EQUILIBRIUM SHIFT OF GOLD ADSORPTION IN A BATCH REACTOR

by

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A dissertation submitted in fulfilment of the requirements for the Masters Degree in Chemical Engineering Technology at the Cape Technikon

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Cape Technikon
April 2001

DECLARATION

I hereby declare that the work contained in this thesis is my own original work, except where acknowledged in the text.

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ABSTRACT

Over the years the carbon-in-pulp technology has been refined to become the highly efficient process that is used in our present-day system of recovering dissolved gold from cyanide leached pulps. The efficiency of a CIP circuit mainly depends on the effectiveness of the adsorption section as it not only determines the amount of soluble gold lost in the residues, but also indirectly affects the function of the other processes in the plant. Research in this area has declined over the past few years as a result of a decrease in the gold price. It is now more than ever important to investigate the operating conditions of the adsorption process to ensure that a highly effective system is maintained.

The adsorption of gold cyanide onto activated carbon is to a large extent dependent on maintaining operating conditions well above those of equilibrium. The Freundlich and the Langmuir isotherms have been used by many researchers to describe the equilibrium conditions of the adsorption process. The general practice in the carbon-in-pulp technology is to use an isotherm for the prediction of a circuit's performance. As confidence has increased in the reliability of these predictions, it has become important to acquire knowledge of the equilibrium condition that is driving the process. Previous research findings have indicated that the equilibrium isotherm of gold cyanide adsorption onto activated carbon is influenced by changes in the adsorption conditions down the adsorption train. This equilibrium or isotherm shift may lead to errors in the prediction of gold adsorption rates, which results in the fact that the simulations of the performance of the CIP circuits are not reliable. In this study the aim was to investigate the combined influence of various operating conditions on the adsorption equilibrium.

Experiments were carried out where the change in pH, oxygen and cyanide concentration, ionic strength in solution and competing ions were investigated simultaneously. In order to investigate the influence of changes in these experimental conditions, equilibrium isotherms were determined by using standard synthetic solutions prepared in 1 litre batch reactors with different concentrations of potassium gold cyanide. Through factorial design the three most sensitive factors were determined. Further experiments were then carried out to test the effect of changes in free cyanide concentration, pH and competing ions (50 ppm nickel) on the equilibrium isotherm as well as the adsorption profile. A relationship was postulated between the cyanide profile in the adsorption circuit and the initial cyanide concentration, which yielded an expression for a first order decay in free cyanide. A linear relationship was also established between the free cyanide concentration and the equilibrium A parameter at a solution pH of 10.5. This resulted in a modified A parameter when the two proposed expressions were combined. The modified A parameter can be substituted in the existing Freundlich isotherm which will modify the isotherm.

A surface diffusion/film diffusion model was fitted to the experimental data to estimate the adsorption profile. The modified A parameter was incorporated into the model and it proved that a better fit (51 % improvement) could be obtained when a change in pH and free cyanide concentration was accounted for. As a result of limited experimental data the competition factor for gold and nickel could not be determined. It is suggested that future work should include the effect of competing ions, in order to include this factor in the modified Freundlich isotherm. It is assumed that if this additional effect were added to the model, an even greater fit of the model predictions would be obtained.

ACKNOWLEDGEMENTS

The work contained in this thesis was performed at the Faculty of Engineering at the Cape Technikon between May 1998 and May 2000.

I wish to thank the following people/institutions for their assistance and contributions in the completion of this thesis:

- The Departments of Chemical Engineering and Analytical Chemistry at the Cape Technikon for the use of their laboratory facilities and instrumentation.

- The National Research Foundation (NRF) for their financial contributions.

- The Agricultural Research Institute, Infruitec, for their assistance in analyses.

- My supervisor, Prof. Francis Petersen, for his guidance and support. The excellent example he sets in his work has encouraged me to reach for higher goals.

- The staff and fellow students at the Cape Technikon, for all their assistance.

- My parents for their encouragement, financial support and for always being proud of me.

- Moray, my fiancee, for his love and faith in me.

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CHAPTER 1

INTRODUCTION & LITERATURE REVIEW

The recovering and acquiring of gold have fascinated man almost since the beginning of time. One of the oldest gold recovery processes available is amalgamation, which relies upon the contact of ore with mercury to form a gold-mercury amalgamate. Although this process is still being used by artesian mines in third world countries due to its simplicity, the toxic nature of mercury has made it an unpopular route for gold recovery. Today, cyanide leaching is the method of choice for the recovery of most of the world's gold production.

