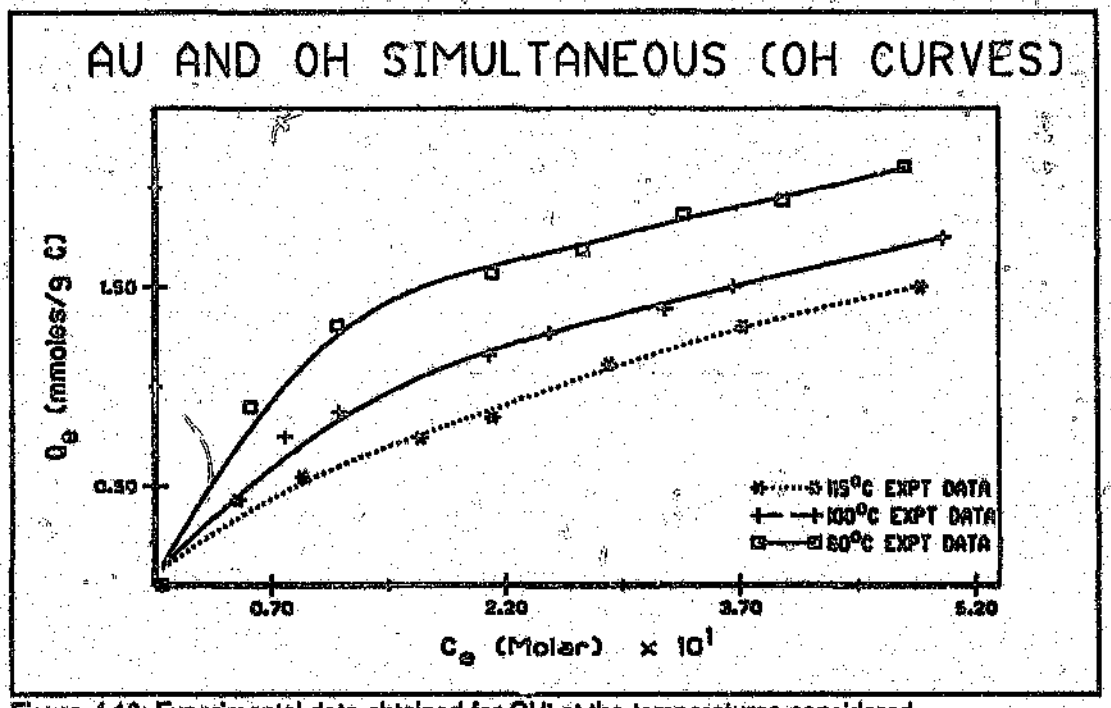


Figure 4.10: Experimental data obtained for OH^- at the temperatures considered.

The gold isotherms show a wider deviation with respect to temperature as compared to the hydroxide ion isotherms. This is due to reactions between the OH^- ion and some of the phenolic groups on the surface of the carbon structure[6].

Adams[3] has shown that the resultant effect is an increase in the effective dielectric constant within the pores of the carbon as well as formation of hydrophillic negatively charged surface. There is therefore a decrease in the affinity for neutral species as well as anions such as $Au(CN)_2^-$. Coupling this effect to the temperature effects as a result of the exothermic nature of the adsorption reaction, it is not surprising that such a wide deviation has been experienced. Apart from this factor both components have clearly shown an inverse adsorption dependence on temperature since the adsorption reaction is exothermic.

Comparison between the multi-component adsorption and the single component adsorption isotherms have been made and this has been presented in Appendix 5 (samples are shown below in Figures 4.11 and 4.12). The general trend is that the multi-component isotherms for each component and temperature have been found to lie below the single component ones. This could

be probably be due to the reduction in the adsorption capacity for the carbon for each component in the presence of the other.

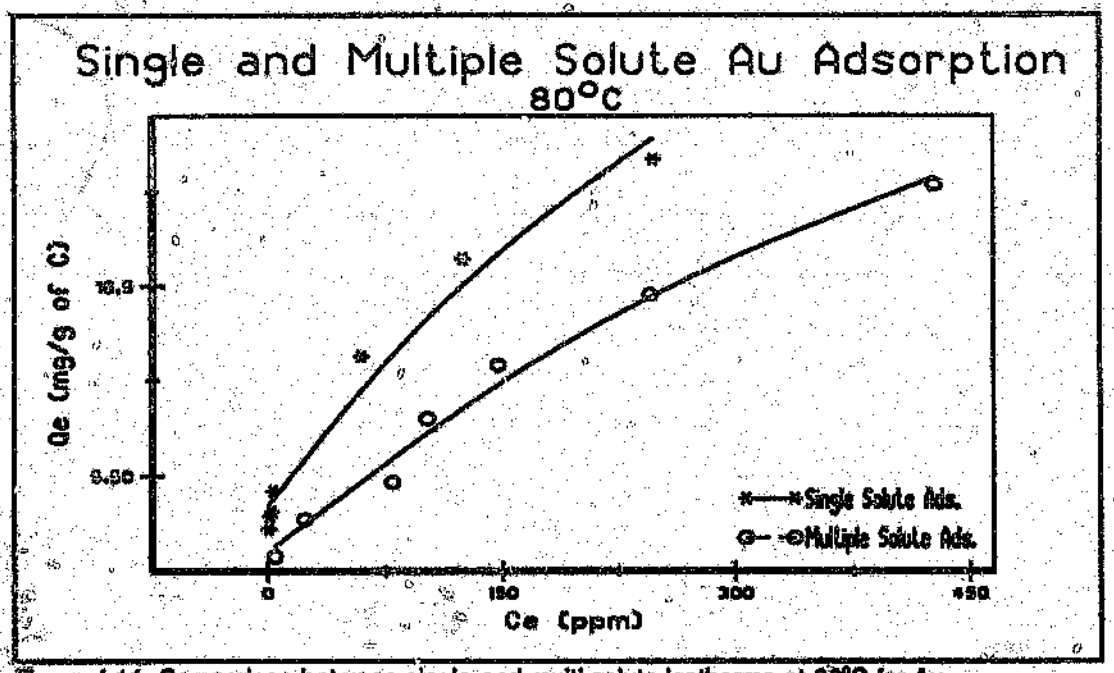


Figure 4.11: Comparison between single and multi-solute isotherms at 80°C for Au.

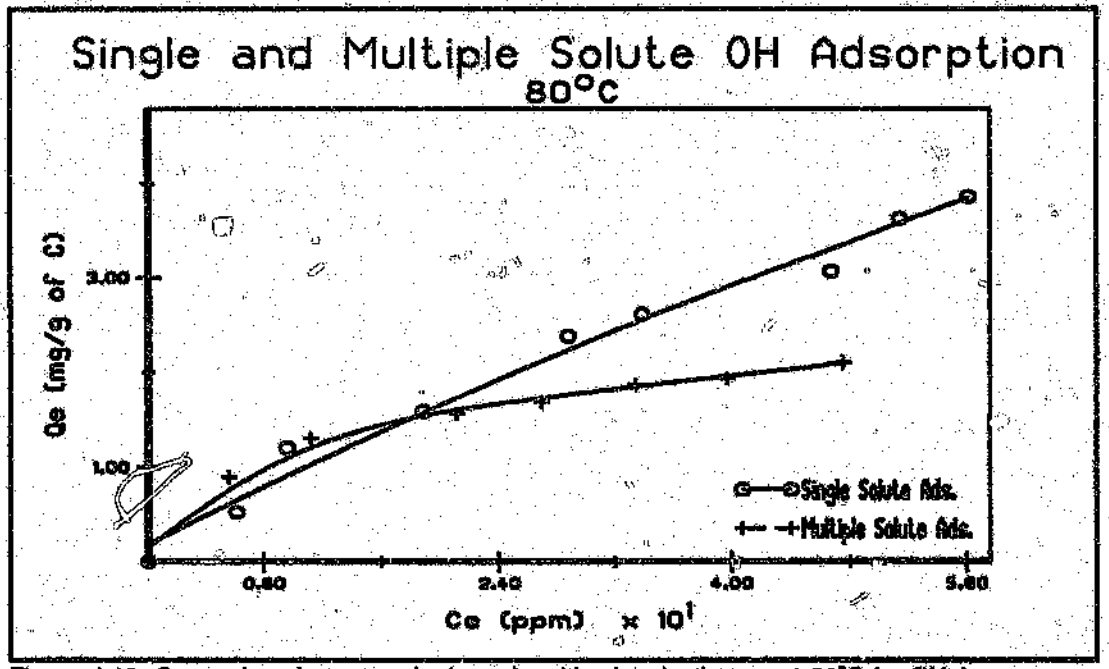


Figure 4.12: Comparison between single and multi-solute isotherms at 80°C for OH^- ion.

The two models described above were applied to the multi-component experimental data by estimation of the unknown parameters using the SAS Non-Linear Regression Sub-Routine[34].

Model 1 is the application of Equations 4.8 and 4.9 with the estimation of only $a_{i,k}$. The values of A_i, ΔH_i and n_i values obtained from single component data (Table 3) were substituted into the equations before the parameter estimation. After parameter estimation the following equations were obtained:

$$Q_{Au} = \frac{1.42x10^{-6}EXP\left(\frac{4.26x10^4}{R*T}\right)C_{Au}}{[C_{Au}+6.22x10^2C_{OH}]^{0.62}}$$

and

$$Q_{OH} = \frac{3.53x10^{-2}EXP\left(\frac{1.49x10^4}{R*T}\right)C_{OH}}{[C_{OH}+2.90x10^{-3}C_{Au}]^{0.30}}$$

Model 2 is the application of the Fritz et al[23] equation from Equations 4.11 and 4.12 with the single component parameters substituted from Table 3 before the determination of other unknown parameters to yield (ie after parameter estimation):

$$Q_{Au} = \frac{1.42x10^{-6}EXP\left(\frac{4.26x10^4}{R*T}\right)C_{Au}^{0.38}}{[-23.84+27.34C_{Au}^{0.02}+0.03C_{OH}^{-1.83}]}$$

and

$$Q_{OH} = \frac{3.53x10^{-2}EXP\left(\frac{1.49x10^4}{R*T}\right)C_{OH}^{0.70}}{[-4.93+5.80C_{OH}^{0.03}+0.37C_{Au}^{0.12}]}$$

These equations were used to fit the experimental data. The results obtained for each component are shown below.

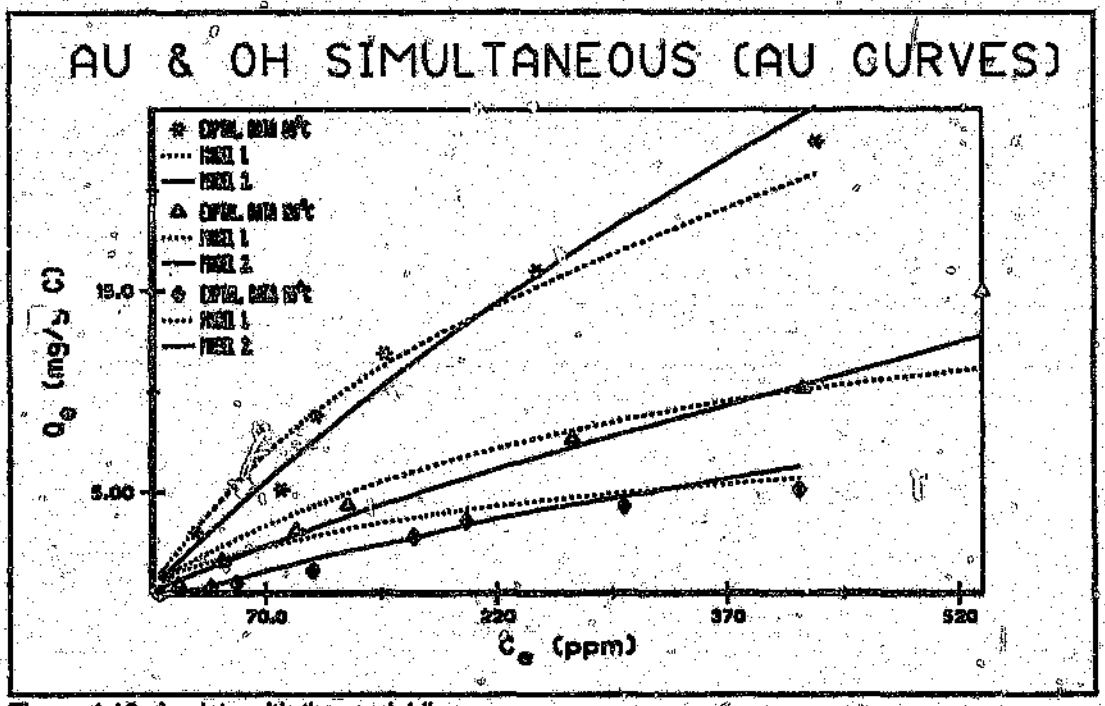


Figure 4.13: Au data with the model lines.

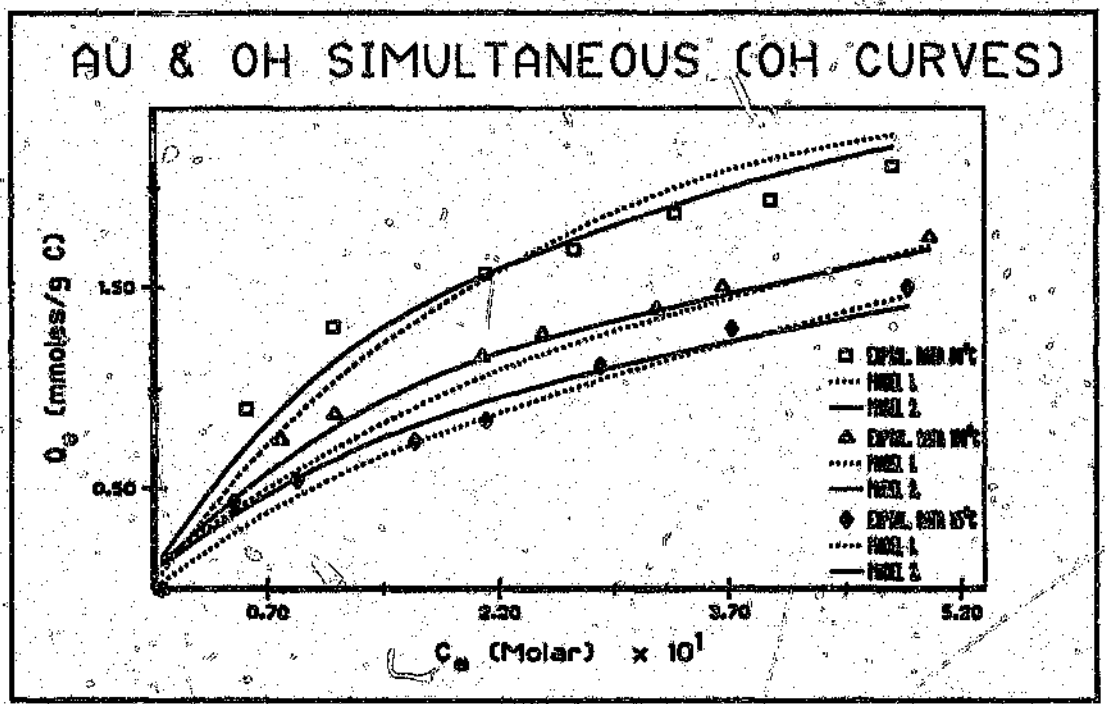


Figure 4.14: OH data with the model lines.

4.3 STATISTICAL DISCRIMINATION BETWEEN THE MODELS

Many workers use the plot of the predicted value against the observed value as the measure to discriminate between models. In this work the above plots have been made as shown below.

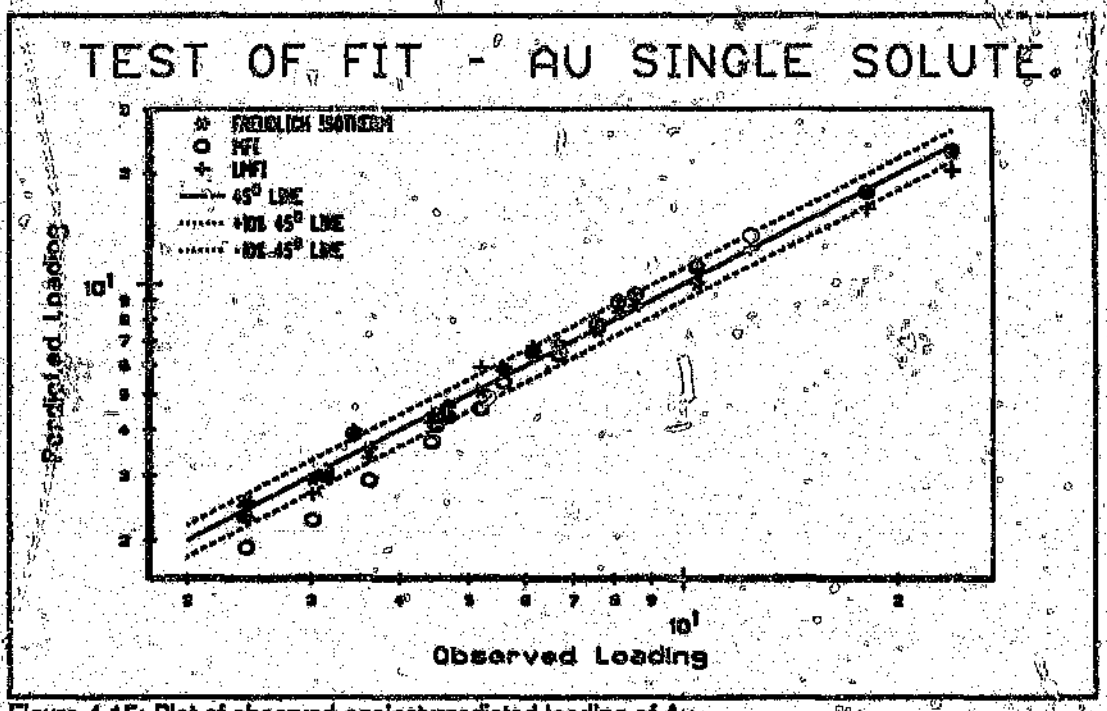


Figure 4.15: Plot of observed against predicted loading of Au

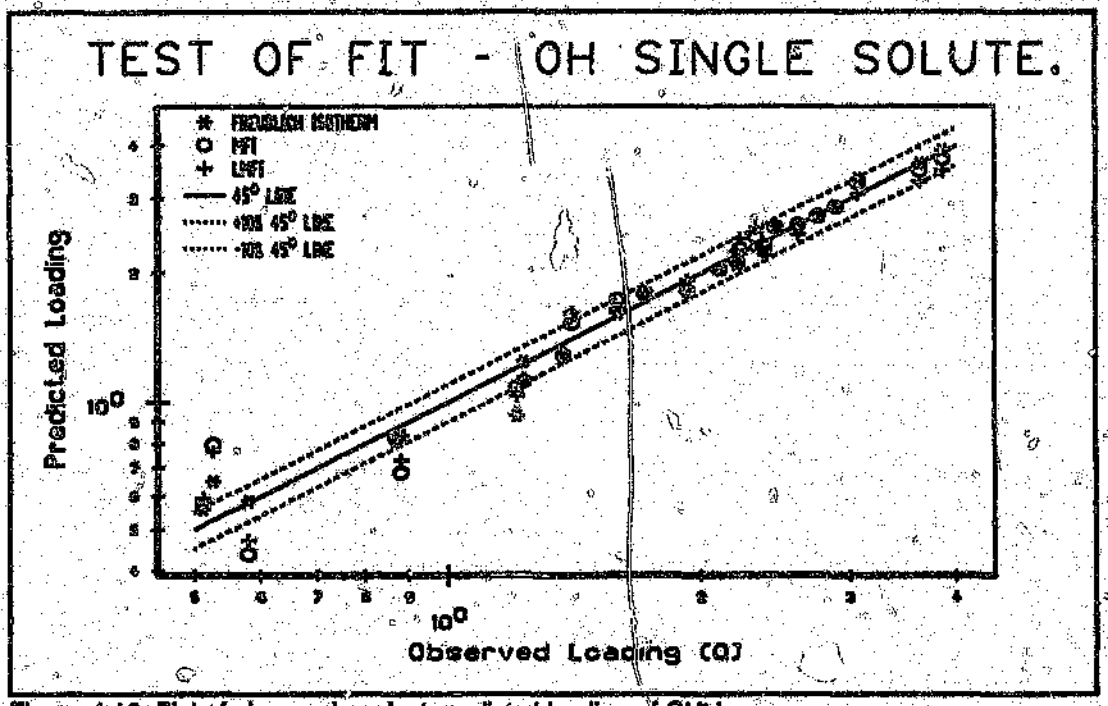


Figure 4.16: Plot of observed against predicted loading of OH^- ion.

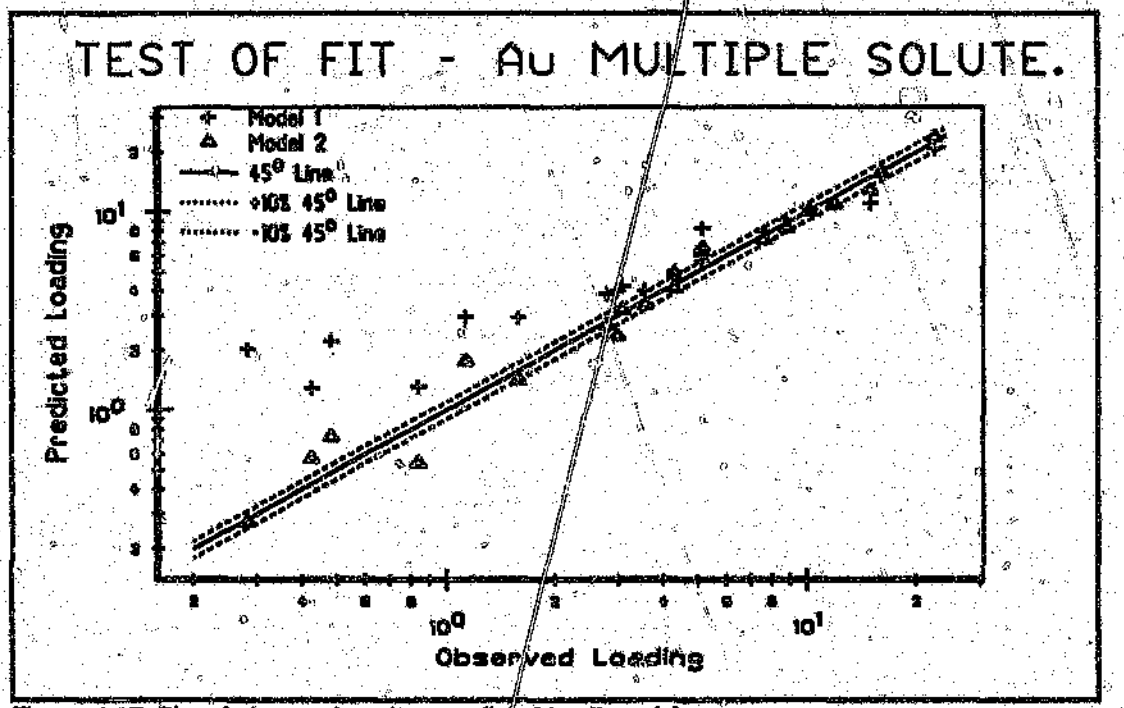


Figure 4.17: Plot of observed against predicted loading of Au.

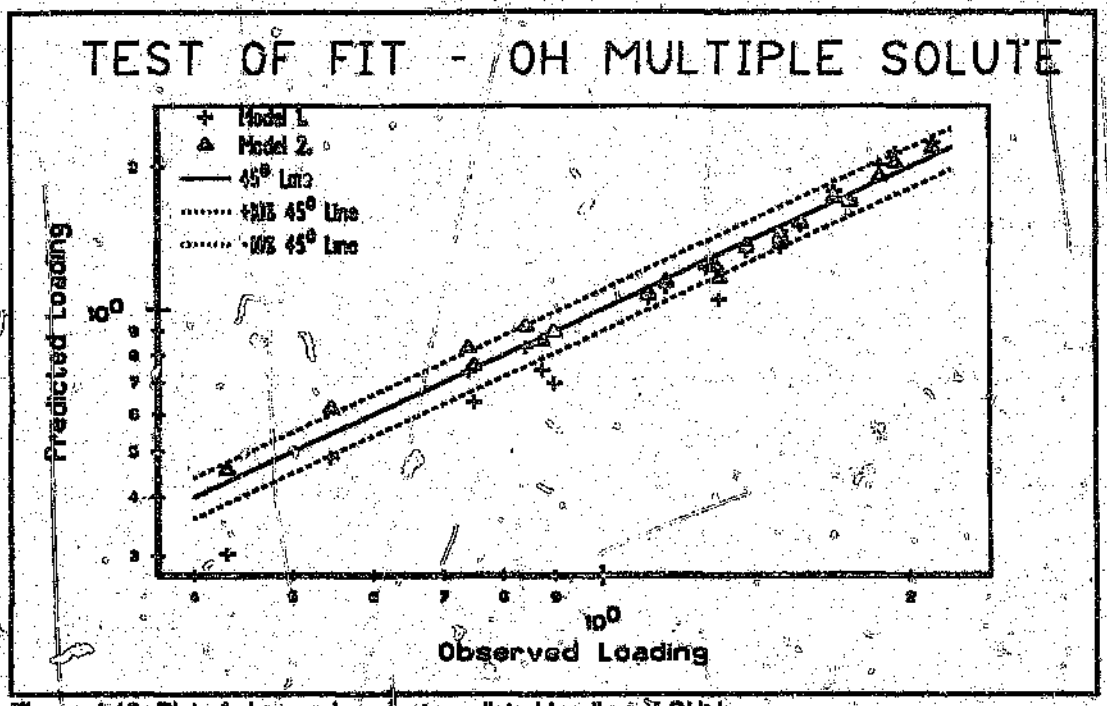


Figure 4.18: Plot of observed against predicted loading of OH^- ion.

A glance at the plots for the single solute adsorption set of experiments revealed that the Freundlich isotherm predictions seems to be better than that of MFI and LMFI (single component models). This seems to be confirmed by the sums of squares of the residuals obtained for the isotherms as seen from Table 4.4. One of the interesting points is the way LMFI does not fit the data especially at high loadings (see Figure 4.3). This is a result of logarithmic transformation and this shows that this is not a good approach even though it makes fitting much easier.

Table 4.4: Table showing the models and their respective variables [single-solute].

	Au		OH^-	
M	S	m	S	m
FI	3.5930	6	0.2883	6
MFI	6.4478	3	0.3447	3
LMFI	19.4066	3	0.6023	3

Note: S = Sum of Squares of the residuals.

m = Number of parameters estimated.

In the case of the multiple-solute adsorption good fits have been obtained and it seems that Model 2 is better than Model 1 as shown by Figures 4.17 and 4.18.

Statistically, this is not an acceptable way of comparing models. This is because the models do not have the same number of parameters and hence do not possess the same degree of freedom. Comparing them on the basis of the sum of squares of the residuals alone may be misleading. Two statistical methods have therefore been employed to perform this comparison in a more rigorous manner.

a. Method 1.

Moys and King[11] have used a simple statistical analysis for comparing models and this method has been discussed and employed in this work.

Assume that we have models A and B such that A has m_A number of parameters while B has m_B parameters to be estimated. If m_B is less than m_A then a value λ_{AB} could be determined as

$$\lambda_{AB} = \frac{(S_B - S_A) / (m_A - m_B)}{S_A / (N - m_A)}$$

where,

S_A = Sum of squares of the residuals due to model A

S_B = Sum of squares of the residuals due to model B

and N = Number of experimental points involved in the modelling (For Au N=21 while N=24 for OH^- for the single solute data).

Supposing that λ_{AB} is less than $F(m_A - m_B, N - m_A)$ at say 95% confidence level, then the fit of model B is more significant than that of model A.

The above test is strictly exact for linear models but it gives a very good basis for comparison of

the models in this particular work also. The test was therefore carried out between the FI and MFI and between FI and LMFI. MFI and LMFI have the same number of parameters therefore they could be compared on the basis of the sum of squares of the residuals. Below shows the values obtained and the F values obtained from tables.

From the Table it can be concluded that the MFI is a better model statistically than FI at both 95 and 99% confidence levels for the adsorption of OH^- while MFI is better than FI for the adsorption of Au at only the 99% level.

Table 4.5: Table showing the calculated λ values and the F table readings at 95 and 99% confidence levels.

COMPARISON	λ_{Au}	λ_{OH^-}
FI & MFI	3.86	1.18
FI & LMFI	6.81	6.54
F TABLE VALUE	**Au**	**OH^-**
95%	3.29	3.16
99%	5.42	5.09

Similar calculations were performed for the models used for the multiple solute data and Table 4.6 shows the variables used and λ_{21} value calculated.

Table 4.6: Values of the variables used for the Multiple-solute data and the λ_{21} values determined for each component.

VARIABLES	Au	OH
S_1	45.9827	0.2972
S_2	12.0426	0.0875
m_1	1	1
m_2	5	5
N	21	21
λ	11.2733	9.5863

At the 95% confidence level the F value from the Tables for 4 and 16 degrees of freedom is 3,01 while it is 4,77 for the 99% confidence level. Hence the λ_{21} values calculated are significantly larger than the $F_{(4,16)}$ values obtained from the Tables. Therefore, it can be concluded that the General empirical model is a better model, in terms of this test, than the Freundlich-type model.

b. Method 2.

For any experimental data set, the deviations of the predicted values using a model could be represented by

$$(y_i - \bar{y}) = (\hat{y}_i - \bar{y}) + (y_i - \hat{y}_i)$$

where;

y_i = experimental data i,

$\bar{y}$ = mean of the experimental data and

$\hat{y}_i$ = the predicted value of y_i using the model.

The equation above could therefore be written as

DATA = MODEL FIT + RESIDUAL.

Variation within the data set is quantified by squaring and summing the deviations to yield

$$\sum (y_i - \bar{y})^2 = \sum (\hat{y}_i - \bar{y})^2 + \sum (y_i - \hat{y}_i)^2$$

This is equivalent to

$$SST = SSM + SSE,$$

where the variables are defined as,

$SST = \Sigma(y_i - \bar{y})^2$,

$SSM = \Sigma(\hat{y}_i - \bar{y})^2$

$SSE = \Sigma(y_i - \hat{y}_i)^2$

Assuming that the model has m parameters to be estimated and N number of experimental points (all these values have been given in the section above), the number of degrees of freedom of SST is (N-1), that of SSE is (N-m) while that of SSM is (m-1)[35]. Θ is defined as;

$$\Theta = \frac{SSM/(m-1)}{SSE/(N-m)}$$

If Θ is greater than the $F_{(m-1,N-m)}$ statistic at say 95% confidence level then the model's fit is significant.

Secondly if

$$R^2 = \frac{SSM}{SST}$$

is very close to 1 then the fit of the model is adequate.

Since it has been concluded from the previous section that FI and MFI are the "best" models for the single solute adsorption data the above tests were carried out on them. The same test was also conducted on the models for the multi-component adsorption models and the Tables below are indicative of the figures obtained.

It can be seen that the calculated values of ⊖ shown in Table 4.7 compared to the F Table readings in Table 4.9 reveal that for the two models considered the fits obtained are statistically sound since the ⊖ values are higher than the appropriate F values. Further, the R^2 values calculated for the two models as shown in Table 4.8 are very close to unity substantiating the goodness of fit obtained from the two models.

Table 4.7: Calculated ⊖ values for the single solute models.

MODEL	⊖	
	Au	OH^-
FI	478.60	56.09
MFI	928.78	71.31

Table 4.8: Table showing SST, SSM , SSE and R^2 values calculated for the single solute models.

MODEL	SST		SSM		SSE		R^2	
	Au	OH^-	Au	OH^-	Au	OH^-	Au	OH^-
FI	576.7935	20.6044	573.2005	20.3161	3.5930	0.2883	0.9938	0.9860
MFI	576.7935	20.6044	570.3457	20.2597	6.4478	0.3447	0.9888	0.9833

Table 4.9: F-Table readings at 95 and 99% confidence levels and various degrees of freedom as indicated for Au and OH^- single solute data respectively.

CONFIDENCE LIMIT	Au		OH^-	
	$FI_{F_{2,n}}$	$MFI_{F_{2,n}}$	$FI_{F_{2,n}}$	$MFI_{F_{2,n}}$
95%	2.90	3.55	2.77	3.47
99%	4.56	6.01	4.25	5.78

Table 4.10: Table showing SST, SSM, SSE, R^2 and Θ values calculated for the multiple solute data.

MODEL	SST		SSM		SSE		R^2		Θ	
	Au	OH	Au	OH	Au	OH	Au	OH	Au	OH
1	716.57	4.419	670.59	4.122	45.983	0.297	0.936	0.933	UND	UND
2	716.57	4.419	704.53	4.332	12.043	0.087	0.983	0.980	234.0	198.3

Table 4.11: F-Table readings at 95 and 99% confidence levels for the multiple solute models.

CONFIDENCE LIMIT	MODEL $1_{F(0,20)}$	MODEL $2_{F(4,19)}$
95%	UND	3.01
99%	UND	4.77

NOTE : UND means infinite.

In the case of multiple solute adsorption, it can be seen from the two Tables above that model 2 fits the data better than model 1 since the R^2 values calculated are than that of model 1 and very close to 1. Secondly the Θ values determined for model 2 have been much higher than the table readings obtained for each component. Hence the conclusions drawn earlier that model 2 is a better model is strengthened.

4.4. DISCUSSION OF THE ΔH VALUES OBTAINED FROM MFI.

Below shows the ΔH values for Au and OH^- adsorption respectively using MFI.

Table 4.12: ΔH values obtained for gold and hydroxide ion adsorption.

SOLUTE	-ΔH/kJmol^{-1}
Au	42.63
OH^-	14.86

The above values compare very well with ΔH values for physisorption of other species as seen from literature[25] (See Table 4.13 below). Therefore the adsorption of Au and OH^- could be said to be physical. Further the negative nature of the values obtained conform to the fact that the adsorption reaction is exothermic. The higher negative value obtained for gold could be probably attributed to the higher affinity that carbon has for gold.

McDougal et al[26] working between the temperatures of 20 and 60°C have estimated the isosteric heat of reaction for Au adsorption to be 42kJ/mol and this is confirmed by the result obtained in this work.

Table 4.13: Typical observed enthalpies of Physisorption, $-\Delta H/kJmol^{-1}$ reported in literature.

SOLUTE	$-\Delta H$	SOLUTE	$-\Delta H$
H_2	84	CO_2	25
CH_4	21	N_2	21
H_2O	57	C_2H_2	38
O_2	21	C_2H_4	34
Cl_2	36	CO	25

4.5. CONCLUSION

Several models have been discussed in this chapter. The modification of the Freundlich isotherm has been very effective and has helped in determining the heat of the adsorption of both gold cyanide and hydroxide ion to be 42kJ/mol and 14kJ/mol respectively. From these figures it is concluded that the adsorption reaction is a physical one and this further corroborates the conclusions drawn by others.

A statistical comparison has been made between both single and multi-component isotherms. As a result of this it has been deduced that for the adsorption of hydroxide ion at the single component level the modified Freundlich isotherm is better than the Freundlich isotherm, taking into consideration the three temperatures, at both 95% and 99% confidence levels while for the adsorption of gold cyanide the modified Freundlich isotherm is only better at 99% confidence level. In the multi-component system, the General empirical multi-component isotherm has been determined to be better than the Freundlich-type isotherm for the simultaneous adsorption of gold cyanide and hydroxide ion.

This work has developed a firm basis on which to describe the equilibrium behaviour of gold and hydroxide under typical elution conditions. To get a complete model for the elution process mathematical models need to be formulated and kinetic data needs to be generated. The next

chapter describes how the model was formulated using ideas from the literature review. Chapter six describes how kinetics was measured and the way the model was applied to the data.

CHAPTER 5

A MATHEMATICAL MODEL FOR THE ELUTION OF GOLD

CHAPTER 5.

A MATHEMATICAL MODEL FOR THE ELUTION OF GOLD.

This chapter discusses the derivation of the mathematical model for the elution of gold. It also describes how the reactor mass balance was simplified using the method of characteristics. A numerical procedure for the solution of the model is also presented with sensitivity analysis of the model to some of the parameters.

One of the objectives of the project is to develop a comprehensive model to describe the elution process. Therefore the mass balance for the reactor must be carefully derived. All AARL elution processes are done in columns. Hence the mass balance of the reactor reduces to a plug-flow packed-bed reactor problem. As mentioned in the Literature Review (Chapter 2), there are only three published reports on the modelling of the AARL elution[2,8,19]. Two of such reports did not adopt a "full" plug-flow model. In those reports the reactor column was divided into a number of CSTR in series. This approach does not give a good representation of the reactor mass balance. It is only Stange and King[2] who used a "full" plug-flow packed-bed reactor model in their work. From this discussion it could be seen that the nature of the reactor mass balance is very important for the success of the work.

As shown in Chapter 2, under the following conditions:

a. when the adsorbent has a high affinity for the adsorbate,
b. when the adsorbate is reversibly adsorbed, and
c. when the adsorbate has a favourable isotherm.

surface diffusion is assumed to control intraparticle diffusion such that pore diffusion can be neglected[31]. For the aurocyanide-carbon system in this work, these arguments have been shown to be true in Chapter 4 hence pore diffusion is eliminated. It is therefore considered that only surface diffusion controls the intraparticle diffusion. A detailed discussion on the development of the models is given below.

5.1 DERIVATION OF THE MODEL.

Reactor Mass balance

Figure 5.1 shows a schematic diagram of a plug flow reactor.

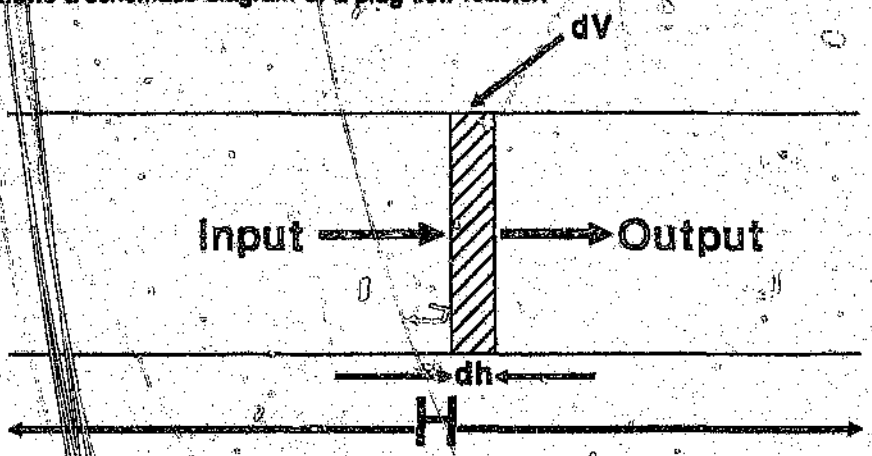


Figure 5.1: A Schematic Diagram of a Plug-flow reactor section dh packed with carbon.

The mass balance over the elemental section *dh* is given as:

$$Input - Output = Reaction\ rate + Accumulation$$

By definition[34]

$$Input\text{-}Output = -\partial(FC)$$

where,

F = Flow rate of the eluant through the column (m^3/s), and

C = Concentration of gold in the solution (g/m^3).

Thus

$$Input\text{-}Output = -F\partial C$$

Because F is constant throughout the column.

The reaction rate over the unit volume ($R\partial V$) consists of only desorption of the gold from the carbon.

This desorption term is given as:

$$\frac{\text{amount of Q desorbing}}{\text{time.volume of carbon particles per unit mass}} * dV$$

where,

$$\frac{\text{amount of Q desorbing}}{\text{time}} = -\frac{\partial Q}{\partial t}$$

$$\text{Volume of carbon particle per unit mass} = \frac{a(1-\varepsilon)H}{M_c}$$

dV = Sectional Volume of ∂h = a.∂h (a is the sectional area of the column),

ε = Carbon bed voidage,

M_c = Mass of carbon in the column (kg), and

H = Length of the column (m).

The desorption term therefore becomes,

$$R\partial V = -\frac{\partial Q}{\partial t}\frac{M_c}{a(1-\varepsilon)H}a\partial h$$

The accumulation term (within the solution phase) can be similarly written as:

$$\frac{\partial C}{\partial t}\frac{M_s}{a\varepsilon H}a\partial h$$

where

M_s = Mass of solution in the column (kg).

a can then be eliminated from the desorption and the accumulation terms. The mass balance over the elemental section *dh* is then given as:

$$-F\partial C = \frac{M_s}{\varepsilon H}\frac{\partial C}{\partial t}.\partial h - \frac{M_s}{(1-\varepsilon)H}\frac{\partial Q}{\partial t}.\partial h$$

Rearranging this equation gives the mass balance over the plug flow system to be

$$\frac{M_s}{(1-\varepsilon)H}\frac{\partial Q}{\partial t} = F\frac{\partial C}{\partial h} + \frac{M_s}{\varepsilon H}\frac{\partial C}{\partial t} \qquad 5.1$$

Mass balance over the Carbon Particle Phase.

The following assumptions were made to develop the surface diffusion model which includes film transfer as well:

1. Mass transfer within the carbon particle is via surface diffusion.
2. Mass transfer between the bulk solution and the particles occur via film diffusion through the stagnant liquid film surrounding the particles.
3. There is accumulation of the solute on the particle surface.
4. The desorption reaction is instantaneous and equilibrium exists between the solute in the liquid phase and in the adsorbed phase throughout the particle.
5. The carbon particles are spherical (See Figure 2.1).

As has been stated in the fifth assumption the carbon particle is being considered as spherical.

Let Q = the loading on the carbon particle at position *r*.

The mass balance over the spherical shell of radius *r* to *r+dr* is given as

$$A_2.Flux\ F_2 - A_1.Flux\ F_1 = V.R_a \qquad 5.2$$

A_1 = Inner area = $4\pi r^2$

A_2 = Outer area = $4\pi (r + dr)^2$

Assuming Fick's law of diffusion since elution is being considered,

Flux $F_1 = -D_s (\partial Q/\partial r)_r$

Flux $F_2 = -D_s (\partial Q/\partial r)_{r+dr}$

D_s = Surface diffusion coefficient,

V = Volume = $4 \pi r^2 dr$ and

R_s = Accumulation per unit volume on the particle surface = $\partial Q/\partial t$

Substituting all these factors into equation 5.1 gives

$$-\left(4\pi (r+dr)^2 D_s \left(\frac{\partial Q}{\partial r}\right)_{r+dr} - 4\pi r^2 D_s \left(\frac{\partial Q}{\partial r}\right)_r\right) = 4\pi r^2 dr \left(\frac{\partial Q}{\partial t}\right) \qquad 5.3$$

This is equivalent to

$$-4\pi\left(D_s R^2 \frac{\partial Q}{\partial R}_{R=r+dr} - D_s R^2 \frac{\partial Q}{\partial R}_{R=r}\right) = 4\pi r^2 dr \frac{\partial Q}{\partial t}$$

Such that,

$$-\left(\frac{D_s R^2 \frac{\partial Q}{\partial R}_{R=r+dr} - D_s R^2 \frac{\partial Q}{\partial r}_{R=r}}{dr}\right) = r^2 \frac{\partial Q}{\partial t} \qquad 5.4$$

The limit as $dr \rightarrow 0$, equation 5.3 becomes,

$$-\frac{\partial}{\partial r}\left(D_s r^2 \frac{\partial Q}{\partial r}\right) = r^2 \frac{\partial Q}{\partial t} \qquad 5.5$$

Solution of this equation is discussed below.

Mass balance over the external particle surface

The mass balance of Q over the external particle phase is given as

$$k_s (C - C_s) = D_s \rho \left(\frac{\partial Q}{\partial r}\right)_{R=r}$$

$$-\left(\frac{\partial Q}{\partial r}\right)_{R-r} = \frac{k_s}{D_s \rho}(C - C_s) \qquad 5.6$$

Equation 5.6 acts a boundary condition for the solution of equation 5.5.

5.1.1. Transformation of the Reactor Mass Balance using the Method of Characteristics.

The reactor mass balance written for the column is a hyperbolic partial differential equation. This can be solved using the method of characteristics as described by previous investigators[38,39,40,41]. The detailed description of the transformation is given below.

Since we have a desorption reaction as indicated from the mass balance derivation, the decrease in the concentration of gold from the carbon particle surface can be simply written as the amount of gold that is being diffused out of it and this is given as:

$$\frac{\partial Q}{\partial t} = -\frac{k_s}{\rho}(C - C_s)$$

Substituting this into the mass balance equation 5.1 derived from the previous section gives

$$F\frac{\partial C}{\partial h} + \frac{M_s}{\varepsilon H}\frac{\partial C}{\partial t} + \frac{M_c k_s}{(1-\varepsilon) H \rho}(C - C_s) = 0 \qquad 5.7$$

The boundary conditions for this equation are:

$C(0,t) = C_o$ and $C(h,0) = 0$.

Let the concentration of gold in the solution be expressed as a function of time, *t*, and height, *h*, on a curve parameterised as *h=h(s)* and *t=t(s)* with *s* being the parameter along the curve. It can therefore be defined that,

$$\Gamma(s) = C(h(s), t(s))$$

Differentiating with respect to s yields

$$\frac{d\Gamma(s)}{ds} = \Gamma(s) = \frac{\partial C}{\partial h} \cdot \frac{dh(s)}{ds} + \frac{\partial C}{\partial t} \cdot \frac{dt(s)}{ds}$$

$$\Gamma(s) = \frac{\partial C}{\partial h} \cdot \dot{h} + \frac{\partial C}{\partial t} \cdot \dot{t} \qquad 5.8$$

Where $\dot{h} = dh(s)/ds$ and $\dot{t} = dt(s)/ds$.

From equation 5.7

$$\frac{\partial C}{\partial t} = -\left[\frac{FeH}{M_s}\frac{\partial C}{\partial h} + \frac{M_c k_s \varepsilon H}{(1-\varepsilon) H \rho M_s}(C - C_s)\right]$$

Also from equation 5.8

$$\frac{\partial C}{\partial t} = \frac{\Gamma(s)}{\dot{t}} - \frac{\partial C}{\partial h}\frac{\dot{h}}{\dot{t}}$$

Combining the two equations above and re-arranging gives

$$\frac{\partial C}{\partial h}\left[\dot{h} - \frac{FeH}{M_s}\dot{t}\right] = \Gamma(s) + \frac{M_c k_s \varepsilon}{(1-\varepsilon)\rho M_s}(C - C_s)\dot{t} \qquad 5.9$$

Assuming that

$$\frac{dh}{ds} = \dot{h} = \frac{FeH}{M_s}$$

Then equation 5.9 becomes

$$\Gamma(s) = -\frac{M_c k_s \varepsilon}{(1-\varepsilon)\rho M_s}(C - C_s)\dot{t}$$

dh/dt therefore becomes the slope of the characteristic such that

$$t = t_o + \frac{M_s h}{F\varepsilon H}$$

Let $h = Ls$ for simplicity, where L is the length of the carbon bed,

$$\Rightarrow t = t_o + \frac{M_s L s}{F\varepsilon H} \qquad 5.10$$

and the differential of t becomes

$$\frac{dt}{ds} = \frac{M_s L}{F\varepsilon H} = \dot{t}$$

Therefore

$$\frac{dC}{ds_I} = -\frac{M_s k_s a}{(1-\varepsilon)\rho M_s}(C-C_s)\dot{t} \qquad 5.11$$

Where I denotes the characteristic t as given in equation 5.11. Figure 5.2 shows the boundary conditions for the model with representative characteristics in the (h,t) plane. A Fortran program to solve equation 5.11 coupled to the diffusion equation and the equilibrium equation,

$$Q_s = A_o EXP(-\Delta H/R*T)\, C_s^n$$

appears in Appendix 4. Detail of the Numerical procedure are given below. The model is a single solute model despite the fact that a multi-solute equilibrium model was developed in Chapter 4. A multi-solute elution model would take the work out of the present scope.

5.2 BOUNDARY CONDITIONS AS A RESULT OF THE TRANSFORMATION

Figure 5.2 shows a schematic diagram of the transformation. Significantly the main variable affected by the transformation is the time variable, t.

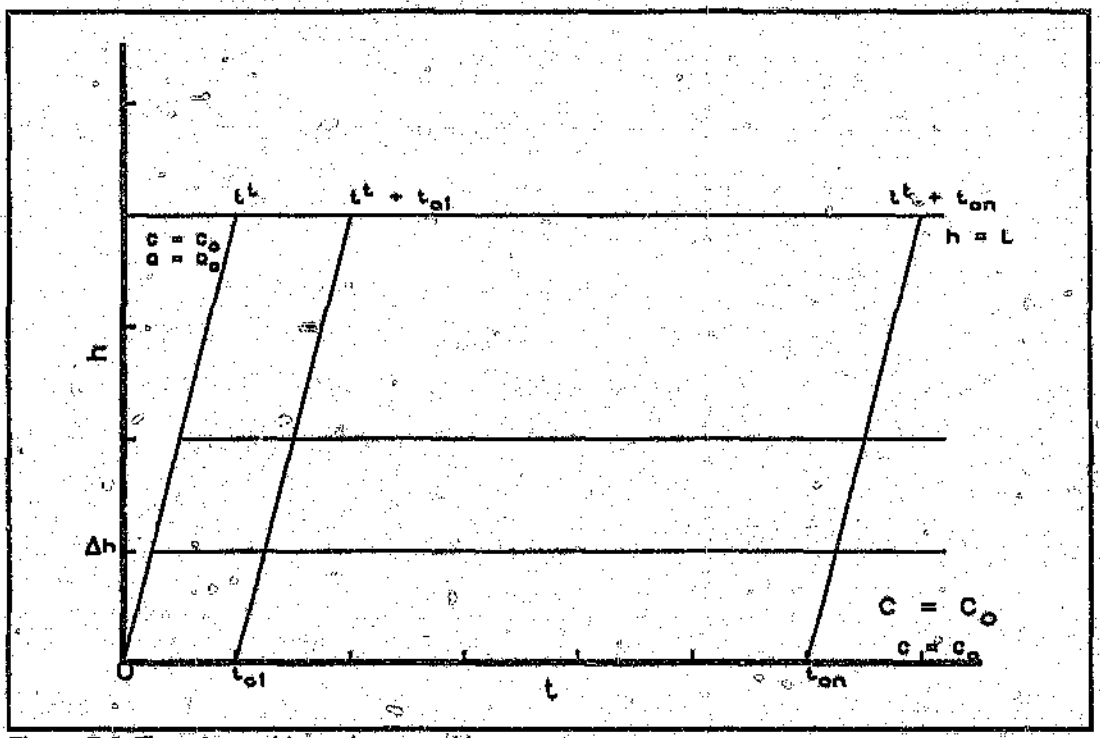


Figure 5.2: Transformed boundary conditions.

t^t seen in the diagram is obtained from equation 5.10 and it is defined as

$$t^t = \frac{M_s L s}{F e H}$$

5.3 NUMERICAL PROCEDURE FOR THE SOLUTION OF THE MODEL

The surface of the elution column is divided into a fine grid of Δh. The surface diffusion model in equation 5.5 is then solved at h=0 ($C = C_o$) at the various grid times for Q_s. This is done using the NAG fortran software library routine D03PGF. The routine integrates a system of nonlinear parabolic partial differential equations in one space variable, using the method of lines and Gear's method. The routine provides the facility for the integration to be done within time and over space interval. The coordinate system in space could either be Cartesian coordinates, cylindrical polars or spherical polars. The routine approximates parabolic equations by a system of ordinary

differential equations in the time variable. The equations are obtained by approximating the space derivatives by finite differences and the result is a set of coupled differential equations at the mesh-points. The interval in the time direction is chosen by the routine to maintain local accuracy specified. The principal disadvantage of the routine is that it does not check the accuracy of the finite-difference approximation in space. This may be of a considerable importance when a high accuracy is demanded. The quadratic approximation method[18,19] is not applied because of the numerous assumptions involved.