It all started with the realization by MacArthur and the Forrest Brothers in the 1890's that gold and silver dissolved in cyanide solutions (Adamson, 1972). The cyanidation process is used in operations such as agitated tank leaching, heap leaching, zinc precipitation recovery and carbon adsorption recovery. The use of activated carbon to adsorb gold from cyanide solutions was patented as early as 1894, but did not receive much attention until the 1950s. Carbon adsorption recovery may include the following alternatives: carbon-in-pulp (CIP), carbon-in-leach (CIL) and carbon-in-column (CIC). The carbon-in-pulp process, which was developed to its present form in South Africa during the 1970's, is currently the most popular process to be employed on gold mines. The adsorption section of the carbon-in-pulp process have been studied by numerous researchers as it is considered the most important part in a CIP circuit.

Through the years, research in gold-extraction processes tended to follow the price of gold. Although the low gold price in the 1990's dampened interest in new research, it is yet important to ensure that existing operations run efficiently even in such difficult times. In this study the adsorption section of the CIP circuit will be investigated to evaluate the equilibrium isotherm used in the models for predicting gold adsorption performance.

1.1 THE CARBON-IN-PULP (CIP) PROCESS

In 1973, the Homestake gold Mine in Nevada began recovering gold directly from cyanide pulp with activated carbon, using and elution method developed at the US Bureau of Mines in the early 1950s. The first full-scale CIP plant in South Africa was commissioned at President Brand Gold Mine in August 1980. CIP has been accepted by industry as being superior to the former technology for its simplicity of operation, reduced capital and operation costs, higher recoveries of gold and versatility for being suited for small and medium scale mining (Bailey, 1987; http://www.mintek.co.za/EMD/CIP/cip.htm).

The gold recovery process begins where the broken ore from the mine is first ground to a fine powder (about 80% - 200 mesh) in large rotary mills. The slurry of the fine ore and water (referred to as the pulp) is treated with about 2 pounds per ton of sodium cyanide and enough quick lime (to keep the pH to about 11) in large tanks that are stirred mechanically or by air-agitation. The process in which the gold is leached from the gold bearing ore through contact with the cyanide solution, is called the cyanidation process. The cyanided pulps are screened to remove any large particles or wood chips that might possibly block the interstage screens, before it enters the CIP circuit (Bailey, 1987; Laxen *et al*, 1994). The CIP process comprises mainly of the following important operations (see Figure 1.1).

1.1.1 Loading of gold onto carbon

The adsorption circuit is the most important operation in the CIP process, since the efficiency of adsorption of gold determines not only the amount of soluble gold lost in the residues, but also the function of the other processes in the plant. Activated carbon is used to adsorb the gold directly from the cyanided pulp in a series of six to eight large adsorption tanks. These tanks are arranged in a cascade to facilitate the use of gravity for continuous movement of the pulp (Bailey, 1987; Yannopoulos, 1990). Pulp flows continually from the first vessel to the last in the series, and the carbon is transferred intermittently by pumping it in the opposite (countercurrent) direction. Interstage screens between the tanks prevent the carbon from moving downstream. The gold value of the pulp decreases downstream, and the gold loading on the carbon increases upstream, with the highest value in the first tank. The pH of the pulp is maintained in the range of 10 to 11 through the addition of lime (Yannopoulos, 1990).

1.1.2 Elution or stripping of gold from the carbon

All elution processes are based on Fick's First Law where mass transfer is a linear function of the molar concentration gradient (high temperature)(Coulson and Richardson, 1990). Two methods of elution are used on South African CIP plants (http://www.mintek.co.za/EMD/CIP/cip.htm). In the Zadra procedure hot, dilute caustic solution is recirculated continuously between the elution column and the electrowinning section (Zadra *et al*, 1952). The AARL procedure involves pre-soaking the loaded carbon in hot, concentrated caustic cyanide solution, followed by elution with hot deionized water (Davidson, 1986).

1.1.3 Reactivation of spent carbon

The carbon leaving the elution process is regenerated before being recycled to the last stage of the adsorption circuit. Thermal reactivation of the carbon occurs at 650°C in the absence of air for about 30 minutes, and then being allowed to cool in air (Bailey, 1987; Laxen *et al*, 1994). Regeneration is necessary to remove organic and inorganic substances accumulated within the pores of activated carbon during adsorption, that are not removed during the elution of gold. The objective is to recover the original porous structure and activity loss, with as little damage as possible to the carbon itself.