After this process C_s is determined using the Modified Freundlich Isotherm specified above. The transformed plug-flow model (equation 5.11) is then solved from h=0 to h=Δh using C_s to obtain C for the grid times (see Figure 5.2). This is done assuming that C_s is constant over the integral step, which is a good assumption if the step length is small. This procedure is repeated until the parameterised variable, s, is equal to 1, that is when h=L.

5.4 SENSITIVITY ANALYSIS OF THE MODEL

Figure 5.3 shows a sensitivity analysis produced as a result of varying the diffusion coefficient.

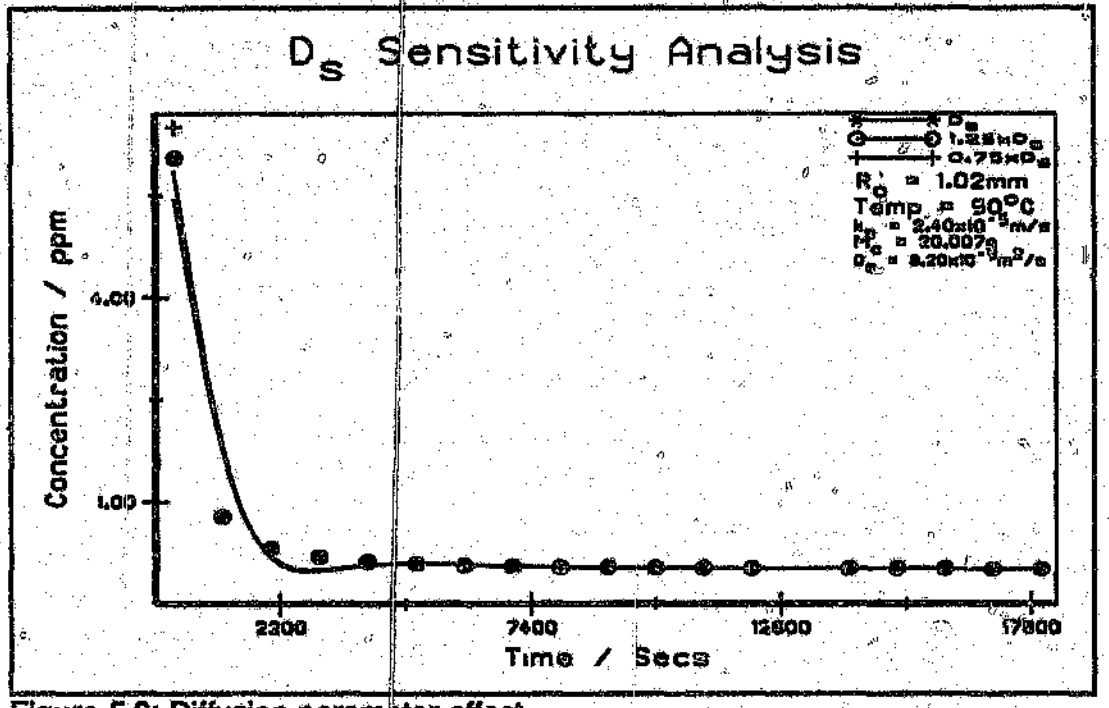


Figure 5.3: Diffusion parameter effect.

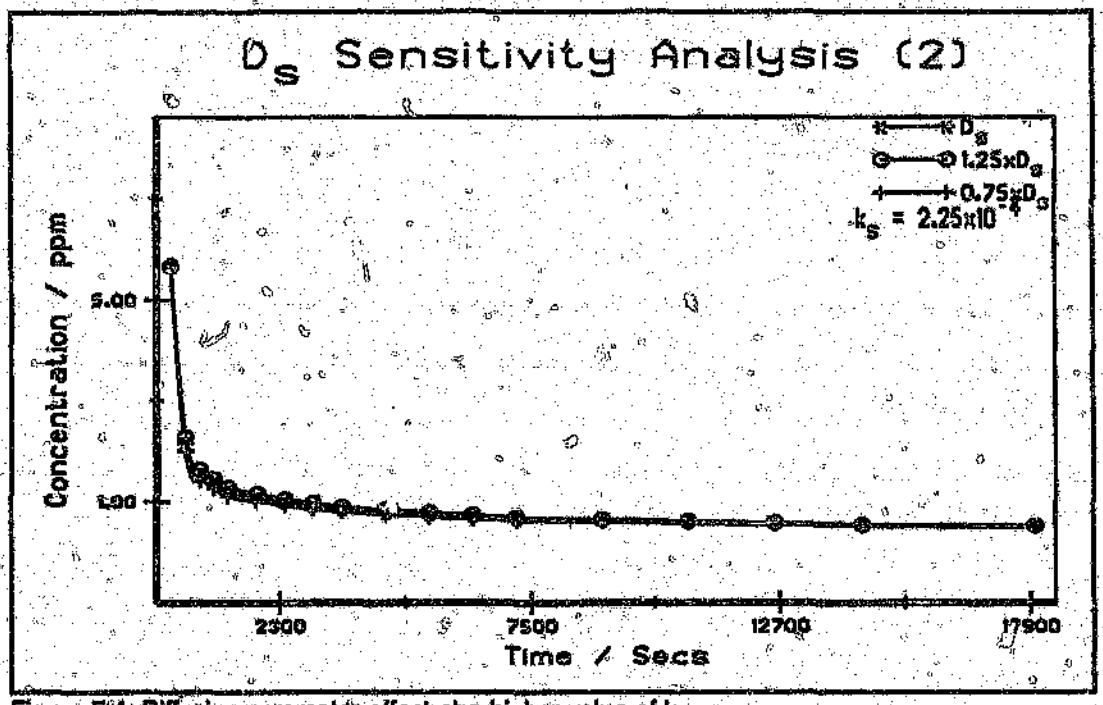


Figure 5.4: Diffusion parameter effect at a higher value of k_s.

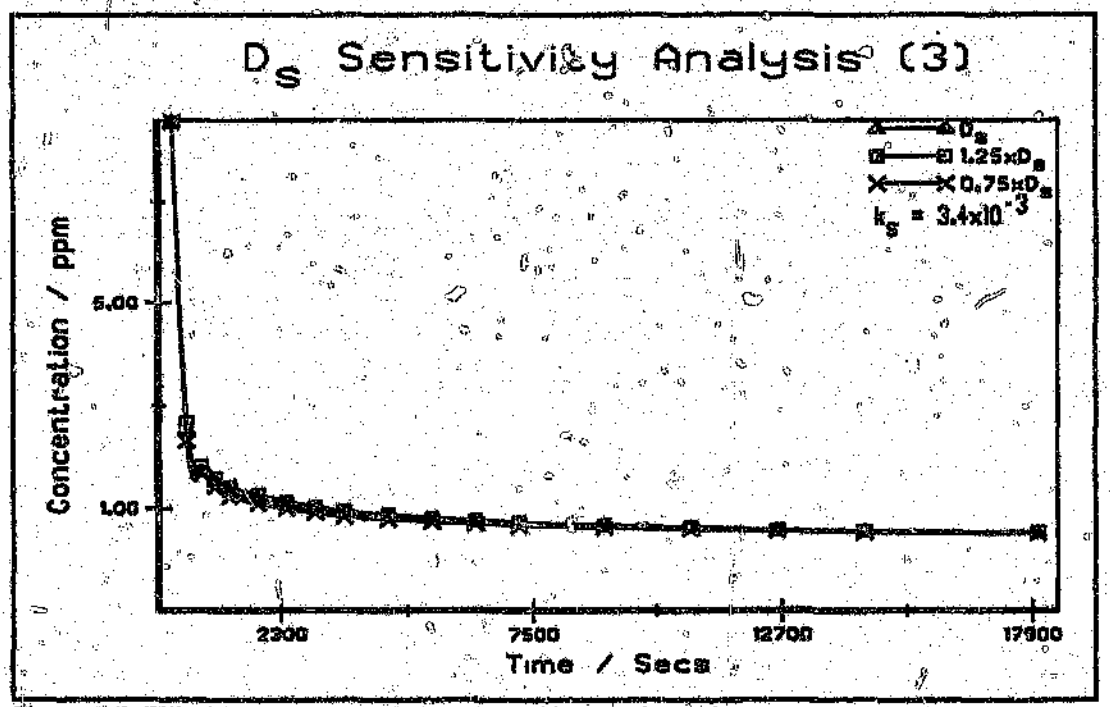


Figure 5.5: Diffusion parameter effect at much higher value of k_s.

From the diagram it can be concluded that model is not sensitive to the diffusion coefficient D_s. To test the adequacy of the above conclusion the sensitivity of the model was tested again with respect to D_s with larger values of k_s. Figures 5.4 and 5.5 show the results obtained. From the two figures it can be concluded that the earlier conclusion drawn is sustained. The observation that the model is not sensitive to D_s suggested that surface diffusion could be playing a fairly small role in the rate of desorption making film transfer the main rate determining factor. Attempt was made to eliminate surface diffusion as a rate determining factor. This was done by setting D_s as high as $3x10^{-4}m^2s^{-1}$. This figure being 10^6 times surface diffusion coefficients reported in the literature[43]. The film transfer coefficient was then estimated by minimizing the sum of squares of the residuals non-linearly using the Nag Fortran Routine E04FCF. The model, as result of this modification, becomes predominantly film transfer controlled.

Sensitivity of k_s to the film transfer controlled model is shown below Figure 5.6. It can be seen that the model is very sensitive to the film transfer coefficient. The effect is dominant at the initial stages as expected. As the film transfer coefficient increases the rate of desorption increases as well.

Figure 5.7 shows sensitivity of the film transfer controlled model to temperature. It can be seen here also that the model is very sensitive to temperature and the effect is dominant at the initial stages. This observation has substantiated the significant change that can occur as a result of increase or decrease in temperature. The effect has demonstrated that increase in temperature of only 10°C can cause a tremendous increase in the kinetics of solution.

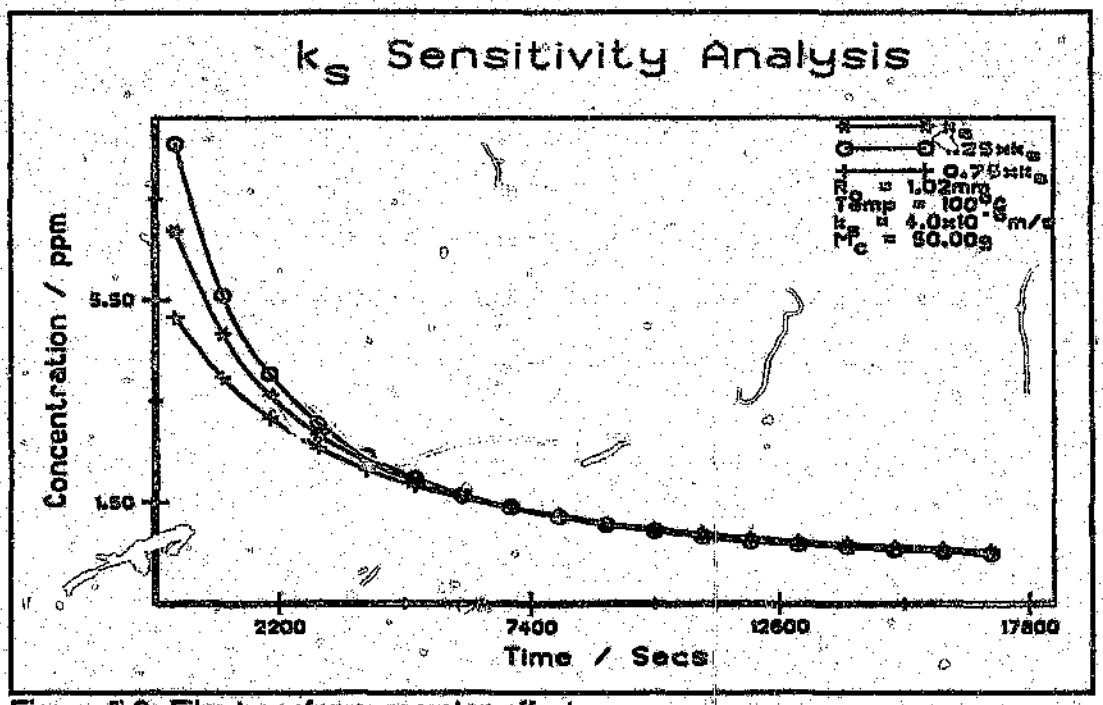


Figure 5.6: Film transfer parameter effect.

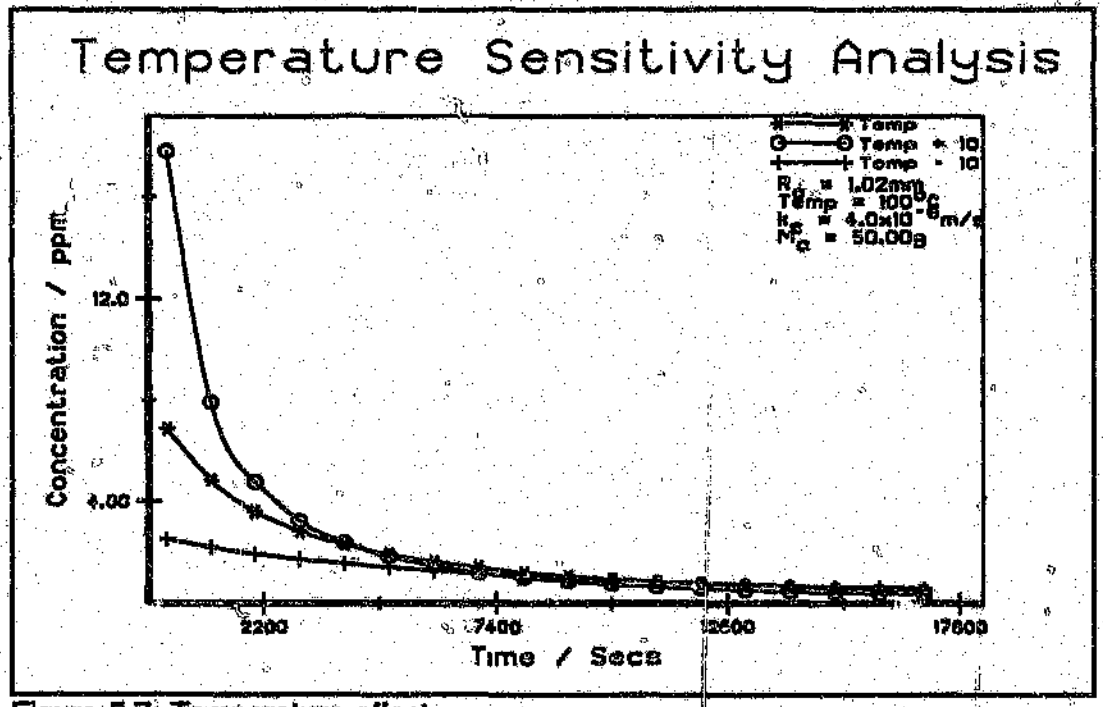


Figure 5.7: Temperature effect.

5.5 CONCLUSION

This Chapter discussed the derivation of the elution model. It has been shown that the method of characteristics is a powerful numerical procedure to transform the hyperbolic plug flow model. Simulation of the model has revealed that the model is less sensitive to the surface diffusion parameter suggesting the surface diffusion is not a rate determining factor. The model was then modified to be film transfer controlled. The film transfer controlled model was found to be very sensitive to the film transfer parameter and temperature.

Application of the film transfer controlled model to experimental data is presented in the next Chapter.

CHAPTER 6

MODELLING OF KINETICS OF ELUTION

CHAPTER 6

MODELLING OF KINETICS OF ELUTION

This chapter presents the generation and modelling of the kinetic data. As mentioned in Chapter 2 increase in temperature results in decrease in the adsorptive power of carbon thus favouring elution. Desorption is also favoured by low ionic strength, while increase in cyanide and hydroxide ion concentrations enhance desorption. All these factors were therefore taken into consideration for the kinetic data generation. To reduce cost industrially loaded carbon from Knights Resources in Germiston was used.

The Chapter describes how the carbon was prepared for the experimental work. It also discusses the approach adopted to generate a good experimental data using the experimental equipment described in Chapter 3. Modelling of the kinetic experimental data is also discussed. Correlations obtained between the film transfer coefficients and the conditions of elution are also presented.

6.1 CARBON PREPARATION AND EXPERIMENTAL DESCRIPTION

The carbon obtained from the plant contained wood chips and was therefore washed with tap water until the bulk of the wood chip was removed. After this, the carbon was acid washed with 3% HCl solution at the temperature of 90°C for 30 minutes. The acid washing step is necessary to remove elements such as Ni, Cu, Ca, et al which are adsorbed at the adsorption stage of the CIP process since their presence may interfere with the kinetics of gold elution. From a gold elution point of view, the effect of acid washing is the partial modification of the $Au(CN)_2^-$ ion pair to AuCN which is very strongly adsorbed onto the carbon and hence very difficult to elute[3].

The acid washed carbon was washed with distilled water to a pH of 7 before being dried at 70°C for 72 hours. The dried carbon was then sized into several size ranges as will be discussed later. Before every experiment a specific weight of the dried and sized carbon was presoaked in cold 2% NaCN and 2% NaOH (ie 20g/l NaCN and 20g/l NaOH) solution for a specific period of time. Presoaking of the carbon in caustic cyanide converts the AuCN formed in the acid washing step to the $Au(CN)_2^-$ complex which is amenable to elution under caustic conditions. Except where otherwise stated, after presoaking the carbon was washed with distilled water to a pH of 7 before the elution.

The elution experiments were conducted with the experimental equipment described in Chapter 3 (see Figure 3.1). Since the investigation focused on the cyanide-free AARL elution, the eluant was not recirculated. Flow rate of the eluant was kept at 4 bed-volumes/hour in all the experiments as in the case of the equilibrium experiment. Samples were taken at specific time intervals for 5 or 6 hours during the elution as indicated by the experimental data in Appendix 3. Analysis for gold was done by the AAS. Where required, samples were taken immediately after the main sample for cyanide titration. The cyanide titration was performed with 0.1M silver nitrate solution. Iodide ion in the form of KI solution was used as the indicator and aqueous ammonia was used to solubilize the silver cyanide formed. The end point of the reaction was indicated by a golden-yellow turbidity. To ensure sharpness of the end point, the solution was continuously stirred with a magnetic stirrer during the titration. Because the work is focused on cyanide-free elution the carbon was washed to a pH of 7 before each test. This therefore eliminated any influence of cations such as Na^+, Ca^{2+} et al. Because of the washing no hydroxide test was performed.

6.2 RESULTS AND DISCUSSION

6.2.1 Effect of Presoaking Period

This experiment was designed to examine the effect of varying presoaking period on elution. Five portions of about 20g of loaded carbon in the size range +1.70 to -2.36mm were presoaked in 200ml of the presoaking solution for different periods of time at 20°C. After the presoaking period the carbon was washed to neutrality before being subjected to elution at the temperature of 125°C for 6 hours. Figure 6.1 shows the result obtained. The graph has indicated effectively the reproducibility of the elution profile at constant temperature using the experimental equipment described earlier.

The data was fitted to the film transfer controlled model and Figure 6.2 shows the fitted film transfer coefficients as a function of the presoaking time. It could be seen that there is a very little relationship between the film transfer coefficient and the presoaking time. The plot is obviously a straight line parallel to the presoaking period axis. A constant k_s can therefore be assumed for all the presoaking periods. Consequently it could be concluded that the presoaking time has no effect on the film transfer coefficient as long as the temperature of elution remains constant. Graphs comparing the predictions from the model and the experimental data are presented with the experimental data in Appendix 3.

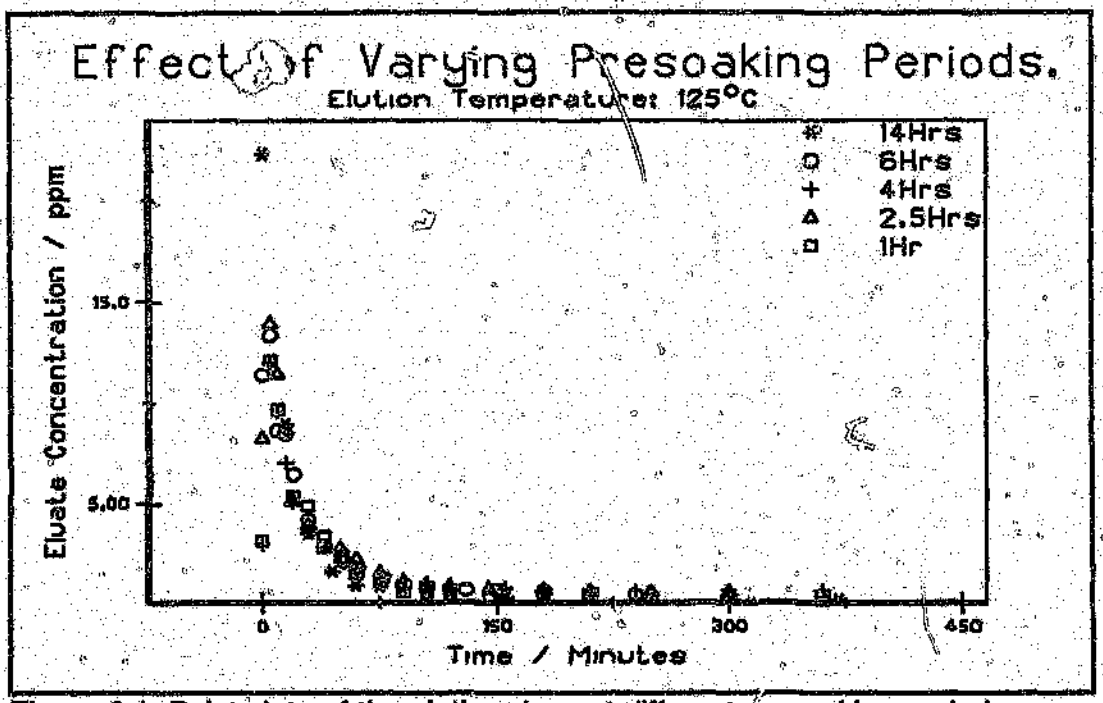


Figure 6.1: Point plots of the elution done at different presoaking periods.

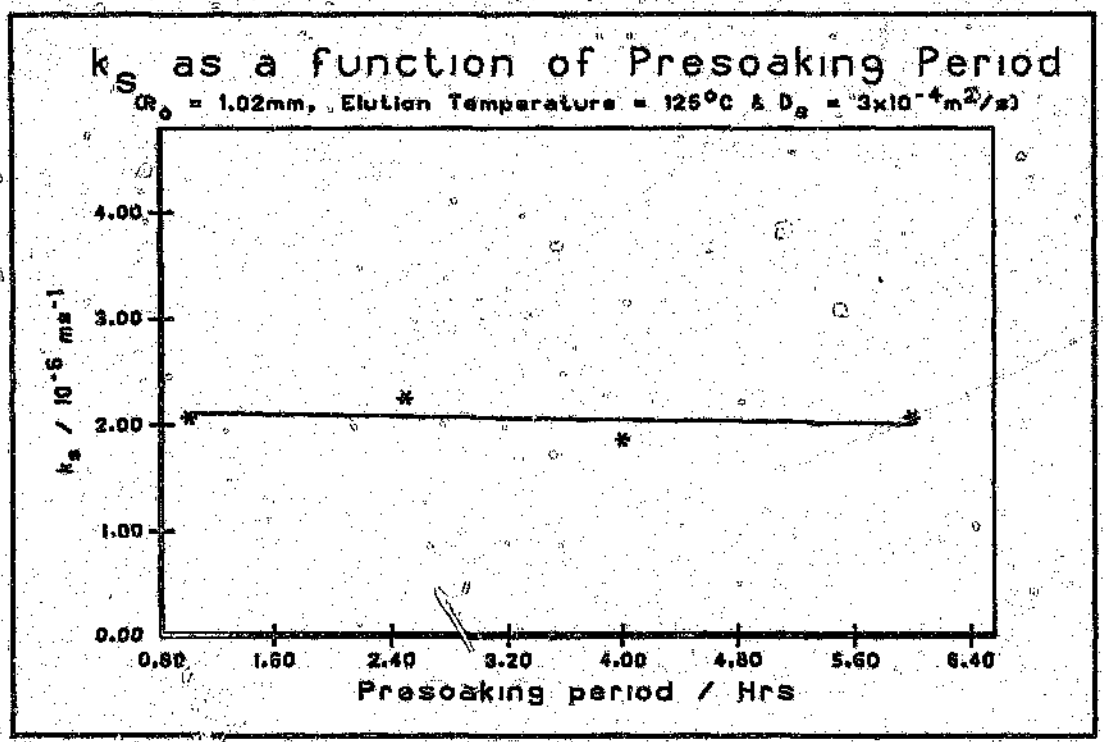


Figure 6.2: Dependence of k_s on Presoaking period.

6.2.2 Effect of Temperature

As indicated in the literature review temperature seems to be the most important factor affecting the elution process. It is therefore expected that high temperatures should enhance the rate of elution.

Two sets of experiments were performed. The difference between the two set of experiments was the mass of carbon that was subjected to elution. In the first set about 20g of carbon was used while 50g of carbon was used for the other set (size range of carbon used was +1.70 to -2.36). However in both cases the carbon was presoaked in 100ml of the presoaking solution for 4 hours. Each set of presoaked carbon was washed to neutrality before elution at the various temperatures.

The data was subjected to the film transfer controlled model and the result from the two experiments is summarised in Figures 6.3.

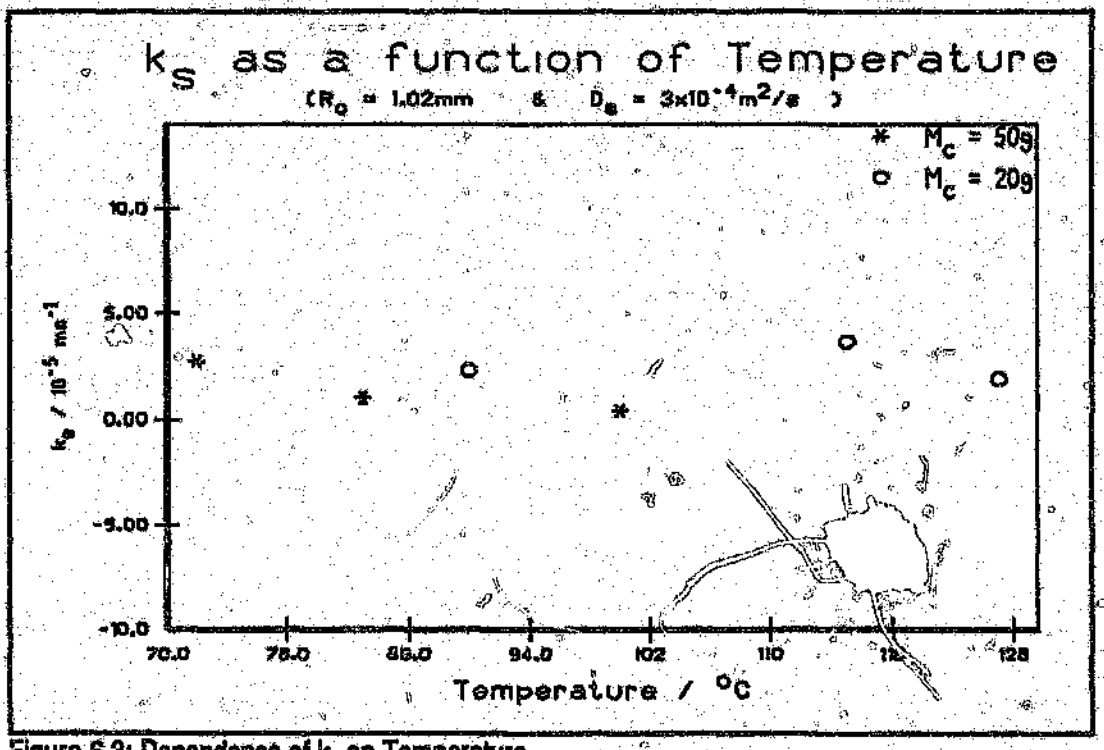


Figure 6.3: Dependence of k_s on Temperature.

From Figure 6.3 it can be seen that there is virtually no correlation between the film transfer coefficient and temperature for each set of data. Within limits of the experimental errors associated with the data the film transfer coefficients obtained at the various temperatures can be said to be constant.

6.2.3 Effect of Particle Size

This experiment was performed to examine the effect of particle size on the rate of elution. About 20g of carbon from three different particle size ranges respectively was presoaked in 100ml of the presoaking solution at 20°C for 4 hours. After presoaking the carbon was washed to a pH of 7 before elution.

The data was subjected to the film transfer controlled model. The effect of particle size on k_s is shown in Figure 6.4.

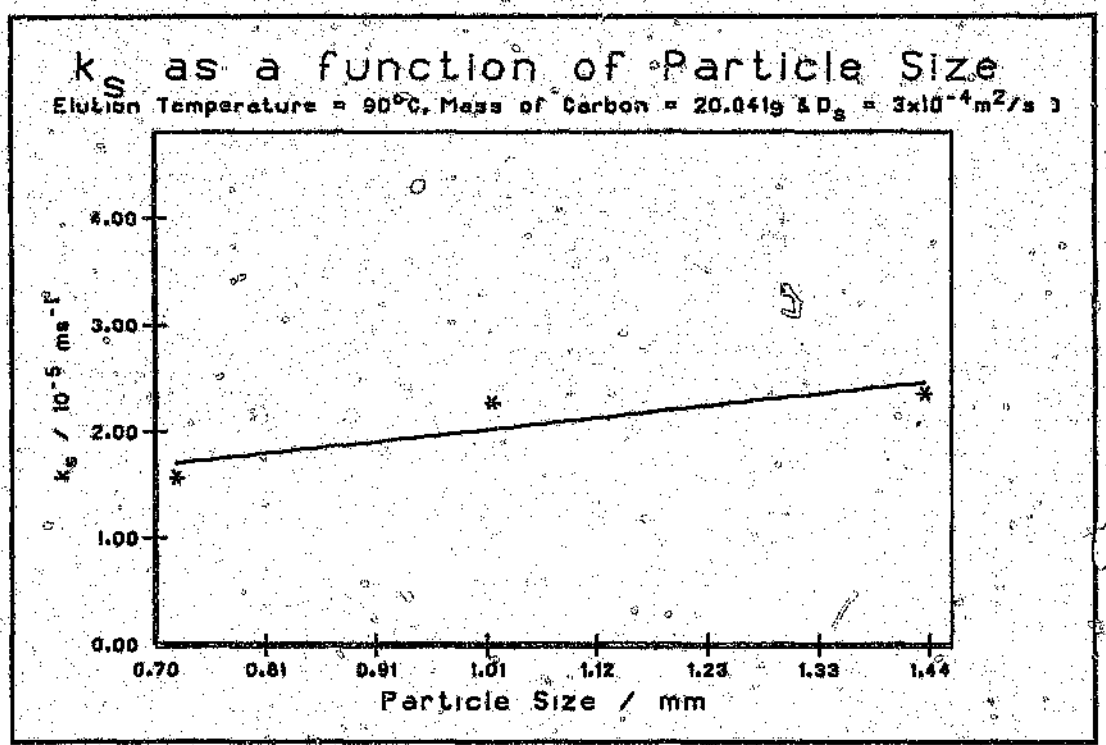


Figure 6.4: Dependence of k_s on Particle size.

It could be seen from the Figure that there is a slight trend between the film transfer coefficient and particle size. Film transfer coefficient is seen to increase with increase in particle size. Similar observations have been made by Afewu[35] and Young[42]. It is suggested that film transfer depends on the surface roughness of the particle and the particle shape. Therefore, film transfer enhancement by surface roughness will be greater for the larger particles than for the smaller particles because of their larger surface area. In fact correlations such as Sherwood and Reynolds numbers for packed columns predict higher film transfer coefficients for larger particles than for smaller particles. Though the result obtained in this work seems to have confirmed the works done earlier the film transfer coefficients obtained can be said to be relatively constant within the errors associated with the data.

6.2.4 Effect of Changing Chemical environment.

An experiment was conducted to examine the effect of the presence of some "measurable cyanide" on the kinetics of elution. In this case the carbon sample was presoaked cold at 20°C for 4 hours. After presoaking the carbon was not washed before elution at 83°C. Figure 6.5 gives a comparative illustration between elution of washed and unwashed carbon at the same temperature.

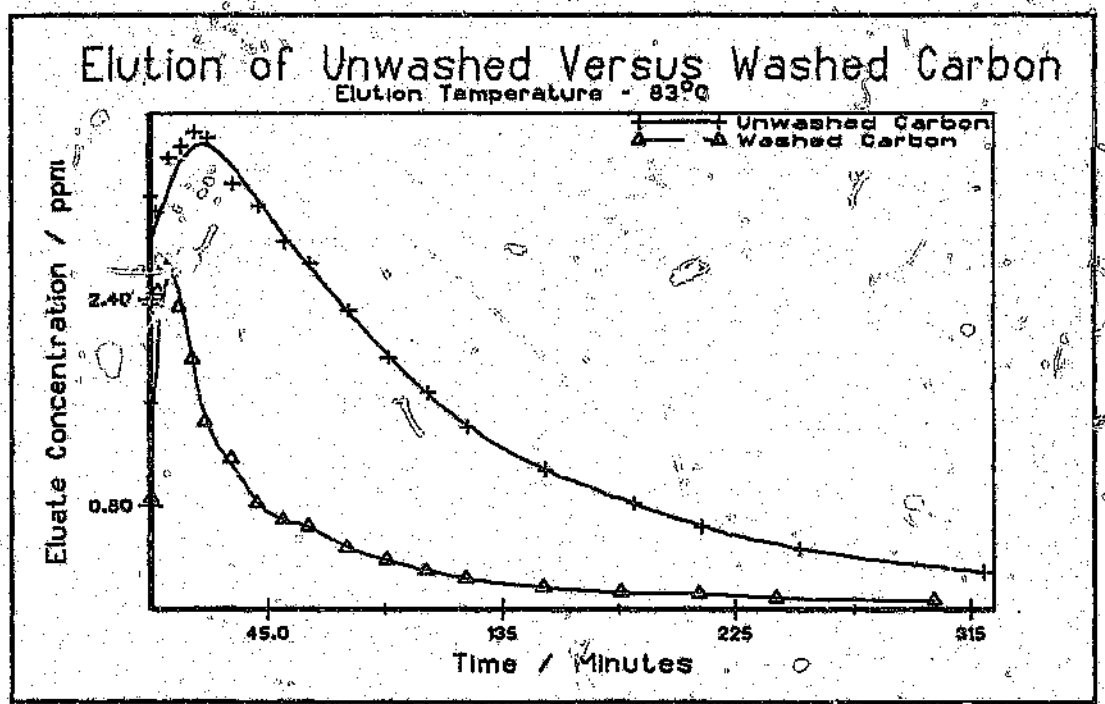


Figure 6.5: Effect of the presence of cyanide on elution at 83°C.

It could be seen that the kinetics of the unwashed carbon was higher than the washed carbon. Adams[3] suggested that the presence of CN^- in the elution environment has a modifying effect on the carbon surface. This is due to reactions between the phenolic groups on the carbon surface and the cyanide ion. This reaction results in making the carbon less receptive to adsorption thus favouring elution. From this, it is expected that the carbon that was not washed must have faster kinetics than the one that was washed because of the presence of cyanide.

It could also be seen that the elution profile of the carbon that was not washed conforms to the typical plant data obtained by Stange and King[2]. The peak of the gold elution only occurs after all the spectator ions, such as Na^+, K^+ et al, in the presoaking solution is washed away. Washing away of such ions results in reduction of ionic strength of the eluate. At that stage, the adsorption equilibrium reaction in equation 2.1 tends to shift to the left thus favouring elution.

The film transfer controlled model was fitted to the experimental data generated without the carbon being washed. The result obtained is shown below in Figure 6.6. It can be seen that the fit obtained is not good. This is due to the nature of the equilibrium isotherm used which does not account for significant changes in ionic strength.

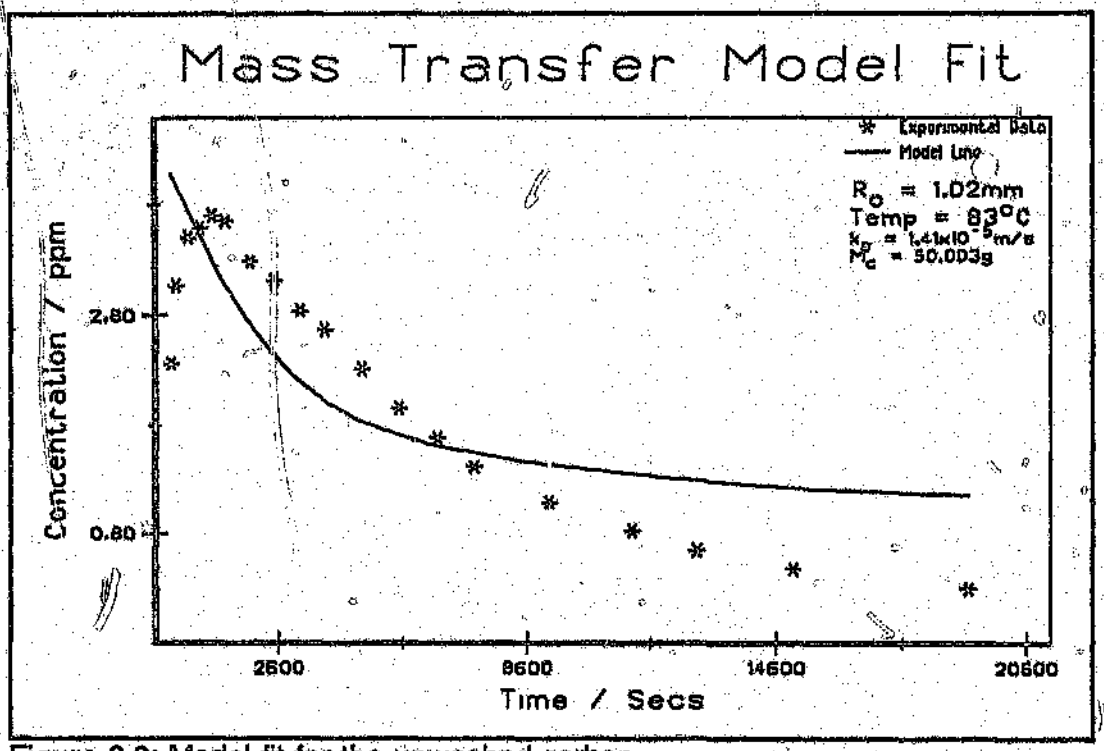


Figure 6.6: Model fit for the unwashed carbon.

Since the carbon was not washed after presoaking before elution, the chemical environment was continuously changing. The change in factors such as ionic strength, cyanide and hydroxide ion concentrations therefore has an influence on gold equilibrium. The equilibrium isotherm used however was a single solute model. Though the influence of OH^- ion on gold equilibrium was studied in this work, the influence of the other factors were not. Thus, the single solute model could not efficiently simulate gold elution in the presence of all these factors.

From Figure 6.6 and the figures shown in Appendix 3 it can be seen that there is a mismatch between the experimental data and the model prediction at the initial stages. This can be explained to be due to the time lag in taking the initial sample in the kinetic experiment because of the time taken to fill the elution column. This effect was not taken into consideration during modelling. But apart from this it can be seen that the fit produced by the model is very good.

6.3 CONCLUSION

It has been shown in this Chapter that the film transfer controlled model could be used to fit experimental data. The period of presoaking has been found to have no influence on the film transfer coefficient as long as the temperature of elution remains constant. There is virtually no relationship between the film transfer coefficient and temperature. It was also found that film transfer increases with increase in carbon particle size very slightly so that the film transfer coefficients obtained can be said to be constant within the errors associated with the data.

The single solute film transfer controlled model did not represent gold elution with changing chemical environment well.

CHAPTER 7

CONCLUSIONS

CHAPTER 7

CONCLUSIONS.

7.1 Conclusions

The following conclusions can be drawn from the work reported above:

- The equilibrium attainment of OH^- is a function of the initial concentration of the OH^- in solution such that the higher the initial concentration the faster the establishment of equilibrium and vice versa. The equilibrium attainment of gold adsorption onto carbon is independent of the initial concentration

- The equilibrium adsorption behaviour of gold and hydroxide ion on to carbon has been found to be physical in nature and exothermic yielding a ΔH of -42.63kJ/mol and -14.86kJ/mol respectively.

- The presence of OH^- ion has significantly suppressed the adsorption of gold on to carbon hence producing a wide deviation with respect to temperature on the gold adsorption profiles. This effect has been suggested to be due to the modifying effect OH^- ion has on the surface of the activated carbon.

- It was shown that statistical analysis can be used to make a choice for the best model which has fitted experimental data especially when the data has been subjected to several models with different number of parameters to be estimated. From such an analysis it was shown that the Modified Freundlich isotherm is the best model for the single solute equilibrium adsorption of gold and OH^- ion respectively. For multi solute equilibrium adsorption, it was found that the General empirical model is better than the Freundlich-type multi-component model.

- An elution model depending on surface diffusion and film transfer has been developed. The reactor mass balance which is a "full" plug flow hyperbolic differential equation was transformed and solved using the method of characteristics.

- The model (which is surface diffusion and film transfer controlled) was found not to be

sensitive to the surface diffusion coefficient. This suggested that surface diffusion was playing a fairly small role as a rate determining factor during the elution process. The model was then modified to be film transfer controlled.

- The film transfer controlled model was found to be very sensitive to the film transfer parameter and temperature. In both cases the effect was found to be dominant at the initial stages of the process. The effect of temperature especially strengthens the conclusion that temperature is the most important factor in the elution process.

- Data for the kinetics of elution was generated and subjected to the film transfer controlled model. It was found that the film transfer controlled model fitted the experimental data very well. Predictions of the model have shown that the dependence of the film transfer coefficient on temperature is virtually non existent within the limits of experimental error generated. It was also found that there is a slight dependence of film transfer coefficient on particle size. This dependence was found to be linear with increase in particle size resulting in a corresponding increase in the film transfer coefficient. No relationship was found between the period of presoaking and the film transfer coefficient.

- The film transfer controlled model was found not to fit gold elution data with a changing chemical environment. This was the result of the equilibrium model used which did not account for the effect of ionic strength and cyanide concentration on the equilibrium adsorption of gold.

7.2 Recommendations

It can be seen that fits obtained with the film transfer controlled model were very good. The model however can not be used for industrial simulation purposes yet. This is because by washing the carbon before elution an artificial situation is created. This situation therefore eliminated the influence that the presence of cations such as Na^+, K^+, Ca^{2+} et al would have on gold elution. Obviously in cyanide-free elution influence by these ionic species would be minimal but worth

measuring, An industrially useful model should be able to predict the influences of temperature, hydroxide ion concentration and the concentration of any of the cations mentioned above simultaneously during the elution process. This is because these factors would have effect on the equilibrium behaviour of gold and therefore could affect the kinetics of gold elution.

It is therefore recommended that the influence of the above mentioned cations on the equilibrium behaviour of gold should also be examined and quantified together with those studied in this work. By so doing a complete model can be developed to simulate cyanide-free AARL elution. A further extension can be made to study the simultaneous desorption of gold and silver. This will strengthen the usefulness of the model industrially since the elution process is a multi-component process.

Also since cyanide free AARL elution process is very similar to Zadra elution process the study can be further extended to take care of the Zadra process. Modifications can be made in the mass balance presented in this work so as to include the recirculation of the eluant as practised in the Zadra process.

Benefits of such an industrially useful model includes easy plant optimization and cost analysis. This is because computer based techniques can be used and this will aid the examination of many scenarios during plant design and operation. By the use of computer based techniques instead of manual process analysis and design techniques, optimum utilization of resources can be achieved.

Finally the elution model developed is still at a preliminary stage and will have to be further worked on to be of value to industry.

REFERENCES.

REFERENCES.

1. **Bailey, P.,** Application of activated carbon to gold recovery. In: Stanley,G.G.(ed), The Extractive Metallurgy of Gold in South Africa, Johannesburg, South Africa Institute of Mining & Metallurgy, 1987, pp 379-614.

2. **Stange, W. & King, R.P.,** The optimization of the CIP process; 22nd International Symposium on the Application of Computer and Operation Research in the Minerals Industry (APCOM), SME, Berlin, Sept 1990.

3. **Adams, M.,** Chemistry of the CIP process, PhD Thesis, WITS University, Johannesburg, 1989.

4. **Adams, M.D. & Nicol, M.J.,** The kinetic of elution of gold from activated carbon, Gold 100, Proceedings of the International Conference on Gold, Vol 2, Extractive Metallurgy of Gold, SAIMM, Johannesburg, 1986.

5. **Nicol, M.J.,** Elution theory, Lecture 14, SAIMM, CIP School, Randburg, October 1985.

6. **Adams, M.D.,** Kinetics of elution of gold from activated carbon by Zadra method, Trans Institution of Mining & Metallurgy, (Sect. C: Mineral Processing & Extractive Metallurgy), IMM, May-August 1990.

7. **Griffin, A.F. & Cortello, M.C.,** Carbon desorption process development at Micron Research (Western Australia). In:Carbon In-Pulp Technology For the Extraction of Gold, Incorporating papers presented at the Seminar on Carbon-In-Pulp Technology in the Extraction of Gold organised by the Perth & Kalgorie Branches, The Aus IMM, July 1982, and Symposium on Carbon-In-Pulp Technology organised by Murdock University, July 1982.

8. **Ruane, M.,** Comparison of the Zadra, Anglo-American and Organic procedures for desorption of gold from activated carbon, As in Reference 7.

9. **Van der Merwe,P.J. & Van Deventer,J.S.J.,** Generalized simulation of Zadra and AARL elution columns, Paper presented at CMMI Conference, Edinburgh, July 1990.

10. **Dement, E.R. & King, N.D.,** Merrill-Crowe/ Carbon-In-Pulp an economic evaluation, As In Reference 7.

11. **Davidson, R.J.,** A review of the AARL process for the elution of gold from activated carbon, Lecture 15, As In Reference 5.

12. **Nicol, M.J., Fleming, C.A. & Cromberge, G.,** The absorption of gold onto activated carbon. I. The kinetics of absorption from pulps, J. S. Afr. Inst. Min. Metall., Vol. 84, No. 2, Feb. 1984, pp 50-54.

13. **Stange, W.,** The optimization of the CIP process using mathematical and economic models, Minerals Engineering, Vol. 4, No. 12, pp 1279-1295, 1991.

14 **Weast, R. C. (Ed),** CRC Hanbook of Chemistry & Physics, 53rd Edition, Chemical Rubber Co., Cleveland, Ohio, 1972 - 1973, pp E12 -E20.

15 **Mantel, C. (Ed),** Chemical Engineering Series - Adsorption, McGraw Hill Book Company Inc., N.Y., 1951, Chapter 2.

16 **Stange, W.,** The modelling and simulation of in-pulp adsorption processes, SAIMM School - Recent Developments in In-pulp Technology, Mintek Randburg, 7-8 Oct., 1991.

17 **Cho, E.H. & Pitt C.H.,** The adsorption of silver cyanide on activated charcoal, Metallurgical Transactions B, Vol 10B, June 1979, pp 159-164.

18 **Van Deventer, J.S.J.,** Kinetic models for the adsorption of metal cyanides on activated carbon, PhD Thesis, University of Stellenbosch, 1984.

19 **Van der Merwe, P.F.,** Fundamentals of the elution of gold cyanide from activated carbon,

RhD Thesis, University of Stellenbosch, June 1991.

20 **Feurstenau, M.C., Nebo, C.O., Kelso, J.R. & Zaragoza, M.,** Rates of adsorption of gold on activated charcoal, Minerals and Metallurgical Processing, Nov. 1987,I pp 177-181.

21 **Dixon, S., Cho, E. & Pitt, C.,** The interaction between gold cyanide, silver cyanide and high surface charcoal, A.I.Ch.E. Symposium Series, No. 173, Vol 74, 1978, pp 75-83.

22 **Woollacott L.C., Stange, W. & King, R.P.,** Towards more effective simulation of CIP and CIL processes.1. The modelling of Adsorption and Leaching, J. S. Afr. Inst. Min. & Metall., Vol 90, No 10, Oct 1990, pp 275-282.

23 **Cho, E.H. & Pitt, C.H.,** Kinetic and thermodynamics of silver adsorption on activated carbon, Metallurgical Transactions B, Vol 10B, June 1979, pp 165-169.

24 **Cho, E.H., Dixon, S.N., & Pitt, C.H.,** The kinetics of gold cyanide adsorption on activated carbon, Metallurgical Transactions B, Vol 10B, June 1979, pp 185-189.

25 **Aitkins, P.W.,** Physical Chemistry, Oxford University Press, 1986-Third Edition, pp 833.

26 **McDougall, G.J., Hancock, R.D., Nicol, M.J., Wellington, O.C. & Copperthwaite, R.G.,** The mechanism of the adsorption of gold cyanide on activated carbon, J. S. Afr. Inst. Min. & Metall., Sept 1980, (9), pp 344-356.

27 **Moys, M.H. & King, R.P.,** Estimation of the parameters in the distributed-constant flotation Model 1, Report 1567, National Institute of Metallurgy, 15 January 1974.

28 **Sheindorf, C.H., Robin N. & Sheintuch, M.,** A Freundlich-type multi-component isotherm, Journal of Colloid and Interface Science, Vol 79, No 1, Jan 1981, pp 136-142.

29 **Fritz, W. & Schlunder, E.,** Simultaneous adsorption equilibria of organic solutes on activated carbon, Chemical Engineering Science, Vol 29, 1974, pp 1279-1282.

30 **Le Roux, J.D.,** Modelling of the effect of organic fouling on the adsorption of gold cyanide by activated carbon in a batch reactor, MSc Dissertation, University of the Witwatersrand, 1989.

31 **Young, B.D., Le Roux, J.D. & Bryson A.W.,** The binary adsorption of gold cyanide and ethyl xanthate onto activated carbon, Hydrometallurgy, 26, 1991, pp 395-401.

32 **Glover, M.R.L.,** The modelling of the binary adsorption of gold and zinc cyanide onto a strong base anion exchange resin, MSc Dissertation, University of the Witwatersrand, 1989.

33 **Young, B.D., Bryson, A.W. & Glover, M.R.L.,** A study of the kinetics of adsorption of gold and zinc cyanide onto a strong base anion exchange resin using a mini-column technique, Hydrometallurgy, 26, 1991, pp 151-162.

34 **SAS/STAT Users Guide,** Version 6, Edition 4, Volume 2, SAS Inc, Cary, NC, USA, 1990.

35 **Moore, D.S. & McCabe, G.P.,** Introduction to the practice of statistics, W.H. Freeman and Company, New York, 1989.

36 **Levenspiel, O.,** Chemical engineering reaction, 2nd Edition, John Wiley & Sons, Inc., New York, 1972.

37 **Afewu, K.I.,** Scale-up of the CIP processes, MSc Dissertation, University of the Witwatersrand, 1992.

38 **Dranoff, J.S. & Lapidus, L.,** Multicomponent ion exchange column calculations, Industrial and Engineering Chemistry, Vol. 50, No. 11, Nov 1958, pp 1648-1653.

39 **Dods, R., Hudson, P.I., Kershenbaum, L. & Streat, M.,** The operation and modelling of a periodic, countercurrent, solid-liquid reactor, Chemical Engineering Science, Vol. 28, 1973, pp 1233-1248.

40 **Wang, M.L., Lio'i, C.T. & Chang, R.Y.,** Numerical technique for solving partial differential equations with applications to adsorption process, Computers and Chemical Engineering, Vol. 4, 1980, pp 85-92.