1.1.4 Electrowinning: metallic gold production

During this procedure, gold metal is recovered from the concentrated solution by an electrolytic process. Although a number of cells have been designed for this purpose (cylindrical cell, rectangular cell, Anglo American cell)(Bailey, 1987), a novel electrowinning cell was designed by Mintek (the Mintek cell), which has become the industry standard (http://www.mintek.co.za/EMD/CIP/cip.htm). This cell, which is manufactured in South Africa, overcame the low efficiencies of existing cells by using six individual steel-wool cathodes instead of the single one normally employed, with an anode placed on each side of the cathodes. The electrochemically active volume of the cell is accordingly increased 12-fold. The electrolyte flows through each of the 12 active sectors in sequence, thus further increasing the efficiency of the design (http://www.mintek.co.za /EMD/CIP/cip.htm).

1.2 GOLD CYANIDE ADSORPTION ONTO ACTIVATED CARBON

1.2.1 Activated carbon

In South Africa the gold-mining industry is the largest single consumer of activated carbon. The important role of activated carbon in the gold recovery process is very clear from the information supplied in the previous section. Aspects relating to the manufacture of activated carbon, as well as the properties of the resultant products are discussed in the following section.

1.2.1.1 Background

Activated carbons can be defined as highly porous, carbonaceous materials. The very large porosity provides a large surface area, which results in exceptional adsorptive properties. The process of activated carbon generation begins with the selection of a raw carbon source. The selection of these sources are based on design specifications since different raw sources will produce activated carbon with different properties. Some of the more common raw sources include wood, sawdust, peat, coal, coconut shells, peach pips and petroleum residues (Balci *et a*l., 1994; McDougall and Hancock, 1981; Mattson and Mark, 1971; AWWA, 1994). Activated carbons are available in powdered or granular form.

Characteristics of importance in choosing carbon types include pore structure, particle size, total surface area and void space between particles. The most ideal activated carbon for applications in gold recovery, is the granular coconut shell carbons with its extremely good impact hardness and wet abrasion resistance (McDougall and Hancock, 1981).

1.2.1.2 Structure

None of the substances which are part of the family of activated carbons can be characterized by a definite structural formula or by chemical analysis (McDougall and Hancock, 1981, Yannopolous, 1990).

It was shown through X-ray diffraction studies that the structure of activated carbon is similar to that of graphite as can be seen in Figure 1.2 (Mattson and Mark, 1971; Bokros, 1969). The structure of activated carbon is believed to be composed of tiny graphite-like plates called basal planes. One such plate is shown in Figure 1.3. The basal planes are flat or somewhat bent, 0.35 nm in thickness and a few nanometres in width and length. The hexagonal carbon rings are randomly orientated resulting in a very disordered overall structure which is often referred to as 'turbostratic'. This highly graphitic structure of activated carbon, aside from its large specific surface area, is the most important property with respect to gold cyanide adsorption (Ibrado and Fuerstenau, 1992).

In any activated carbon, pores of different sizes are found. Pores can be distinguished into:

- Micropores (radius below 1 nm)
- Mesopores (radius 1-25 nm), and
- Macropores (radius larger than 25 nm)

The macropores are used as the entrance to the activated carbon, the mesopores for transportation and the micropores for adsorption (http://www.activated-carbon.com/1-3.html). The pore structure and pore-size distribution are largely predetermined by the nature of the starting material, while the chemical nature of the surface oxides and the surface area of activated carbon is developed during the *carbonization* and *activation* processes.

1.2.1.3 Manufacturing

(a) Carbonisation

The main purpose of the carbonisation process is to reduce the volatile content of the source material (a fixed carbon content of 80% or higher is desirable) to convert it to a suitable form for activation (McDougall and Hancock, 1981). Rearrangement of the carbon atom into graphitic-like structures also occurs during carbonisation. However, the decomposition and deposition of disorganised carbon results in the filling or blocking of the created pores.

An activation step is necessary to enhance the low adsorption properties of the carbon and is basically the development of pores by means of chemical reactions (Balci *et al.*, 1994). There are two main varieties of the activation process, namely thermal/steam activation and chemical activation which give fundamentally different pore structures (http://www.norit.com/carbon/1-0htm).