41 **Acrivos, A.,** Method of characteristic technique - application to heat and mass transfer problems, Industrial and Engineering Chemistry, Vol. 48, No. 4, April 1956, pp 703-710.

42 **Young, B.D.,** The characterisation of particle shape and surface texture and its impact on mass and momentum transfer and particle abrasion, PhD Thesis, University of the Witwatersrand, 1989.

43 **Petersen, F.W. & Van Deventer, J.S.J.,** The interaction between organics and metal complexes in adsorption columns, Minerals Engineering, Vol. 5, No. 1, pp 1-16, 1992.

APPENDIX 1 - Data used for the validation of the Experimental Technique (Chapter 3).

OH KINETIC DATA (SECTION 3.3.1.1)

Figure 3.2

DATA 1: W =50.16g, C_o =0.0992M, V =3litres, T =80°C.

Time	C	C/C_o
0.0	0.0992	1.000
0.5	0.0934	0.942
1.0	0.0926	0.933
1.5	0.0917	0.924
2.0	0.0913	0.920
2.5	0.0905	0.912
3.0	0.0905	0.912
3.5	0.0901	0.908
4.0	0.0880	0.887
4.5	0.876	0.883
5.0	0.876	0.883

DATA 2: W =50.05g, C_o =0.0990M, V =3litres, T =90°C.

Time	C	C/C_o
0.0	0.0990	1.000
0.5	0.0938	0.947
1.0	0.0913	0.922
1.5	0.0913	0.922
2.0	0.0909	0.918
2.5	0.0899	0.908
3.0	0.0888	0.897
3.5	0.0888	0.897
4.0	0.0880	0.889
4.5	0.0876	0.885
5.0	0.0872	0.881

DATA 3: W =50.06g C_o =0.0988M, V =3litres, T =100°C.

Time	C	C/C_o
0.0	0.0988	1.000
0.5	0.0930	0.941
1.0	0.0917	0.928
1.5	0.0905	0.916
2.0	0.0897	0.908
2.5	0.0894	0.905
3.0	0.0892	0.903
3.5	0.0884	0.895
4.0	0.0880	0.891
4.5	0.0867	0.878
5.0	0.0863	0.873

OH^- EQUILIBRIUM DATA (SECTION 3.3.1.1)

Figure 3.3

DATA 1: T = 80°C.

C	Q
0.0992	0.5237
0.1405	1.1432
0.1801	1.7943
0.2194	2.4641
0.2580	0.32596

DATA 2: T = 100°C.

C	Q
0.1006	0.5468
0.1418	1.1302
0.1821	1.8418
0.2200	2.5116
0.2588	3.3328

DATA 3: T = 115°C.

C	Q
0.1070	0.5997
0.1470	1.2293
0.1965	1.9129
0.2248	2.5965
0.2635	3.3461

OH^- EQUILIBRIUM DATA (SECTION 3.3.1.2)

Figure 3.4

DATA 1: T = 60°C, V = 3litres, C_o = 0.3441M.

W	C	Q
70.080	0.3174	1.1430
65.069	0.3283	0.7285
60.010	0.3309	0.6599
55.054	0.3350	0.4959
50.075	0.3389	0.3115
45.021	0.3406	0.2332
40.032	0.3423	0.1349
35.041	0.3435	0.0514

DATA 2: T = 100°C, V = 3litres, C_o = 0.3298M.

W	C	Q
70.108	0.3071	0.9714
65.012	0.3123	0.8075
61.007	0.3158	0.6884
55.034	0.3189	0.5942
50.024	0.3211	0.5217
45.012	0.3239	0.3932
40.045	0.3270	0.2100

DATA 3: T = 115°C, V = 3litres, C_o = 0.3298M.

W	C	Q
70.026	0.3156	0.5998
65.001	0.3175	0.5677
60.177	0.3193	0.6235
55.021	0.3212	0.4689
50.023	0.3246	0.4198
45.130	0.3246	0.3457
40.034	0.3266	0.3298

OH KINETIC DATA (SECTION 3.3.1.3).

Figures 3.5 & 3.6

DATA 1: W = 15.005g, V = 1.5litres, C_o = 0.3738M.

Time	C	C/C_o	Q
0.0	0.3738	1	0.0
2.0	0.3439	0.920	2.9898
4.0	0.3421	0.915	2.9405
6.0	0.3401	0.910	2.8825
8.0	0.3386	0.906	2.8355
10.0	0.3386	0.906	2.6098

DATA 2: W = 14.972g, V = 1.5litres, C_o = 0.3193M.

Time	C	C/C_o	Q
0.0	0.3193	1.000	0.0
2.0	0.2983	0.934	2.1039
4.0	0.2930	0.918	2.4294
6.0	0.2895	0.907	2.5839
8.0	0.2877	0.901	2.5709
10.0	0.2877	0.901	2.792

DATA 3: W = 14.994g, V = 1.5litres, C_o = 0.2070M.

Time	C	C/C_o	Q
0.0	0.2070	1.000	0.0000
2.0	0.1965	0.949	1.0504
4.0	0.1908	0.922	1.4884
6.0	0.1895	0.915	1.4912
8.0	0.1886	0.911	1.4550
10.0	0.1886	0.911	1.5889

DATA 4: W = 15.075g, V = 1.5litres, C_o = 0.1105M.

Time	C	C/C_o	Q
0.0	0.1105	1.000	0.0000
2.0	0.1035	0.937	0.6865
4.0	0.1018	0.921	0.7948
6.0	0.0983	0.890	1.0744
8.0	0.0974	0.881	1.0983
10.0	0.0947	0.857	1.2947

DATA FOR AU KINETIC EXPERIMENT (SECTION 3.3.2.1).

Figure 3.7

DATA 1: W =50.01g, V =3liters, C_o =39.36ppm, T =80°C.

Time	C	C/C_o
0.0	39.36	1.0000
0.5	32.49	0.8255
1.0	25.53	0.6486
1.5	19.66	0.4994
2.0	13.82	0.3510
2.5	11.02	0.2800
3.0	9.67	0.2457
3.5	8.57	0.2177
4.0	7.79	0.1979
4.5	7.12	0.1809
5.0	6.74	0.1710

DATA2: W =50.06g, V =3litres, C_o =40.41ppm, T = 100°C,

Time	C	C/C_o
0.0	40.41	1.0000
0.5	33.38	0.8255
1.0	28.53	0.7060
1.5	25.44	0.6295
2.0	23.55	0.5828
2.5	20.48	0.5068
3.0	17.84	0.4415
3.5	15.38	0.3806
4.0	14.80	0.3662
4.5	14.44	0.3573
5.0	14.17	0.3507

DATA 3: W =50.02g, V = 3litres, C_o =33.84ppm, T =115°C.

Time	C	C/C_o
0.0	33.84	1.0000
0.5	29.72	0.8829
1.0	27.72	0.8191
1.5	25.92	0.7666
2.0	24.36	0.7199
2.5	23.46	0.6933
3.0	21.84	0.6454
3.5	21.06	0.6223
4.0	20.16	0.5957
4.5	19.62	0.5798
5.0	18.87	0.5559

DATA FOR AU EQUILIBRIUM EXPERIMENT (SECTION 3.3.2.1)

Figure 3.8

DATA 1: T = 80°C, C_o = 40.20ppm, V = 3litres.

W	C	Q_e
49.964	8.66	1.892
45.026	8.84	2.090
40.017	9.09	2.332
35.030	9.36	2.641
30.031	9.61	3.056
25.001	10.21	3.60

DATA 2: T = 100°C, C_o = 39.45ppm, V = 3litres.

W	C	Q
50.096	11.93	1.564
45.031	12.09	1.823
40.001	12.18	2.045
35.014	12.63	2.298
30.003	12.97	2.646
25.078	13.50	3.104

DATA 3: T = 115°C, C_0 = 36.95ppm, V = 3litres.

W	C	Q
50.018	15.36	1.295
45.014	16.18	1.384
40.033	17.18	1.482
35.010	17.26	1.687
30.001	17.56	1.939
25.010	17.84	2.292

DATA FOR GOLD KINETIC EXPERIMENT (SECTION 3.3.2.2).

Figures 3.9 & 3.10.

DATA 1: W = 15.019g, V = 1.5l, C_o = 36.80ppm

Time	C	Q	C/C_o
0	36.80	0	1.000
2	6.89	2.987	0.187
4	3.06	3.365	0.083
6	2.21	3.448	0.060
8	1.77	3.493	0.48
10	1.55	3.514	0.042

DATA 2: W = 15.009g, V = 1.5l, C_o = 32.68ppm.

Time	C	Q	C/C_o
0	32.68	0	1.000
2	10.14	2.253	0.307
4	2.63	2.996	0.80
6	1.10	3.148	0.033
8	0.65	3.192	0.020
10	0.47	3.209	0.014

DATA 3: W = 15.009g, V = 1.5l, C_o = 27.01ppm.

Time	C	Q	C/C_o
0	27.01	0	1.000
2	4.36	2.2~~8~~7	0.161
4	1.14	2.584	0.042
6	0.56	2.641	0.021
8	0.37	2.659	0.014
10	0.31	2.665	0.011

DATA 4: W = 15.000g, V = 1.5l, C_o = 184.17ppm.

Time	C	Q	C/C_o
0	184.17	0	1
3	75.83	10.834	0.412
5.5	59.33	12.433	0.322
7.5	48.50	13.477	0.263
9.5	39.00	14.395	0.212

DATA 5: W = 14.999g, V = 1.5l, C_o = 489.25ppm.

Time	C	Q	C/C_o
0	489.25	0	1.000
2	304.50	18.476	0.622
4	252.60	23.464	0.516
6	247.00	23.855	0.505
8	238.20	24.571	0.487
10	230.50	25.182	0.471

DATA 6: W = 15.006g, V = 1.5l, C_o = 49.33ppm.

Time	C	Q	C/C_o
0	49.33	0	1.000
2	10.58	3.873	0.214
4	4.65	4.459	0.094
6	3.01	4.620	0.061
10	2.02	4.717	0.041

NOTE : Time = Time of Sampling (Hours)

C = Concentration of the sample (ppm)

W = Weight of carbon used (g)

C_o = Initial concentration (ppm)

Q = Loading of gold on the carbon (mg/g C)

V = Volume of solution in the system (litres).

APPENDIX 2 - Equilibrium Experimental data - Single and multiple solute data (Chapter 4).

DATA FOR HYDROXIDE ION SINGLE SOLUTE EQUILIBRIUM EXPERIMENT.

DATA 1: Volume of Solution = 1.5l, Temperature = 80°C.

C_o	W	C_b	Q_e
0.0667	15.006	0.0614	0.5261
0.1068	15.008	0.0957	1.2033
0.2070	15.033	0.1886	1.5889
0.3193	15.011	0.2877	2.3792
0.3738	15.001	0.3386	2.6098
0.4974	15.018	0.4667	3.0667
0.5510	15.009	0.5147	3.6278
0.6000	15.002	0.5614	3.8594

$$Q_e = 6.2041 C_e^{0.8090}, \quad R = 0.9806$$

DATA 2: Volume of Solution =1.575l, Temperature =100°C.

C_o	W	C_e	Q_e
0.0618	15.052	0.0569	0.5127
0.1034	15.001	0.0956	0.8673
0.1938	15.006	0.1807	1.3719
0.3041	15.054	0.2895	1.7132
0.3710	15.000	0.3509	2.1054
0.5123	15.001	0.4878	2.4561
0.5551	15.004	0.5315	2.7525
0.5949	15.014	0.5701	2.8906

$$Q_e = 4.3214C_e^{0.7145}, \quad R = 0.9956$$

DATA 3: Volume of Solution =1.5l, Temperature =115°C.

C_o	W	C_e	Q_e
0.0561	15.009	0.0503	0.5797
0.1035	15.002	0.0947	0.8799
0.2053	15.003	0.1930	1.2274
0.3158	15.027	0.3018	1.4011
0.4070	15.032	0.3877	1.9258
0.5103	15.002	0.4881	2.2100
0.5630	15.009	0.5403	2.2269
0.6124	15.011	0.5891	2.3283

$$Q_e = 3.1340 C_e^{0.5614}, \quad R = 0.9928$$

NOTE: C_o = Initial concentration of OH^- ion (Molar).

W = Weight of Carbon used (g).

C_e = Equilibrium concentration of OH^- (Molar).

V = Volume of Solution used.

Q_e = Equilibrium loading (mmoles/g of Carbon).

$Q_e = V (C_o - C_e) / W.$

DATA FOR GOLD SINGLE SOLUTE EQUILIBRIUM EXPERIMENT.

DATA 1: Volume of Solution = 1.5l, Temperature = 80°C.

C_e	Q_e
0.56	2.641
1.10	3.148
2.21	3.448
3.01	4.620
59.33	12.433
124.00	18.082
247.00	23.855

$$Q_e = 2.9866 C_e^{0.3675}, \quad R = 0.9959$$

DATA 2: Volume of Solution =1.5l, Temperature =100°C.

W	C_o	C_e	Q_e
15.020	65.17	20.16	4.495
15.026	72.00	23.17	4.675
15.004	128.67	67.30	6.135
15.017	182.50	106.86	7.555
15.005	236.16	155.17	8.096
15.019	261.50	175.83	8.556
15.002	383.84	279.25	10.458

$$Q_e = 1.7383\ C_e^{0.3108},\quad R = 0.9951$$

DATA 3: Volume of Solution =1.5l, Temperature =115°C.

W	C_o	C_e	Q_e
15.053	95.15	10.75	2.431
15.002	47.14	17.00	3.014
15.017	69.12	32.83	3.625
15.009	106.75	62.33	4.439
14.999	160.87	109.00	5.187
15.000	223.47	167.75	5.572
15.049	333.60	266.75	6.663

$$Q_e = 1.2520\ C_o^{0.2996},\quad R = 0.9959$$

NOTE: C_o = Initial concentration of Gold (ppm).

W = Weight of Carbon used (g).

C_e = Equilibrium concentration of Gold (ppm).

V = Volume of Solution used.

Q_e = Equilibrium loading (mg/g of Carbon).

$Q_e = V (C_o - C_e) / W.$

SIMULTANEOUS ADSORPTION OF GOLD AND HYDROXIDE ION EQUILIBRIUM DATA DATA 1: Volume of Solution = 1.5l, Temperature = 80°C..

W	AU			OH		
	C_c	C_e	Q_e	C_c	C_e	Q_e
15.031	12.887	4.51	0.836	0.0650	0.056	0.898
15.038	53.46	23.50	2.988	0.1251	0.112	1.307
15.023	131.07	79.61	5.138	0.2267	0.211	1.568
15.004	189.92	101.90	8.800	0.2859	0.269	1.690
14.999	265.49	146.50	11.900	0.3527	0.334	1.870
15.020	405.50	245.19	16.010	0.4164	0.397	1.937
15.032	652.02	427.54	22.400	0.4961	0.475	2.106

AU DATA

$$Q_e = 0.2789 C_e^{0.7290}, \quad R = 0.9931$$

OH DATA

$$Q_e = 2.8140 C_e^{0.3807}, \quad R = 0.9930$$

DATA 2: Volume of Solution =1.5l, Temperature =100°C.

W	AU			OH		
	C_o	..... C_e	Q_e	C_o	C_e	Q_e
15.016	16.75	12.50	0.425	0.085	0.078	0.749
15.012	56.80	41.00	1.579	0.125	0.113	0.874
15.024	120.48	99.5	3.093	0.221	0.209	1.159
15.028	166.20	122.85	4.327	0.261	0.248	1.270
15.022	344.63	268.40	7.612	0.336	0.322	1.391
15.088	512.00	418.75	10.165	0.361	0.366	1.501
15.033	684.75	535.00	14.942	0.516	0.499	1.750

AU DATA

$$Q_e = 0.0491C_e^{0.9071}, \quad R=0.9962$$

OH DATA

$$Q_e = 2.372C_e^{0.455}, \quad R = 0.9993$$

DATA 3: Volume of Solution =1.5l, Temperature =115°C.

W	AU			OH		
	C_o	C_e	Q_e	C_o	C_e	Q_e
15.005	37.07	34.25	0.282	0.055	0.048	0.431
15.009	55.77	50.95	0.482	0.095	0.089	0.545
15.040	111.31	100.01	1.127	0.172	0.165	0.740
15.013	193.34	165.34	2.798	0.219	0.211	0.842
15.008	235.12	199.50	3.560	0.298	0.286	1.112
15.012	345.29	302.25	4.301	0.385	0.372	1.299
15.002	467.74	416.52	5.121	0.500	0.485	1.500

AU DATA

$$Q_e = 0.0040C_e^{1.2308}, \quad R = 0.9852$$

OH DATA

$$Q_e = 2.160C_e^{0.555}, \quad R = 0.9913$$

APPENDIX 3 - Kinetics of Elution data and the Model Fits (Chapter 6).

DATA ON THE EFFECT OF VARYING PRESOAKING PERIODS.

The elution of gold from Knight's loaded carbon after preatreatment with 20g/l NaCN and 20g/l NaOH solution.

Condition of Presoaking: Cold presoaking for the period indicated according to the experiment followed by washing of the carbon with distilled water to a pH of 7 before elution.

Elution Temperature = 125°C.

Volume of Presoaking solution = 200ml.

% Aveerge CN consumed per gram of carbon during presoaking = 0.0254

Particle size of Carbon = +1.70 to -2.36mm

Experiment 1 - Presoaking period = 14 hours.

Weight of Loaded Carbon treated = 20.084g

Time/Minutes	C_e/ppm
00	22.34
15	8.91
30	3.48
45	1.58
60	0.85
75	0.80
90	0.74
105	0.56
120	0.50
156	0.26
210	0.24
246	0.19
303	0.12
370	0.12

Experiment 2 - Presoaking period = 6 hours.
Weight of carbon treated = 20.060g.

Time/Minutes	C_o/ppm
00	11.40
05	13.35
10	8.64
15	8.44
20	6.42
30	4.15
40	2.85
52	2.07
60	1.76
77	1.17
90	0.89
105	0.77
130	0.64
150	0.62
180	0.55
210	0.41
240	0.37
[illegible]	0.28
360	0.22

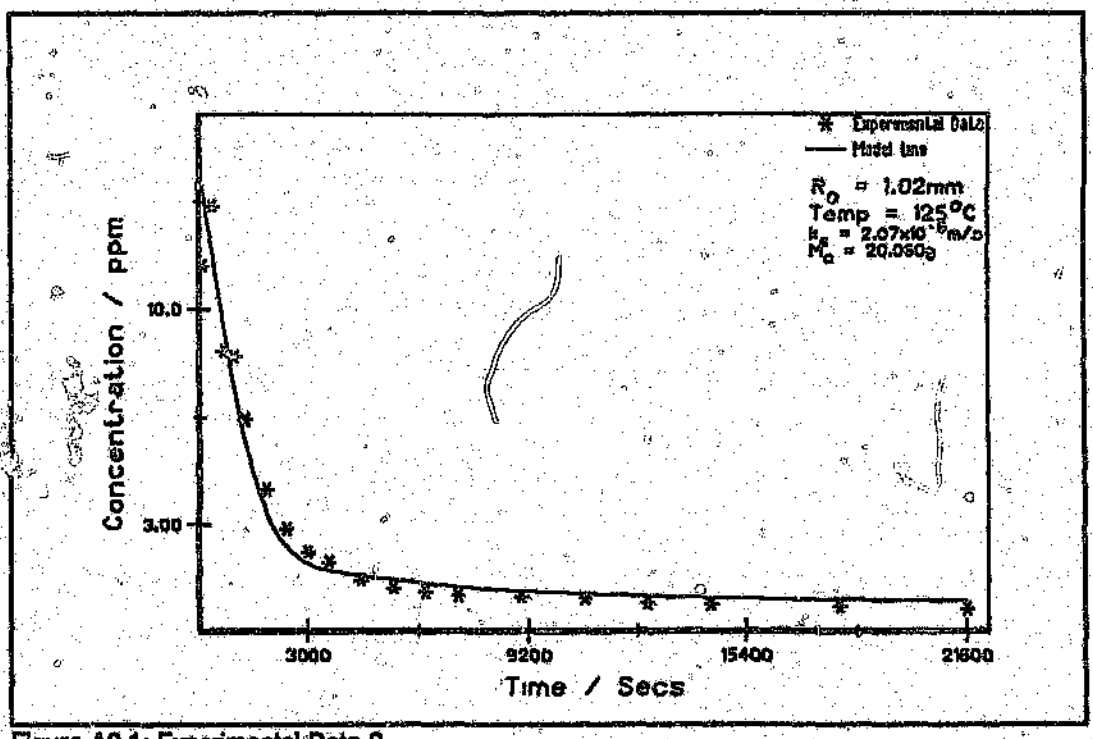


Figure A3.1: Experimental Data 2.

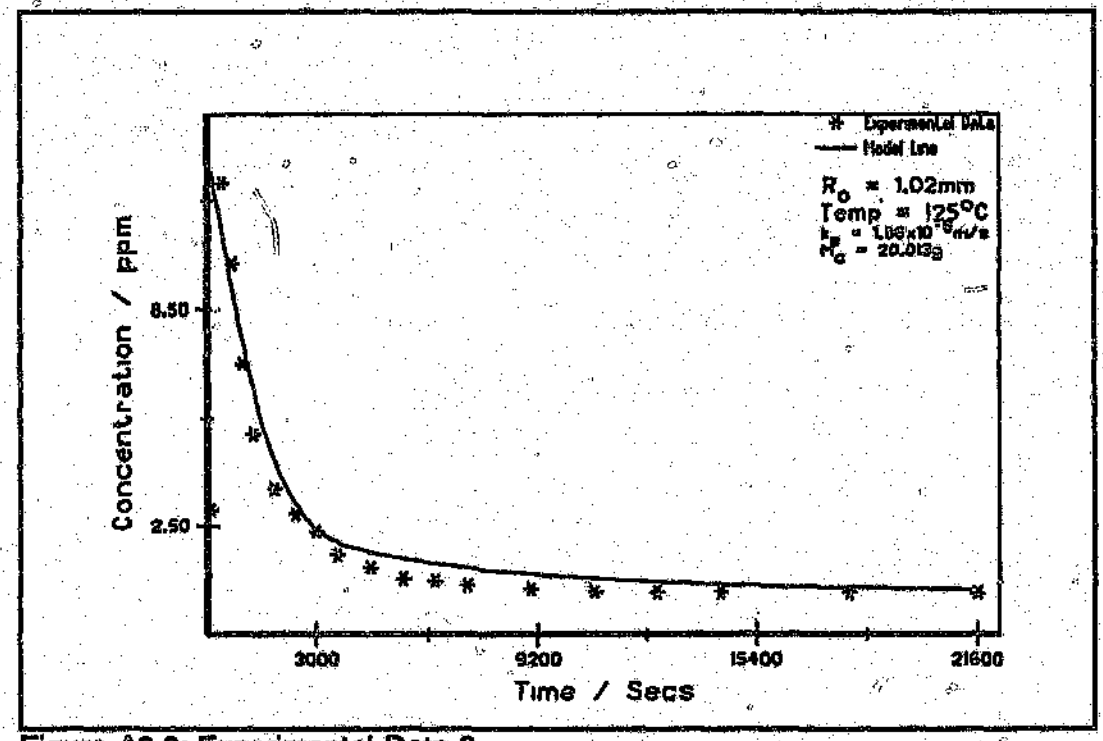


Figure A3.2: Experimental Data 3.

Experiment 3 - Presoaking Period = 4 hours.
Weight of carbon treated =20.013g.

Time/Minute	C_o/ppm
00	2.94
05	11.98
10	9.75
15	7.01
20	5.04
30	3.52
40	2.82
50	2.34
60	1.67
75	1.33
90	1.02
105	0.96
120	0.83
155	0.73
180	0.66
210	0.65
240	0.64
300	0.63
360	0.62

Experiment 4 - Presoaking Period = 2.5 hours.
Weight of Carbon treated = 20.014g.

Time/Minute	C_e/ppm
00	8.23
05	13.94
10	11.43
15	8.65
20	5.08
30	3.86
40	2.73
50	2.70
60	2.14
75	1.47
90	1.06
105	0.88
120	0.82
150	0.66
180	0.63
210	0.57
240	0.53
300	0.48
360	0.47

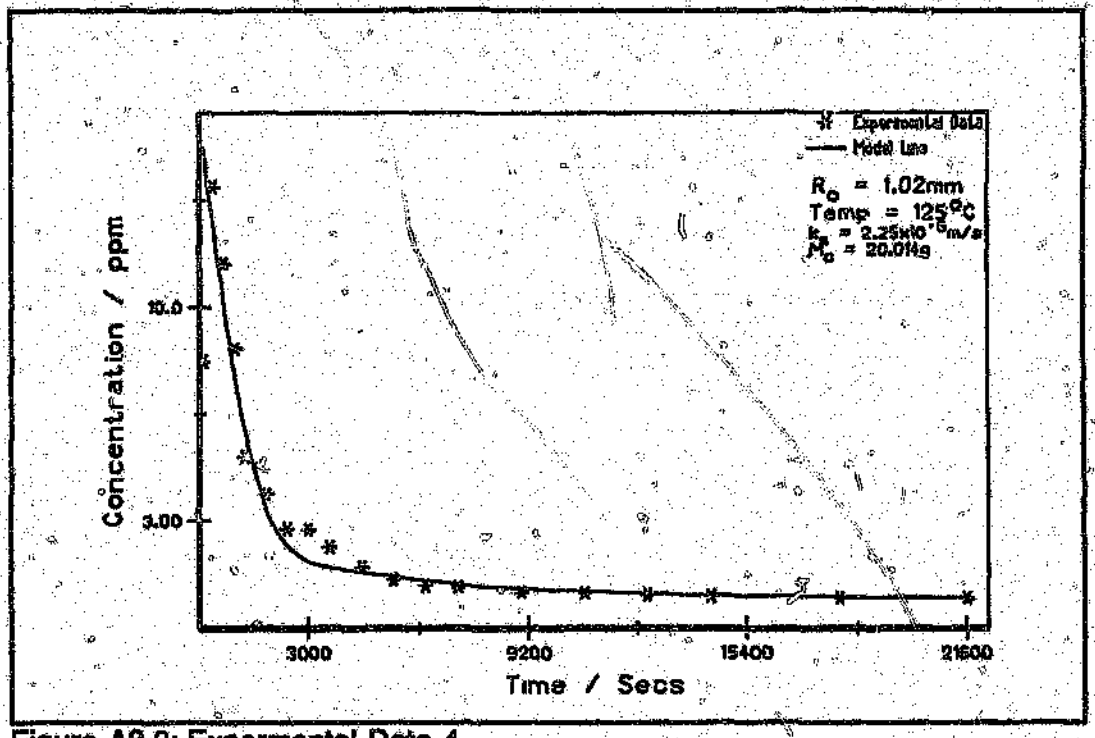


Figure A3.3: Expermental Data 4.

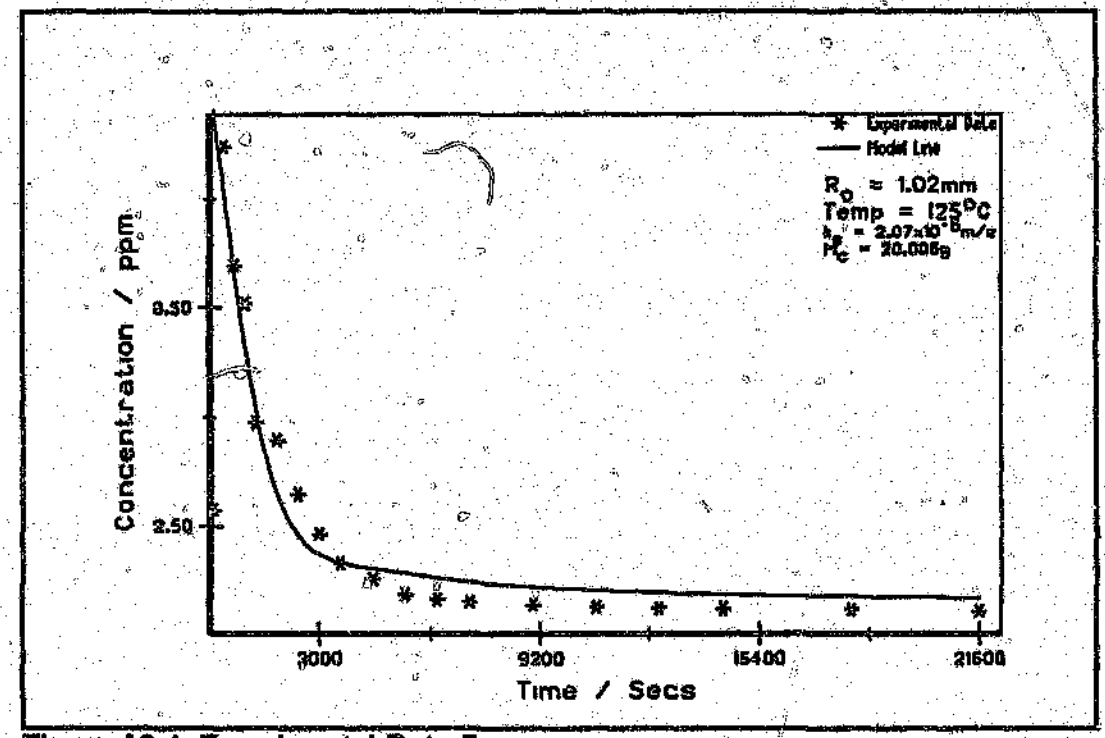


Figure A3.4: Experimental Data 5.

Experiment 5 - Presoaking Period = 1 hour.
Weight of Carbon treated = 20.006g.

Time/Minute	C_t/ppm
00	3.08
05	12.98
10	9.66
15	8.60
20	5.35
30	4.86
40	3.36
50	2.27
60	1.45
75	1.02
90	0.57
105	0.44
120	0.36
150	0.29
180	0.23
210	0.20
240	0.18
300	0.16
360	0.12

Experiment 6.

Weight of Carbon = 20.007g.

Particle size of carbon treated = +1.7 to -2.36mm.

Volume of Presoaking solution = 100mls.

Period of presoaking = 4 hours.

Temperature of presoaking = 20±1°C.

%tage NaCN consumed per gram of Carbon = 0.1522.

Temperature of Elution = 90°C.

Time/Minutes	C_e/ppm
00	5.51
05	4.18
10	1.92
15	1.52
20	1.23
30	1.05
40	0.76
50	0.54
60	0.41
75	0.27
90	0.21
105	0.16
120	0.13
150	0.08
180	0.05
210	0.05
240	0.05
300	0.02

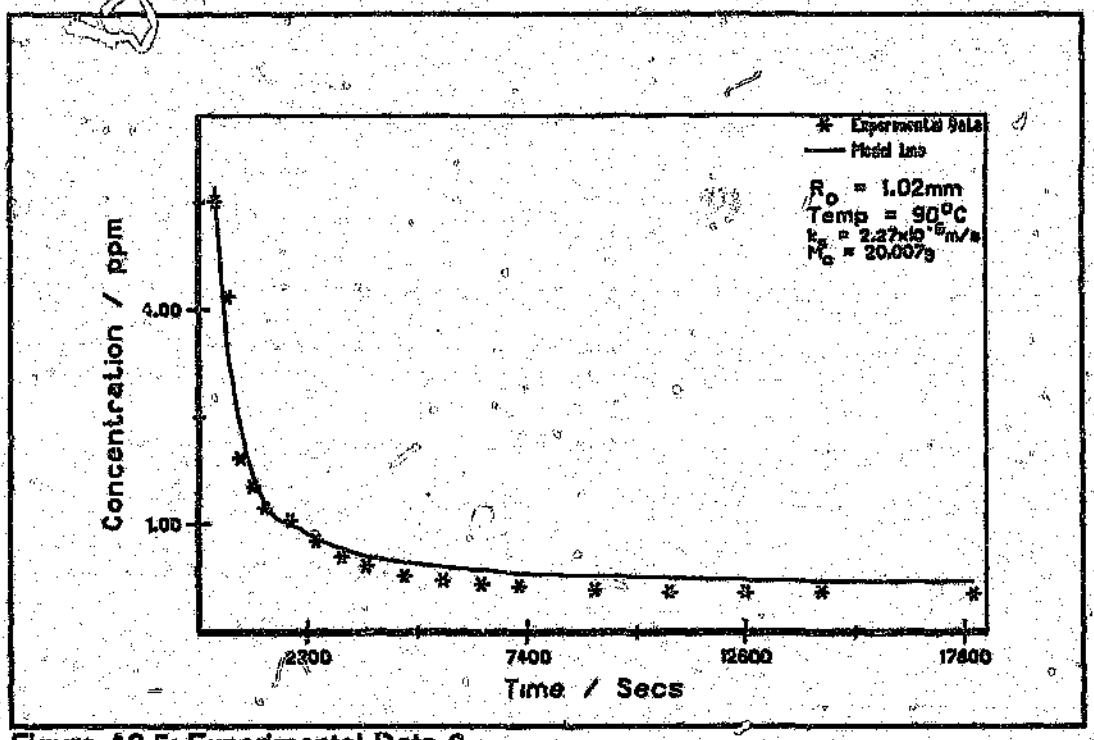


Figure A3.5: Experimental Data 6.

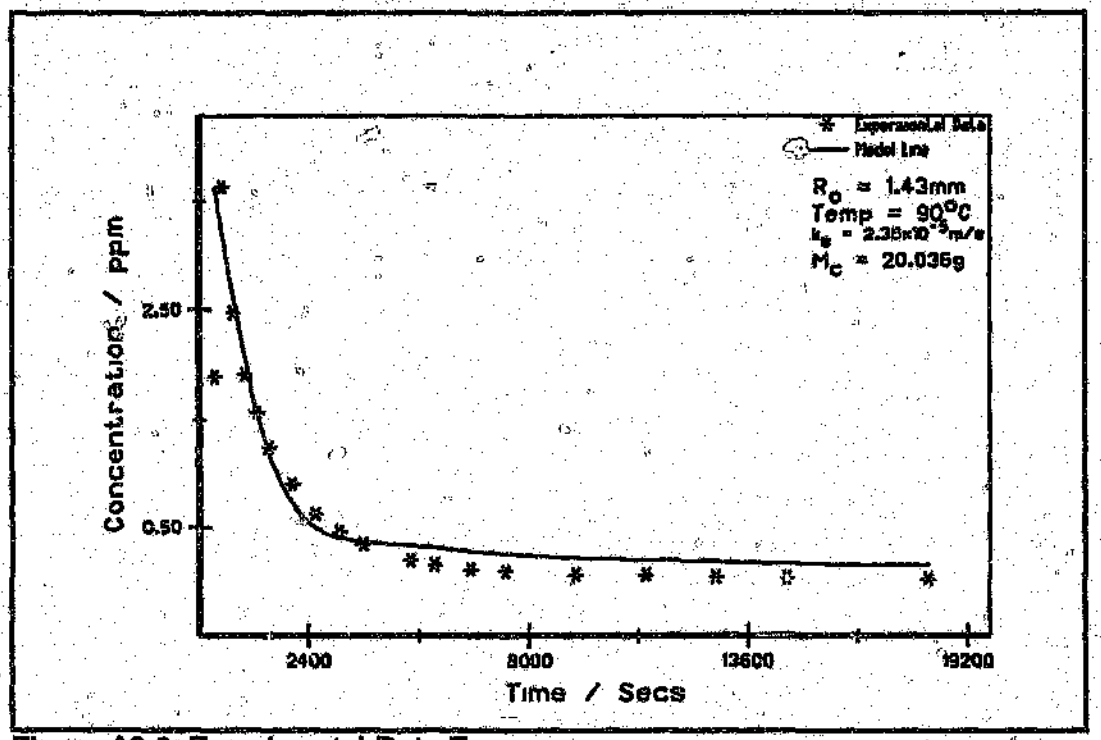


Figure A3.6: Experimental Data 7.

Experiment 7.

Weight of Carbon = 20.036g.

Particle size of carbon treated = +2.36 to -3.35mm.

Volume of Presoaking solution = 100mls.

Period of presoaking = 4 hours.

Temperature of presoaking = 20±1°C.

%tage NaCN consumed per gram of Carbon = 0.1621.

Temperature of Elution = 90°C.

Time/Minutes	C_o/ppm
00	1.69
03	3.63
08	2.47
13	1.91
18	1.56
23	1.24
33	0.90
43	0.62
53	0.46
63	0.34
83	0.19
93	0.15
108	0.11
123	0.09
153	0.06
183	0.06
213	0.04
243	0.03
303	0.02

Experiment 8.

Weight of Carbon = 20.078g.

Particle size of carbon treated = +1.18 to -1.70mm.

Volume of Presoaking solution = 100mls.

Period of presoaking = 4 hours.

Temperature of presoaking = 20±1°C.

%tage NaCN consumed per gram of Carbon = 0.0506.

Temperature of Elution = 90°C.

Time/Minutes	C_n/ppm
00	4.67
03	5.52
08	5.01
13	3.67
18	2.63
23	2.03
33	1.50
43	1.15
53	0.84
63	0.63
78	0.36
93	0.27
108	0.19
123	0.15
153	0.09
213	0.05
243	0.05
	0.05

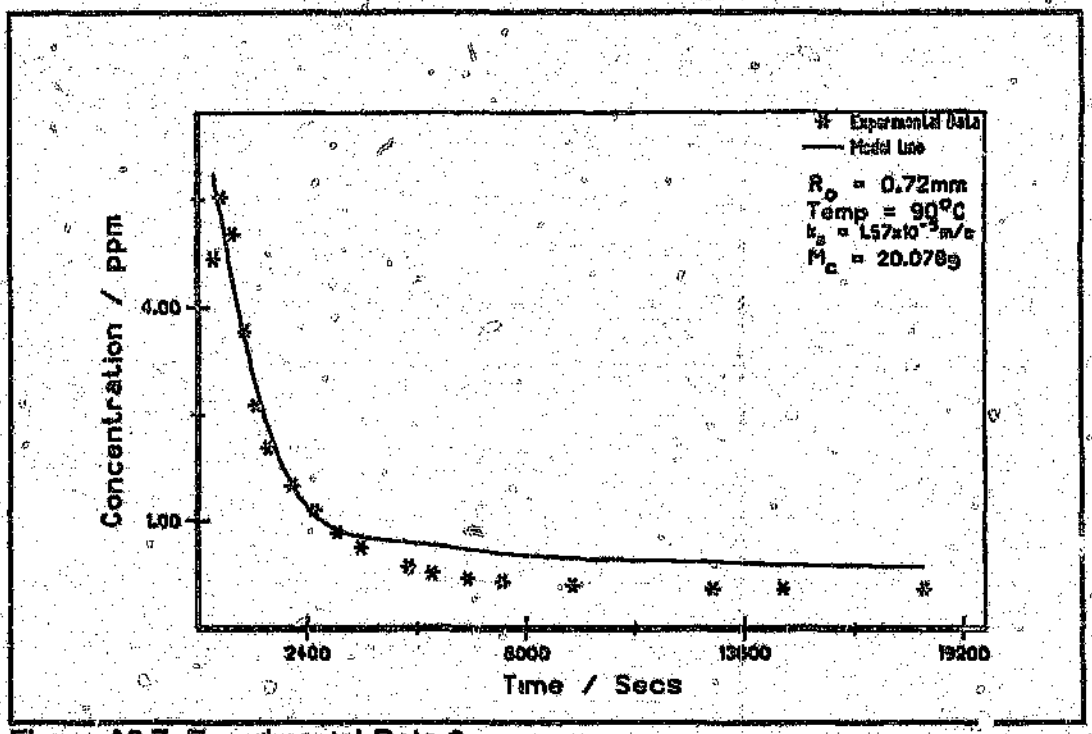


Figure A3.7: Experimental Data 8.

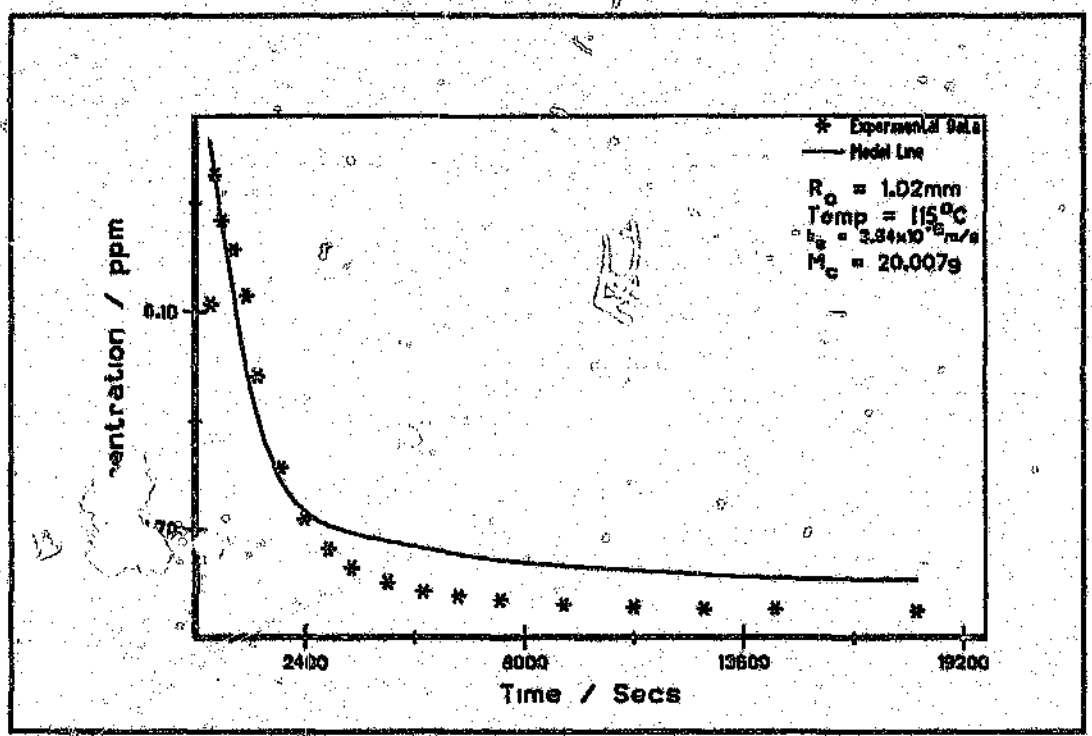


Figure A3.8: Experimental Data 9.

Experiment 9.

Weight of Carbon = 20.007g.

Particle size of carbon treated = +1.70 to -2.36mm.

Volume of Presoaking solution = 100mls.

Period of presoaking = 4 hours.

Temperature of presoaking = 20±1°C.

%tage NaCN consumed per gram of Carbon = 0.1901.

Temperature of Elution = 115°C.

Time/Minutes	C_o/ppm
00	6.26
02	8.87
05	7.94
10	7.35
15	6.43
20	4.80
30	2.95
40	1.90
50	1.29
60	0.91
75	0.61
90	0.43
105	0.33
123	0.26
150	0.16
180	0.12
210	0.08
240	0.08
300	0.05

Experiment 10.

Weight of Carbon = 50.001g.

Particle size of carbon treated = +1.70 to -2.36mm.

Volume of Presoaking solution = 100mls.

Period of presoaking = 4 hours.

Temperature of presoaking = 20±1°C.

Temperature of Elution = 100°C.

Time/min	C_d/ppm
0.00	4.67
06	5.70
11	5.59
16	5.36
21	5.26
31	4.47
41	3.74
51	3.20
61	2.58
76	1.88
91	1.44
106	1.11
121	0.86
151	0.55
181	0.38
211	0.27
241	0.24
301	0.18

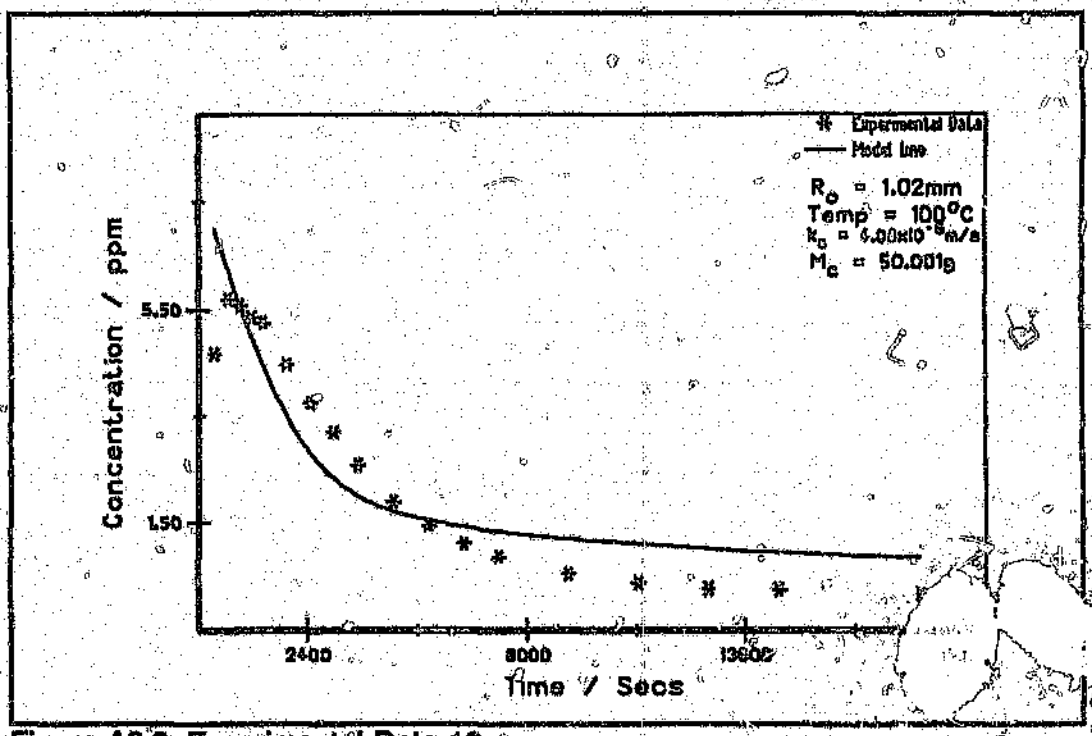


Figure A3.9: Experimental Data 10.

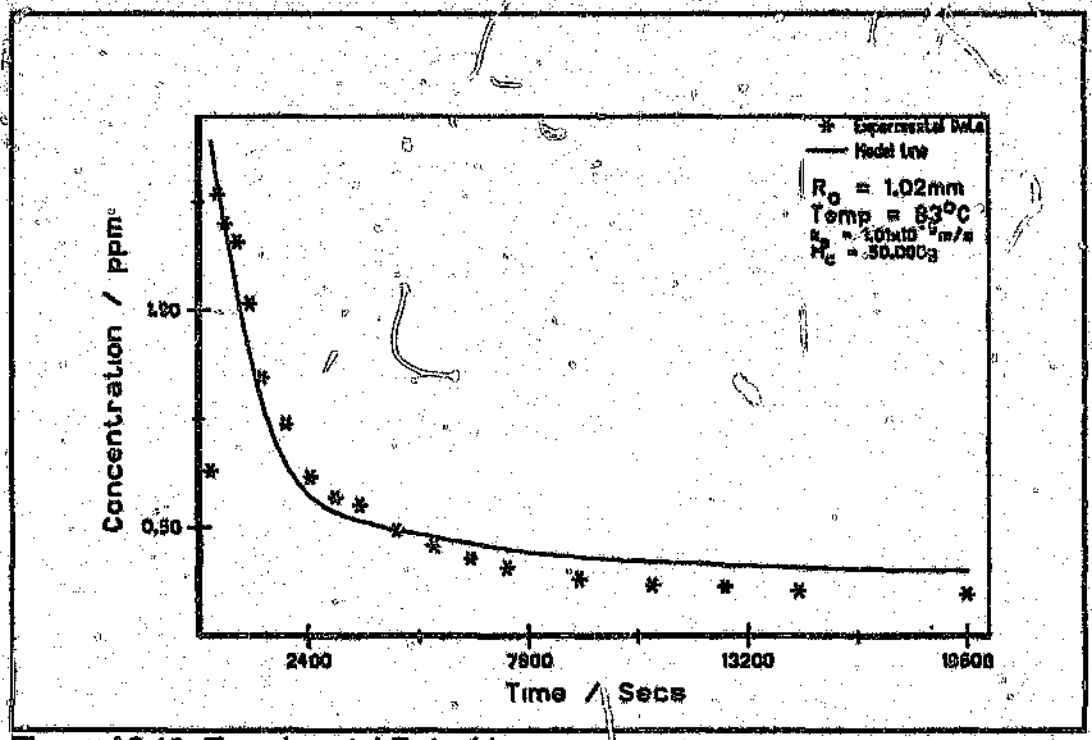


Figure A3.10: Experimental Data 11.

Experiment 11.

Weight of Carbon = 50.006g.

Particle size of carbon treated = +1.70 to -2.36mm.

Volume of Presoaking solution = 100mls.

Period of presoaking = 4 hours.

Temperature of presoaking = 20±1°C.

Temperature of Elution = 83°C.

Time/min	C_t/ppm
0.00	0.86
03	2.65
06	2.46
11	2.34
16	1.94
21	1.46
31	1.16
41	0.82
51	0.69
61	0.64
76	0.48
91	0.38
106	0.30
121	0.24
151	0.17
181	0.13
211	0.12
241	0.09
301	0.07

Experiment 12.

Weight of Carbon = 50.036g.

Particle size of carbon treated = +1.70 to -2.36mm.

Volume of Presoaking solution = 100mls.

Period of presoaking = 4 hours.

Temperature of presoaking = 20±1°C.

Temperature of Elution = 72°C.

Time/Minutes	C_e/ppm
0.00	1.69
05	2.15
10	1.99
15	1.62
20	1.49
30	1.14
40	0.95
50	0.85
60	0.70
75	0.55
90	0.45
105	0.39
120	0.35
150	0.25
180	0.18
210	0.14
240	0.11
300	0.08

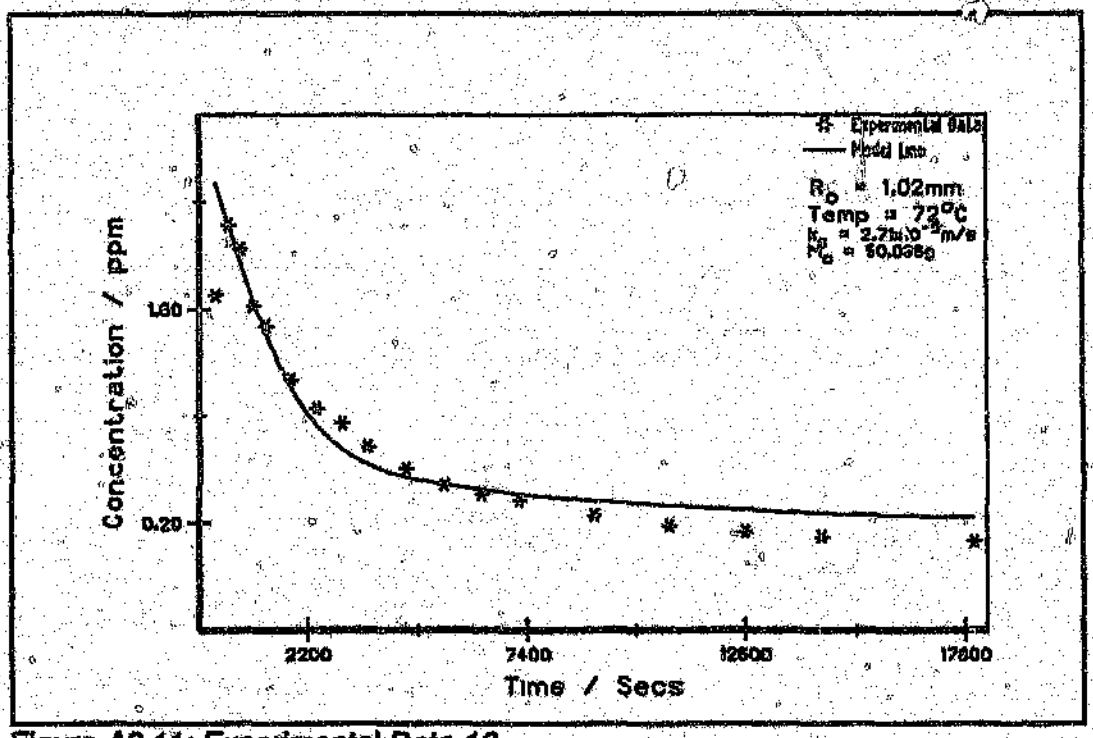


Figure A3.11; Experimental Data 12.

Elution of Unwashed Carbon - Experiment 15.

Weight of Carbon =.50.003g.

Particle size of carbon treated = +1.70 to -2.36mm.

Volume of Presoaking solution = 100mls.

Period of presoaking = 4 hours.

Temperature of presoaking = 20±1°C.

Temperature of Elution = 83°C.

Time/Minutes	C_d/ppm
0.00	2.36
02	3.07
07	3.50
12	3.59
17	3.70
22	3.65
32	3.29
42	3.12
52	2.84
62	2.67
77	2.31
92	1.95
107	1.68
122	1.41
152	1.08
186	0.82
212	0.64
250	0.47
320	0.29

APPENDIX 4 - Computer programmes used.

SAS PROGRAMME TO ESTIMATE THE PARAMETERS OF THE MODIFIED FREUNDLICH ISOTHERM AND THE LINEARIZED FORM BY MINIMIZATION OF THE SUM OF SQUARES OF THE RESIDUALS.

```
GOPTIONS DEVICE = IBM3279;
*GOPTIONS DEVICE = A4AB;
FILENAME IN 'ELI1 DATA';

DATA ELI1;
INFILE IN FIRSTOBS = 1;
INPUT T C Q;
R = 8.31441;

PROC NLIN METHOD = DUD EFORMAT MAXITER = 300;
PARM A0=0.000034 A1=-42500 A2=0.32;
MODEL Q=A0*EXP(-A1/(R*T))*(C**A2);
OUTPUT OUT=B P=Q2HAT R=Q2RESID;
RUN;
PROC PRINT;
SYMBOL1 V='A' C=RED;
SYMBOL2 V='P' C=GREEN;
SYMBOL3 V='STAR' C=RED;
PROC GPLOT DATA=B;
TITLE 'AU SINGLE-SOLUTE MODEL';
  PLOT Q*C Q2HAT*C / OVERLAY;
   PLOT Q2RESID*C=3 / VREF=0;
RUN;
PROC UNIVARIATE DATA=B NORMAL PLOT;
   VAR Q2RESID;
```

CORRELATIONS OBTAINED FROM THE PARAMETERS

Table A4.1: MODEL-MFI, DATA-OH

CORRELATION	A_0	ΔH	n
A_0	1	0.9962	0.0197
ΔH	0.9962	1	-0.0582
n	0.0198	-0.0582	1

Table A4.2: MODEL-MFI, DATA-AU

CORRELATION	A_0	ΔH	n
A_0	1	0.9867	-0.1734
ΔH	0.9867	1	-0.0138
n	-0.1734	-0.0138	1

Table A4.3: MODEL-LMFI, DATA-OH.

CORRELATION	B_0	B_1	B_2
B_0	1	0.9872	-0.2241
B_1	0.9872	1	-0.0941
B_2	-0.2241	-0.0941	1

Table A4.4: MODEL-LMFI, DATA-AU.

CORRELATION	A_0	B_1	B_2
B_0	1	0.9895	-0.3322
B_1	0.9895	1	-0.1971
B_2	-0.3322	-0.1973	1

SAS PROGRAMME TO ESTIMATE THE PARAMETERS OF THE MULTIPLE-SOLUTE ISOTHERMS BY MINIMIZATION OF THE SUM OF SQUARES OF THE RESIDUALS.

```
GOPTIONS DEVICE = IBM3279;
*GOPTIONS DEVICE = A4AB;
FILENAME IN 'ELI DATA';

DATA ELI;
INFILE IN FIRSTOBS = 3;
INPUT T C1 Q1 C2 Q2;
R = 8.31441;
B0 = 3.530515E-2;
B1 = -14854.8;
B3 = 0.6984184;
RT = R*T;
LF = B0*EXP(-B1/RT);

PROC NLIN METHOD = DUD EFORMAT MAXITER = 300;
PARM A1=0.34 A5=100 A6=0.62 A7=0.09 A8=0.07;
MODEL Q2=(LF*C2**B3)/(A1+A5*C2**A6+A7*C1**A8);
OUTPUT OUT=B P=Q2HAT R=Q2RESID;
RUN;
PROC PRINT;
SYMBOL1 V='A' C=RED;
SYMBOL2 V='P' C=GREEN;
SYMBOL3 V='STAR' C=RED;
PROC GPLOT DATA=B;
TITLE 'AU & OH SIMULTANEOUS OH1 MULTIPLE-SOLUTE MODEL';
  PLOT Q2*C2 Q2HAT*C2 / OVERLAY;
  PLOT Q2RESID*C2=3 / VREF=0;
```

```
RUN;
PROC UNIVARIATE DATA=B NORMAL PLOT;
   VAR Q2RESID;
```

PROGRAM TO SOLVE DIFFUSION AND MASS TRANSFER PROBLEM.

```
C
      PROGRAM ELUTE
C
C  STANDARD FORTRAN 77 PROGRAMME USING THE NAG LIBRARY
C
C  INTEGER NAMED CONSTANTS:
C
      INTEGER IU, NPDES, MAXITR, MAXNX, IWK
      PARAMETER ( IU = 1, NPDES = 1, MAXITR = 1000, MAXNX =
     +            100, IWK = 500 )
C
C  DOUBLE PRECISION NAMED CONSTANTS:
C
C  R   - ISOTHERM PARAMETER
C
      DOUBLE PRECISION R, ONE
      PARAMETER ( R = 8.3144D0, ONE = 1.0D0 )
C
C  LOCAL INTEGER SCALARS:
C
C  NX   - THE NUMBER OF RADIAL POINTS IN THE CARBON
C  NBED - THE NUMBER OF DESCRITISED COLUMN HEIGHTS
C  ITR  - THE MAXIMUM NUMBER OF ITERATIONS
C
      INTEGER I, L, K, IND, IFAIL, NX, NBED, ITR, INORM, IMON,
     +        IBAND, M, INDIN, IFIN
C
C  LOCAL DOUBLE PRECISION ARRAYS AND SCALARS:
C
C  AL   - LENGTH OF THE CARBON BED
C  H1   - LENGTH OF THE COLUMN
C  RF   - FLOWRATE OF SOLUTION THROUGH THE COLUMN
C  RO   - CARBON PARTICLE SIZE
C  MS   - MASS OF SOLUTION IN THE COLUMN
C  EPS  - COLUMN VOIDAGE
C  MC   - MASS OF CARBON
C  H2, SIGMA, TEMP, AO - ISOTHERM PARAMETERS
```

```
C
      DOUBLE PRECISION X(MAXNX), Y(IU,MAXNX), CCC(MAXITR),
     +                 WK(IWK), CS, SO, TO, TEND, AL, YINIT,
     +                 H1, RF, RO, MS, EPS, H2, TEMP, AO,
     +                 RELERR, ABSERR, MC, SIGMA, CONS1,
     +                 CONS2, CONS3, CONS4, CONS5, DNBED,
     +                 TIMINC, TIME, CCINIT
C
C  LOCAL CHARACTER ARRAYS:
C
      CHARACTER*24 W1(33), CS2*7
C
C  GLOBAL DOUBLE PRECISION SCALARS:
C
C  DS   - DIFFUSSION COEFFICIENT OF THE CARBON
C  RHO  - PARTICLE DENSITY
C  KS   - THE FILM MASS TRANSFER COEFFICIENT
C  CC   - INLET CONCENTRATION
C
      DOUBLE PRECISION DS, RHO, KS, CC, A, BETA
      COMMON / CM1 / DS,
     +     / CM2 / RHO, KS, CC, A, BETA
C
      EXTERNAL D03PGF, PDEF, BNDY, D03PAZ
C
      INTRINSIC SIN, EXP, DBLE
C
      DATA W1(1)  / '(T2,"NX    = ",I22,/,  ' /,
     +     W1(2)  / 'T2,"NBED  = ",I22,/,  ' /,
     +     W1(3)  / 'T2,"ITR   = ",I22,/,  ' /,
     +     W1(4)  / 'T2,"IU    = ",I22,/,  ' /,
     +     W1(5)  / 'T2,"NPDES = ",I22,/,  ' /,
     +     W1(6)  / 'T2,"INORM = ",I22,/,  ' /,
     +     W1(7)  / 'T2,"IMON  = ",I22,/,  ' /,
     +     W1(8)  / 'T2,"IBAND = ",I22,/,  ' /,
     +     W1(9)  / 'T2,"IWKMIN = ",I22,/,  ' /,
     +     W1(10) / 'T2,"M     = ",I22,/,  ' /,
     +     W1(11) / 'T2,"INDIN = ",I22,/,  ' /,
```

```
     +    W1(12) / 'T2,"IFIN   = ",I22,/,   ' /,
     +    W1(13) / 'T2,"H1     = ",E22.15,/,' /,
     +    W1(14) / 'T2,"AL     = ",E22.15,/,' /,
     +    W1(15) / 'T2,"RF     = ",E22.15,/,' /,
     +    W1(16) / 'T2,"RO     = ",E22.15,/,' /,
     +    W1(17) / 'T2,"MS     = ",E22.15,/,' /,
     +    W1(18) / 'T2,"EPS    = ",E22.15,/,' /,
     +    W1(19) / 'T2,"H2     = ",E22.15,/,' /
     DATA W1(20) / 'T2,"TEMP   = ",E22.15,/,' /,
     +    W1(21) / 'T2,"AO     = ",E22.15,/,' /,
     +    W1(22) / 'T2,"R      = ",E22.15,/,' /,
     +    W1(23) / 'T2,"RELERR = ",E22.15,/,' /,
     +    W1(24) / 'T2,"ABSERR = ",E22.15,/,' /,
     +    W1(25) / 'T2,"X(1)   = ",E22.15,/,' /,
     +    W1(26) / 'T2,"DS     = ",E22.15,/,' /,
     +    W1(27) / 'T2,"RHO    = ",E22.15,/,' /,
     +    W1(28) / 'T2,"KS     = ",E22.15,/,' /,
     +    W1(29) / 'T2,"SIGMA  = ",E22.15,/,' /,
     +    W1(30) / 'T2,"CCINIT = ",E22.15,/,' /,
     +    W1(31) / 'T2,"YINIT  = ",E22.15,/,' /,
     +    W1(32) / 'T2,"MC     = ",E22.15,/,' /,
     +    W1(33) / 'T2,"CS2    = ",A7     )' /
C
      OPEN ( 2, FILE = '/ELUTE INDATA A', STATUS = 'OLD' )
      READ ( 2, 5 ) NX, INORM, IMON, IBAND, M, INDIN, IFIN,
     +              NBED, ITR, RELERR, ABSERR, CCINIT, AL,
     +              YINIT, DS, KS, H1, RF, RO, MS, EPS, H2,
     +              TEMP, AO, SIGMA, X(1), MC, CS2
C
      IWKMIN = NPDES*(3*IBAND*NX+12*NX+2*NPDES+5)+40
      RHO = 900.0D0
C
      OPEN ( 1, FILE = '/ELUTE RES1 A', STATUS = 'OLD' )
      WRITE ( 1, W1 ) NX, NBED, ITR, IU, NPDES, INORM, IMON,
     +                IBAND, IWKMIN, M, INDIN, IFIN, H1, AL,
     +                RF, RO, MS, EPS, H2, TEMP, AO, R, RELERR,
     +                ABSERR, X(1), DS, RHO, KS, SIGMA, CCINIT,
     +                YINIT, MC, CS2
```

```
C
      A = AO*EXP(-H2/(R*TEMP))
      BETA = ONE/SIGMA
      DNBED = DBLE(NBED)
      CONS1 = RF*H1
      CONS2 = MS*AL/(CONS1*EPS)/(DNBED-ONE)
      CONS4 = 1.57079633D0/(DBLE(NX)-ONE)
      SO = -(MC*KS*AL)/((ONE-EPS)*RHO*CONS1)
      CONS5 = EXP(SO*(ONE/DNBED))
      TIMINC = (18000.0D0-000.0D0)/(05.0D0*DBLE(ITR))
C
      DO 1, I = 1,ITR,1
        CCC(I) = CCINIT
    1 CONTINUE
C
      DO 10, I = 2,NX,1
        X(I) = RO*SIN(CONS4*(DBLE(I)-ONE))
   10 CONTINUE
C
      DO 12, L = 1,NBED,1
        CONS3 = CONS2*(DBLE(L)-ONE)
        TO = CONS3
C
        DO 17, I = 1,NX,1
          Y(IU,I) = YINIT
   17   CONTINUE
C
        DO 2, K = 1,ITR,1
          TEND = CONS3+(DBLE(K)-ONE)*TIMINC
          IND = INDIN
          IFAIL = IFIN
          CC = CCC(K)
          CALL D03PGF ( NPDES, M, PDEF, BNDY, TO, TEND, Y, IU,
         +              NX, X, RELERR, ABSERR, INORM, D03PAZ,
         +              IMON, IBAND, WK, IWK, IND, IFAIL )
          IF ( IFAIL .NE. 0 ) THEN
            WRITE ( 6, '(T2,2I2,3(1X,E22.15))' ) IFAIL, IND,
         +        TO, TEND, Y(IU,NX)
```

```
      END IF
      IF ( CS2 .EQ. 'SIMPLE' ) THEN
        CS = (Y(IU,NX)/A)**BETA
      ELSE
        CS = (Y(IU,NX)/A)**BETA
      END IF
      CCC(K) = CS+(CCC(K)-CS)*CONS5
      TO = TEND
    2 CONTINUE
C
   12 CONTINUE
C
      WRITE ( 1, 4 )
      OPEN ( 7, FILE = '/ELUTE RES2 A', STATUS = 'OLD' )
C
      DO 13, I = 1,ITR,1
        TIME = 000.0D0+DBLE(I-1)*05.00000D0*TIMINC
        WRITE ( 1, 3 ) TIME, CCC(I)
        WRITE ( 7, 3 ) TIME, CCC(I)
   13 CONTINUE
C
      STOP
C
    3 FORMAT ( T6, F9.1, 12X, E22.15 )
    4 FORMAT ( //, T5, 'TIME (SECONDS)', 10X, 'CONCENTRATION
   +          (PPM)', /, T5, 14('*'), 10X, 19('*'), // )
    5 FORMAT ( 9(I4,/), 18(E15.8,/), A7 )
C
      END
      SUBROUTINE PDEF ( NPDES, X, T, UX, DUX, F, G, C )
C
C  INTEGER SCALAR ARGUMENTS:
C
      INTEGER NPDES
C
C  DOUBLE PRECISION ARRAY AND SCALAR ARGUMENTS:
C
      DOUBLE PRECISION UX(NPDES), DUX(NPDES), F(NPDES),
```

```
G(NPDES,NPDES),C(NPDES), X, T
C
C  GLOBAL DOUBLE PRECISION SCALARS:
C
      DOUBLE PRECISION DS
      COMMON / CM1 / DS
C
      C(1) = 1.0D0/DS
      F(1) = 0.0D0
      G(1,1) = 1.0D0
C
      RETURN
C
      END
C
      SUBROUTINE BNDY ( NPDES, T, UX, IBND, P, Q, R )
C
C  INTEGER SCALAR ARGUMENTS:
C
      INTEGER NPDES, IBND
C
C  DOUBLE PRECISION ARRAY AND SCALAR ARGUMENTS:
C
      DOUBLE PRECISION UX(NPDES), P(NPDES), Q(NPDES), R(NPDES), T
C
C  GLOBAL DOUBLE PRECISION SCALARS:
C
      DOUBLE PRECISION DS, RHO, KS, CC, A, BETA
      COMMON / CM1 / DS,
     +       / CM2 / RHO, KS, CC, A, BETA
C
      IF ( IBND .EQ. 0 ) THEN
        P(1) = 0.0D0
        Q(1) = 1.0D0
        R(1) = 0.0D0
      ELSE
        P(1) = 0.0D0
        Q(1) = 1.0D0
```

```
      R(1) = (KS*(CC-(UX(1)/A)**BETA))/(RHO*DS)
      END IF
C
      RETURN
C
      END
```

SAMPLE OF THE INPUT FILE.

```
11              NX      not > 100
1               INORM
2               IMON
1               IBAND
2               M
0               INDIN
-1              IFIN
11              NBED
18              ITR     not > 1000
0.0001          RELERR
0.0001          ABSERR
0.0             CCINIT
0.48500         AL
712.0           YINIT
0.3000E-03      DS
0.400E-05       KS
0.485           H1
8.333E-6        RF
0.001015        RO
0.686           MS
0.8500          EPS
-42627.0        H2
373.0           TEMP
0.14239E-0(     AO
0.877           SIGMA
0.1E-10         X(1)
0.050000        MC
COMPLEX         CS2
```

SAMPLE OF THE OUTPUT FILE.

NX	=	11
NBED	=	11
ITR	=	18
IU	=	1
NPDES	=	1
INORM	=	1
IMON	=	2
IBAND	=	1
IWKMIN	=	212
M	=	2
INDIN	=	0
IFIN	=	-1
H1	=	0.485000000000000E+00
AL	=	0.485000000000000E+00
RF	=	0.833300000000000E-05
RO	=	0.101500000000000E-02
MS	=	0.686000000000000E+00
EPS	=	0.850000000000000E+00
H2	=	-0.426270000000000E+05
TEMP	=	0.373000000000000E+03
AO	=	0.142390000000000E-04
R	=	0.831440000000000E+01
RELERR	=	0.100000000000000E-03
ABSERR	=	0.100000000000000E-03
X(1)	=	0.100000000000000E-10
DS	=	0.300000000000000E-03
RHO	=	0.900000000000000E+03
KS	=	0.400000000000000E-05
SIGMA	=	0.377000000000000E+00
CCINIT	=	0.000000000000000E+00
YINIT	=	0.712000000000000E+03
MC	=	0.500000000000000E-01
CS2	=	COMPLEX

TIME (SECONDS)	CONCENTRATION (PPM)
0.0	0.688184833367905E+01
1000.0	0.483982003466645E+01
2000.0	0.362184084433375E+01
3000.0	0.284263839153937E+01
4000.0	0.230804603493380E+01
5000.0	0.191785506247925E+01
6000.0	0.162370277175432E+01
7000.0	0.139144357245550E+01
8000.0	0.121[illegible]4231778564E+01
9000.0	0.106780650112796E+01
10000.0	0.950045932909234E+00
11000.0	0.852848566461944E+00
12000.0	0.769678617970385E+00
13000.0	0.699177458703900E+00
14000.0	0.638805058765399E+00
15000.0	0.5[illegible]6387827997953E+00
16000.0	0.540328609051755E+00
17000.0	0.500067836848643E+00

PROGRAM TO SOLVE THE MASS TRANSFER PROBLEM.

```
C  STANDARD FORTRAN 77 PROGRAMME USING THE NAG LIBRARY
C  BEGINNING OF MAIN PROGRAMME UNIT ELUTE
   PROGRAM ELUTE
C  NON-EXECUTABLE STATEMENTS
C  INTEGER NAMED CONSTANTS:
C  N    - NAG VARIABLE
C  LIW  - NAG VARIABLE
C  LW   - NAG VARIABLE
     INTEGER N, LIW, LW
     PARAMETER ( N = 1, LIW = 1, LW = 200 )
C  DOUBLE PRECISION NAMED CONSTANTS:
     R    - ISOTHERM PARAMETER
   DOUBLE PRECISION R
     PARAMETER ( R = 8.3144D0 )
C  LOCAL INTEGER ARRAYS AND SCALARS:
C  IW   - NAG VARIABLE
C  I    - NAG VARIABLE
C  IFAIL -   -DO-
C  IBTYPE -  -DO-
C  MAXFCN -  -DO-
C  NEXP  - NO OF EXPERIMENTAL POINTS
C  NITER - NAG VARIABLE
C  NF    -  -DO-
C  LWMIN -  -DO-
     INTEGER IW(LIW), I, IFAIL, IBTYPE, MAXFCN, NEXP, NITER,
    +        NF, LWMIN
C  LOCAL DOUBLE PRECISION ARRAYS AND SCALARS:
C  Y    - NAG CARBON LOADING REPRESENTATION
C  XGUESS - GUESS OF KS
C  FVEC  - NAG VARIABLE
C  FJAC  -  -DO-
C  S     -  -DO-
C  W     -  -DO-
C  CS    - SURFACE SOLUTION CONCENTRATION
C  SO    - PARAMETRISED CHARACTERISTIC VARIABLE
C  TO    - CHARACTERISTIC INITIAL TIME
```

```
C  TEND   - CHARACTERISTIC TIME
C  H1     - LENGTH OF THE COLUMN
C  RF     - FLOWRATE OF SOLUTION THROUGH THE COLUMN
C  RO     - CARBON PARTICLE SIZE
C  MS     - MASS OF SOLUTION IN THE COLUMN
C  H2     - ISOTHERM PARAMETER
C  TEMP   - ISOTHERM PARAMETER
C  AO     - ISOTHERM PARAMETER
C  SIGMA  - ISOTHERM PARAMETER
C  FTOL   - NAG VARIABLE
C  FVALUE -   -DO-
C  ETA    -   -DO-
C  STEPMX -   -DO-
      DOUBLE PRECISION Y(1,100), XGUESS(N), FVEC(19),
     +                 FJAC(19,N), S(N), V(N,N), W(LW), CS,
     +                 SO, TO, TEND, H1, RF, RO, MS, H2,
     +                 TEMP, AO, SIGMA, CONS3, CONS4, CONS5,
     +                 FTOL, FVALUE, ETA, STEPMX
C  LOCAL CHARACTER ARRAYS:
C  W1     - NAG VARIABLE
      CHARACTER*35 W1(42)
C  GLOBAL INTEGER SCALARS:
C  NBED   - THE NUMBER OF DESCRITISED COLUMN HEIGHTS
C  NX     - THE NUMBER OF RADIAL POINTS IN THE CARBON
C  IU     - NAG VARIABLE
C  INDIN  -   -DO-
C  IFIN   -   -DO-
C  IBAND  -   -DO-
C  IMON   -   -DO-
C  INORM  -   -DO-
C  M      -   -DO-
C  NPDES  -   -DO-
      INTEGER NBED, NX, IU, INDIN, IFIN, IBAND, IMON, INORM, M,
     +        NPDES
      COMMON / I1 / NBED, NX, IU, INDIN, IFIN, IBAND, IMON,
     +          INORM, M, NPDES
C  GLOBAL DOUBLE PRECISION ARRAYS AND SCALARS:
C  ECCC   - PREDICTED CONCENTRATION
```

```
C  CCC    - OBSERVED CONCENTRATION
C  DS     - DIFFUSSION COEFFICIENT OF THE CARBON
C  RHO    - PARTICLE DENSITY
C  KS     - THE FILM MASS TRANSFER COEFFICIENT
C  CC     - INLET CONCENTRATION
C  EPS    - COLUMN VOIDAGE
C  AL     - LENGTH OF THE CARBON BED
C  MC     - MASS OF CARBON
C  YINIT  - INITIAL LOADING ON CARBON
C  CCINIT - INITIAL SOLUTION CONCENTRATION
C  ABSERR - NAG VARIABLE
C  RELERR -   -DO-
       DOUBLE PRECISION X(100), EXDATA(19), ECCC(19), CCC(19),
      +                 DS, RHO, KS, CC, A, BETA, CONS1, EPS,
      +                 ONE, AL, MC, DNBED, CONS2, YINIT, CCINIT,
      +                ABSERR, RELERR
       COMMON / DP1 / DS,
           / DP2 / RHO, KS, CC, A, BETA,
           / DP3 / X, EXDATA, ECCC, CCC, CONS1, EPS, ONE, AL,
      +          MC, DNBED, CONS2, YINIT, CCINIT, ABSERR,
      +          RELERR
C  EXTERNAL PROCEDURES
       EXTERNAL E04FCF, LSQFUN, E04FDZ
C  INTRINSIC FUNCTIONS
       INTRINSIC SIN, EXP, DBLE
C  INITIALIZATION OF VARIABLES
       DATA W1(1) /' ( T2,"NX      = ", I22,   /, ' /,
      +   W1(2) /'  T2, "NBED    = ", I22,   /, ' /,
      +   W1(3) /'  T2, "IU      = ", I22,   /, ' /,
      +   W1(4) /'  T2, "NPDES   = ", I22,   /, ' /,
      +   W1(5) /'  T2, "INORM   = ", I22,   /, ' /,
      +   W1(6) /'  T2, "IMON    = ", I22,   /, ' /,
      +   W1(7) /'  T2, "IBAND   = ", I22,   /, ' /,
      +   W1(8) /'  T2, "M       = ", I22,   /, ' /,
      +   W1(9) /'  T2, "INDIN   = ", I22,   /, ' /,
      +   W1(10) /'  T2, "IFIN   = ", I22,   /, ' /,
      +   W1(11) /'  T2, "NEXP   = ", I22,   /, ' /,
      +   W1(12) /'  T2, "IBTYPE  = ", I22,   /, ' /,
```

```
     +    W1(13) / '  T2, "MAXFCN   = ", I22,    /,  ',
     +    W1(14) / '  T2, "N       = ", I22,    /,  ',
     +    W1(15) / '  T2, "LWMIN    = ", I22,    /,  ',
     +    W1(16) / '  T2, "LIW     = ", I22,    /,  ',
     +    W1(17) / '  T2, "LW      = ", I22,    /,  ',
     +    W1(18) / '  T2, "IFAIL   = ", I22,    /,  ',
     +    W1(19) / '  T2, "H1      = ", E22.15, /,  ',
     +    W1(20) / '  T2, "AL      = ", E22.15, /,  '/
      DATA W1(21) / '  T2, "RF      = ", E22.15, /,  ',
     +    W1(22) / '  T2, "RO      = ", E22.15, /,  ',
     +    W1(23) / '  T2, "MS      = ", E22.15, /,  ',
     +    W1(24) / '  T2, "EPS     = ", E22.15, /,  ',
     +    W1(25) / '  T2, "H2      = ", E22.15, /,  ',
     +    W1(26) / '  T2, "TEMP    = ", E22.15, /,  ',
     +    W1(27) / '  T2, "AO      = ", E22.15, /,  ',
     +    W1(28) / '  T2, "R       = ", E22.15, /,  ',
     +    W1(29) / '  T2, "RELERR  = ", E22.15, /,  ',
     +    W1(30) / '  T2, "ABSERR  = ", E22.15, /,  ',
     +    W1(31) / '  T2, "X(1)    = ", E22.15, /,  ',
     +    W1(32) / '  T2, "RHO     = ", E22.15, /,  ',
     +    W1(33) / '  T2, "SIGMA   = ", E22.15, /,  ',
     +    W1(34) / '  T2, "CCINIT  = ", E22.15, /,  ',
     +    W1(35) / '  T2, "YINIT   = ", E22.15, /,  ',
     +    W1(36) / '  T2, "MC      = ", E22.15, /,  ',
     +    W1(37) / '  T2, "ONE     = ", E22.15, /,  ',
     +    W1(38) / '  T2, "XGUESS(1) = ", E22.15, /,  ',
     +    W1(39) / '  T2, "FTOL    = ", E22.15, /,  ',
     +    W1(40) / '  T2, "ETA     = ", E22.15, /,  '/
      DATA W1(41) / '  T2, "STEPMX  = ", E22.15, /,  ',
     +    W1(42) / '  T2, "DS      = ", E22.15, / ) '/
C  FORMAT STATEMENTS
      3 FORMAT ( T7, F7.1, 13X, E22.15 )
      4 FORMAT ( //, T5, 'TIME (SECONDS)', 10X, 'CONCENTRATION
     +       (PPM)', /, T5, 14("*"), 10X, 19("*"), // )
      5 FORMAT ( 11(I4,/), 21(E15.8,:,/) )
      6 FORMAT ( 2E22.15 )
C EXECUTABLE STATEMENTS
      OPEN ( 2, FILE = '/ELUTE1 INDATA A', STATUS = 'OLD' )
```

```
      READ ( 2, 5 ) NX, INORM, IMON, IBAND, M, INDIN, IFIN,
     +              NBED,IBTYPE, MAXFCN, IFAIL, RELERR, ABSERR,
     +              CCINIT, AL, YINIT, H1, RF, RO, MS, EPS, H2,
     +              TEMP, AO, SIGMA, X(1), MC, XGUESS(1), FTOL,
     +              ETA, STEPMX, DS
      OPEN ( 3, FILE = '/ELUTE1 INEXP A', STATUS = 'OLD' )
        DO 7, I = 1,20,1
      READ ( 3, 6, END = 8 ) EXDATA(I), ECCC(I)
    7 CONTINUE
        8 NEXP = I-1
          ONE = 1.0D0
          RHO = 900.0D0
          IU = 1
          NPDES = 1
          LWMIN = 6*N+NEXP*N+2*NEXP+N*(N-1)/2
      OPEN ( 1, FILE = '/ELUTE1 RES1 A', STATUS = 'OLD' )
      WRITE ( 1, W1 ) NX, NBED, IU, NPDES, INORM, IMON,
     +              IBAND, M, INDIN, IFIN, NEXP, IBTYPE,
     +              MAXFCN, N, LWMIN, LIW, LW, IFAIL, H1,
     +              AL, RF, RO, MS, EPS, H2, TEMP, AO, R,
     +              RELERR, ABSERR, X(1), RHO, SIGMA,
     +              CCINIT, YINIT, MC, ONE, XGUESS(1),
     +              FTOL, ETA, STEPMX, DS
        WRITE ( 1, 4 )
          DO 20, I = 1,NEXP,1
        WRITE ( 1, 3 ) EXDATA(I), ECCC(I)
   20 CONTINUE
      A = AO*EXP(-H2/(R*TEMP))
      BETA = ONE/SIGMA
      DNBED = DBLE(NBED)
      CONS1 = RF*H1
      CONS2 = MS*AL/(CONS1*EPS)/(DNBED-ONE)
      CONS4 = 1.57079633D0/(DBLE(NX)-ONE)
        DO 10, I = 2,NX,1
           X(I) = RO*SIN(CONS4*(DBLE(I)-ONE))
   10 CONTINUE
      CALL E04FCF (NEXP, 2), LSQFUN, E04FDZ, IBTYPE, MAXFCN,
     +              ETA, FTOL, STEPMX, XGUESS, FVALUE, FVEC,
```

```
     +          FJAC, NEXP, S, V, N, NITER, NF, IW, LIW,
     +          W, LW, IFAIL )
      WRITE ( 1, 4 )
      OPEN ( 7, FILE = '/ELUTE1 RES2 A', STATUS = 'OLD' )
        DO 13, I = 1,NEXP,1
      WRITE ( 1, 3 ) EXDATA(I), CCC(I)
      WRITE ( 7, 3 ) EXDATA(I), CCC(I)
13 CONTINUE
      WRITE ( 1, '( /, T2, "KS    = ", E22.15,
     +          /, T2, "SSR   = ", E22.15,
     +          /, T2, "NITER = ", I22,
     +          /, T2, "NF    = ", I22,
     +          /, T2, "IFAIL = ", I22 )' ) XGUESS(1),
     +            FVALUE, NITER, NF, IFAIL
      STOP
C  END OF MAIN PROGRAMME UNIT ELUTE
      END

C  BEGINNING OF SUBROUTINE PROGRAMME UNIT LSQFUN
      SUBROUTINE LSQFUN ( IFLAG, NEXP, N, XC, FVECC, IW, LIW, W,          LW )
      INTEGER IW(LIW), IFLAG, NEXP, N, LIW, LW
      DOUBLE PRECISION XC(N), FVECC(NEXP), W(LW)
C  INTEGER NAMED CONSTANTS:
      INTEGER IWK
      PARAMETER ( IWK = 500 )
C  LOCAL INTEGER SCALARS:
C  I     - DO LOOP VARIABLE
C  L     -    -DO-
C  K     -    -DO-
      INTEGER I, L, K, IND, IFAIL, IWKMIN
C  LOCAL DOUBLE PRECISION SCALAR:
C  TIMINC - TIME INTERVAL
      DOUBLE PRECISION Y(1,100), WK(IWK), SO, CONS5, CONS3,
     +          TO, TEND, CS, TIMINC
C  GLOBAL INTEGER SCALARS:
      INTEGER NBED, NX, IU, INDIN, IFIN, IBAND, IMON, INORM,
     +          M, NPDES
      COMMON / I1 / NBED, NX, IU, INDIN, IFIN, IBAND, IMON,
```

```
     +          INORM, M, NPDES
C  GLOBAL DOUBLE PRECISION ARRAYS AND SCALARS:
      DOUBLE PRECISION X(100), EXDATA(19), ECCC(19), CCC(19),
     +          DS, RHO, KS, CC, A, BETA, CONS1, EPS,
     +          ONE, AL, MC, DNBED, CONS2, YINIT,
     +          CCINIT, ABSERR, RELERR
      COMMON / DP1 / DS,
     +     / DP2 / RHO, KS, CC, A, BETA,
     +     / DP3 / X, EXDATA, ECCC, CCC, CONS1, EPS, ONE,
     +          AL, MC, DNBED, CONS2, YINIT, CCINIT,
     +          ABSERR, RELERR
C  EXTERNAL PROCEDURES
      EXTERNAL D03PGF, PDEF, BNDY, D03PAZ
C  INTRINSIC FUNCTIONS
      INTRINSIC EXP, DBLE
C  EXECUTABLE STATEMENTS
      IWKMIN = NPDES*(3*IBAND*NX+12*NX+2*NPDES+5)+40
      KS = XC(1)
      SO = -(MC*KS*AL)/((ONE-EPS)*RHO*CONS1)
      CONS5 = EXP(SO*(ONE/DNBED))
      DO 9, I = 1,NEXP,1
        CCC(I) = CCINIT
9 CONTINUE
      TIMINC = (EXDATA(NEXP)-EXDATA(1))/(10.0D0*DBLE(NEXP))
      DO 12, L = 1,NBED,1
        CONS3 = CONS2*(DBLE(L)-ONE)
        TO = CONS3
        DO 17, I = 1,NX,1
          Y(IU,I) = YINIT
17 CONTINUE
        DO 2, K = 1,NEXP,1
          TEND = CONS3+(DBLE(K)-ONE)*TIMINC
          IND = INDIN
          IFAIL = IFIN
          CC = CCC(K)
      CALL D03PGF ( NPDES, M, PDEF, BNDY, TO, TEND, Y,
     +          IU, RELERR, ABSERR, INORM, D03PAZ,
     +          IMON, IBAND, WK, IWK, IND, IFAIL )
```

```
          IF ( IFAIL .NE. 0 ) THEN
         WRITE ( 6, '( T2, 2I2, 3(1X,E22.15) )' ) IFAIL,
     +          IND, TO, TEND, Y(IU,NX)
          END IF
            CS = (Y(IU,NX)/A)**BETA
            CCC(K) = CS+(CCC(K)-CS)*CONS5
            TO = TEND
2  CONTINUE
12 CONTINUE
       DO 1, I = 1,NEXP,1
            FVECC(I) = CCC(I)-ECCC(I)
1 CONTINUE
       RETURN
C  END OF SUBROUTINE PROGRAMME UNIT LSQFUN
       END


C  BEGINNING OF SUBROUTINE PROGRAMME UNIT PDE
   SUBROUTINE PDEF ( NPDES, X, T, UX, DUX, F, G, C )
C  NON-EXECUTABLE STATEMENTS
C  INTEGER SCALAR ARGUMENTS:
C  NPDES  - NAG VARIABLE
       INTEGER NPDES
C  DOUBLE PRECISION ARRAY ARGUMENTS:
C  F      - NAG VARIABLE
C  G      -  -DO-
C  C      -  -DO-
       DOUBLE PRECISION UX(NPDES), DUX(NPDES), F(NPDES),
     +                  G(NPDES,NPDES), C(NPDES), X, T
C  GLOBAL DOUBLE PRECISION SCALARS:
       DOUBLE PRECISION DS
       COMMON / DP1 / DS
C  EXECUTABLE STATEMENTS
       C(1) = 1.0D0/DS
       F(1) = 0.0D0
       G(1,1) = 1.0D0
       RETURN
C  END OF SUBROUTINE PROGRAMME UNIT PDEF
```

```
      END

C  BEGINNING OF SUBROUTINE PROGRAMME UNIT BNDY
      SUBROUTINE BNDY ( NPDES, T, UX, IBND, P, Q, R )
C  NON-EXECUTABLE STATEMENTS
      INTEGER SCALAR ARGUMENTS:
C  NPDES - NAG VARIABLE
C  IBND  -  -DO-
      INTEGER NPDES, IBND
C  DOUBLE PRECISION ARRAY AND SCALAR ARGUMENTS:
C  UX    - NAG VARIABLE
C  P     -  -DO-
C  Q     -  -DO-
C  R     -  -DO-
C  T     -  -DO-
      DOUBLE PRECISION UX(NPDES), P(NPDES), Q(NPDES), R(NPDES),
     +                 T
C  GLOBAL DOUBLE PRECISION SCALARS:
      DOUBLE PRECISION DS, RHO, KS, CC, A, BETA
      COMMON / DP1 / DS,
     +     / DP2 / RHO, KS, CC, A, BETA
C  EXECUTABLE STATEMENTS
      IF ( IBND .EQ. 0 ) THEN
        P(1) = 0.0D0
        Q(1) = 1.0D0
        R(1) = 0.0D0
      ELSE
        P(1) = 0.0D0
        Q(1) = 1.0D0
        R(1) =(KS*(CC-(UX(1)/A)**BETA))/(RHO*DS)
      END IF
      RETURN
C  END OF SUBROUTINE PROGRAMME UNIT BNDY
      END
```

SAMPLE OF THE INPUT FILE.

11	NX not > 100
2	INORM
2	IMON
1	IBAND
2	M
0	INDIN
-1	IFIN
11	NBED
-1	IBTYPE
400	MAXFCN
-1	IFAIL
0.0001	RELERR
0.0001	ABSERR
0.0	CCINIT
0.485	AL
712.0	YINIT
0.485	H1
8.333E-06	RF
0.001015	RO
0.686	MS
0.85	EPS
-42627.0	H2
356.0	TEMP
0.14239E-04	AO
0.377	SIGMA
0.1E-12	X(1)
0.050003	MC
0.50E-04	XGUESS(1)
0.0	FTOL
0.0	ETA
100000.0	STEPMX
0.3E-03	DS

SAMPLE OF THE OUTPUT FILE

NX	=	11
NBED	=	11
IU	=	1
NPDES	=	1
INORM	=	2
IMON	=	2
IBAND	=	1
M	=	2
INDIN	=	0
IFIN	=	-1
NEXP	=	18
IBTYPE	=	-1
MAXFCN	=	400
N	=	1
LWMIN	=	60
LIW	=	1
LW	=	200
IFAIL	=	-1
H1	=	0.485000000000000E+00
AL	=	0.485000000000000E+00
RF	=	0.833300000000000E-05
RO	=	0.101500000000000E-02
MS	=	0.686000000000000E+00
ERS	=	0.850000000000000E+00
H2	=	-0.426270000000000E+05
TEMP	=	0.356000000000000E+03
AO	=	0.142390000000000E-04
R	=	0.831440000000000E+01
RELERR	=	0.100000000000000E-03
ABSERR	=	0.100000000000000E-03
X(1)	=	0.100000000000000E-12
RHO	=	0.900000000000000E+03
SIGMA	=	0.377000000000000E+00
CCINIT	=	0.000000000000000E+00
YINIT	=	0.712000000000000E+03
MC	=	0.500030000000000E-01
ONE	=	0.100000000000000E+01

XGUESS(1)	=	0.500000000000000E-04
FTOL	=	0.000000000000000E+00
ETA	=	0.000000000000000E+00
STEPMX	=	0.100000000000000E+06
DS	=	0.300000000000000E-03

EXPERIMENTAL

TIME (SECONDS)	CONCENTRATION (PPM)
120.0	0.307000000000000E+01
420.0	0.350000000000000E+01
720.0	0.359000000000000E+01
1020.0	0.370000000000000E+01
1320.0	0.365000000000000E+01
1920.0	0.326000000000000E+01
2520.0	0.312000000000000E+01
3120.0	0.284000000000000E+01
3720.0	0.267000000000000E+01
4620.0	0.231000000000000E+01
5520.0	0.195000000000000E+01
6420.0	0.168000000000000E+01
7320.0	0.141000000000000E+01
9120.0	0.108000000000000E+01
11600.0	0.820000000000000E+00
12720.0	0.640000000000000E+00
14500.0	0.470000000000000E+00
19200.0	0.290000000000000E+00

TIME (SECONDS)	PREDICTED CONCENTRATION (PPM)
120.0	0.424425965631235E+01
420.0	0.379248622172054E+01
720.0	0.341610643993772E+01
1020.0	0.309484750918273E+01
1320.0	0.281726562292806E+01
1920.0	0.257905217720690E+01
2520.0	0.236990258270117E+01
3120.0	0.218727832893569E+01
3720.0	0.202745636269719E+01
4620.0	0.188497283603220E+01
5520.0	0.175619066900941E+01
6420.0	0.164036026391409E+01
7320.0	0.153776534080265E+01
9120.0	0.144412686734142E+01
11600.0	0.136013646738576E+01
12720.0	0.128255484767402E+01
14500.0	0.121181730456266E+01
19200.0	0.114785803840135E+01

KS	=	0.140715306428379E-04
SSR	=	0.677910423545492E+01
NITER	=	5
NF	=	82
IFAIL	=	3

APPENDIX 5 - Comparison between single and multiple solute isotherms.

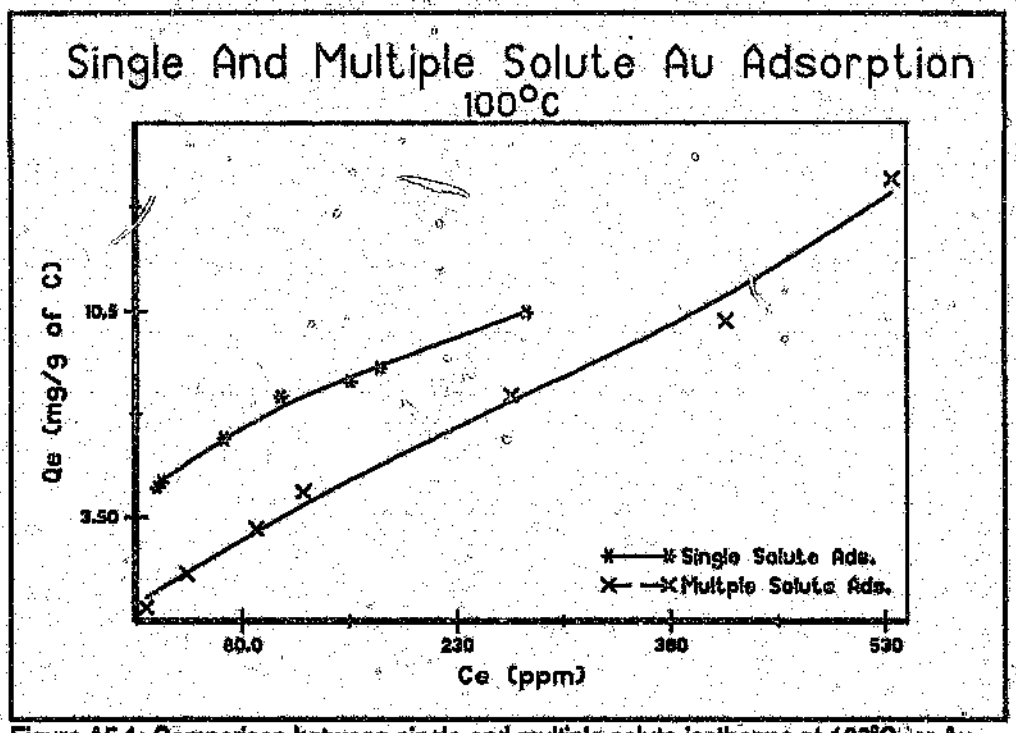


Figure A5.1: Comparison between single and multiple solute isotherms at 100°C for Au

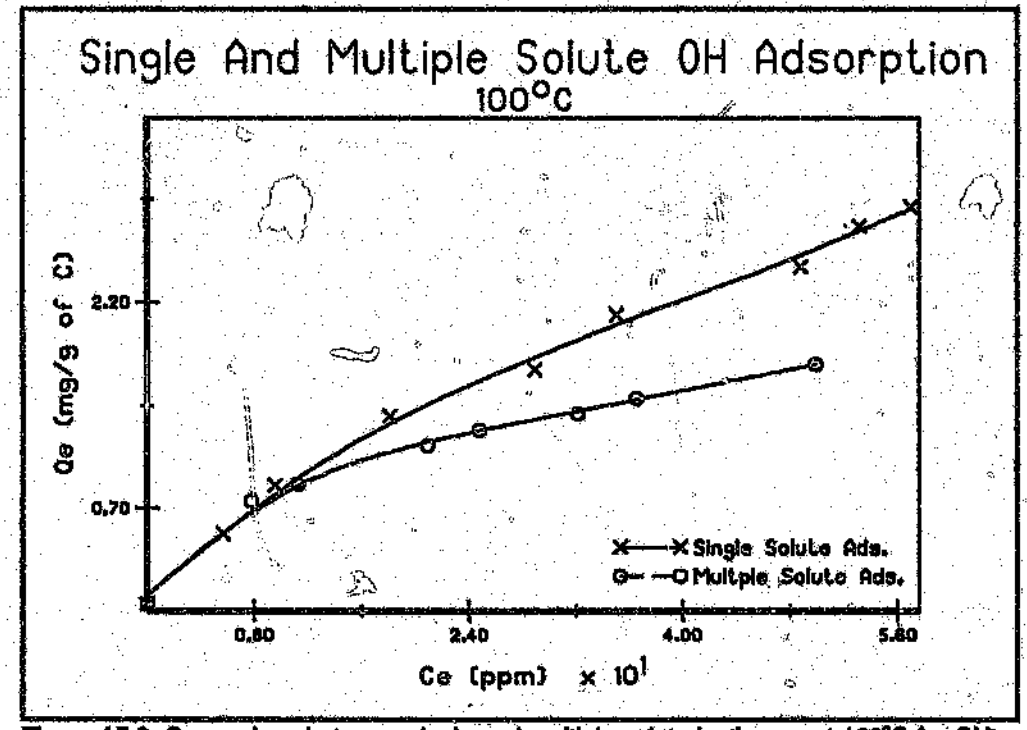


Figure A5.2: Comparison between single and multiple solute isotherms at 100°C for OH

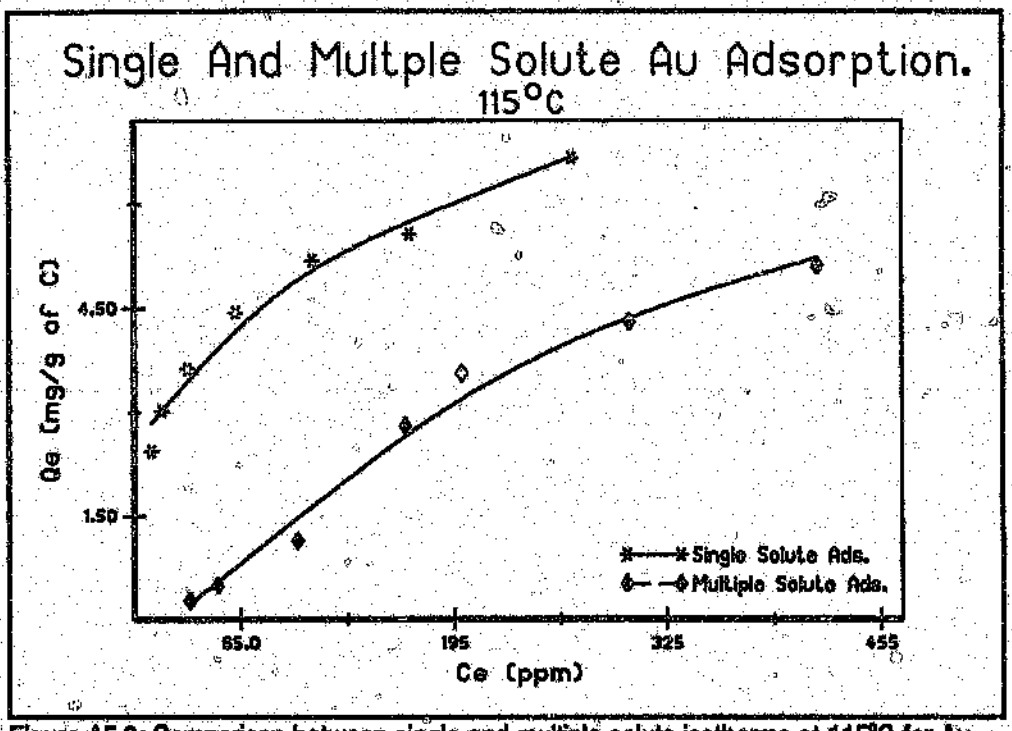


Figure A5.3: Comparison between single and multiple solute isotherms at 115°C for Au

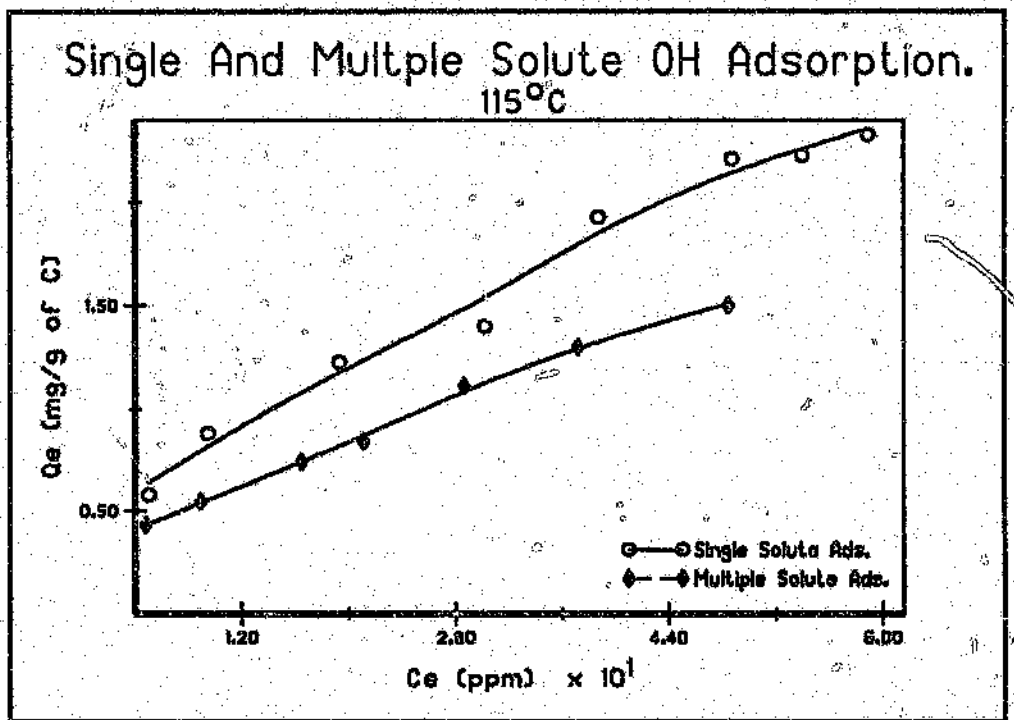


Figure A5.4: Comparison between single and multiple solute isotherms at 115°C for OH^-