(b) Thermal/steam activation

In the steam activation process, the carbonised material is reacted with steam, air, flue gas, or mixtures of these at temperatures between 800°C and 1100°C for a period of time. At these conditions, part of the carbon atoms are removed by 'gasification' (http//www.norit.com/carbon/1-0htm):

$$C\ (solid) + H_2O\ (gas) \rightarrow CO\ (gas) + H_2\ (gas)$$

Due to many factors, the different basal planes in the carbonised material show different reactivities towards this gasification reaction. As a result, some plates are removed, while others are not. This yields a very porous structure consisting of micro- and mesopores which gives the carbon its adsorptive capacity. As a result of this method of production, micropores are usually more-or-less slit shaped. The micropore walls are largely the flat sides of adjacent basal planes. Progressive activation can enlarge the micropores into mesopores. In this process, the pore shape becomes more random as seen in Figure 1.4.

One of the most important structural characteristics of activated carbon produced through steam activation from coconut shells, is that it is extremely microporous (the major portion of its pore volume being represented by pores with a radius of 10°A). For this reason coconut-shell products are ideal for the adsorption of the small gold-dicyanoarate complex. The graphitic zones that are believed to exist in thermally activated carbon also playes an important role in the mechanism of gold extraction from a cyanide medium (McDougall, 1991).

(c) Chemical activation

The chemical activation process is different from the steam activation process, in that carbonisation and activation occur at the same time, and at lower temperatures. Chemically activated carbons are produced by mixing an activation chemical with a young carbonaceous material (usually sawdust) and carbonising the resulting mixture. The most commonly used activating agents include zinc chloride, phosphoric acid and salts of sodium and magnesium (Hassler, 1974; McDougall, 1991).

The carbonisation temperature is relatively low between 200° C and 650° C. As a result of the relatively low process temperature, graphitic basal planes are not found in chemically activated carbons. Instead, each particle can be seen as a partly aromatic, partly aliphatic organic molecule (http://ww.norit.com/carbon/1-0htm). Chemically activated carbons are characterized by their generally macroporous structure making them suitable for the adsorption of large molecules (McDougall, 1991).

1.2.1.4 Chemical properties

As already stated, the overall structure of activated carbon is very disordered resulting in a high levels of structural imperfections. For this reason there are many possibilities for reactions with carbon atoms at the edges of the planar layers. Oxygen-containing organic functional groups are present on the surface of the carbon as a result of these reactions (Mattson and Mark, 1971; McDougall, 1991). These surface oxides are mostly located at the edges of broken graphitic ring systems and their exact chemical structures are not known with certainty. It has been suggested though that they may belong to the following groups:

carboxyl, phenolic hydroxyl, quinone-type carbonyl, normal lactones, fluorescein, carboxylic acid anhydrides and cyclic peroxides. The chemical nature of activated carbon however, depends on conditions during and after manufacture (Mattson and Mark, 1971; McDougall, 1991).

1.2.1.5 Adsorptive properties

Generally, it is understood that activated carbon owes its adsorptive properties primarily to its large internal surface area, as well as to its pore-size distribution, and that the external surface area and the nature of the surface oxides play minor roles (Mattson and Mark, 1971).

Adsorption is a removal process where certain particles are bound to an adsorbent particle surface by either chemical or physical attraction (http://www.ce.vt.edu/enviro2/wtprimer/carbons/sketcarb.html). Activated carbon uses the physical adsorption process, whereby attractive Van der Waals forces (also dipole-dipole interactions and hydrogen bonding) pull the solute out of solution and onto its surface, and which are generally reversible (Reynolds and Richard, 1996). Chemical adsorption refers to processes involving homopolar forces (as in ionic or covalent bonds), and such processes are generally irreversible. Adsorption requires three processes: macrotransport, microtransport and sorption (http://www.activated-carbon.com/1-3.html). The first step involves diffusion through a liquid phase to reach the carbon granule. Mictrotransport involves diffusion of molecules through macropores in the carbon granule to an adsorption site. The third step involves adsorption of the molecule to the surface.

Activated carbon is a very versatile substrate with respect to its interactions with various organic and inorganic compounds. It can function for instance as a reducing agent or, in the presence of excess oxygen, as an oxidation catalyst (McDougall, 1991). As a result, the adsorption of inorganic species such as the gold dicyanoaurate anion onto activated carbon, may occur by several mechanisms, making its identification extremely difficult.

1.2.2 Cyanide

The introduction of the cyanide leaching process in the 1890's made a mark in extractive hydrometallurgy due to the high degree of efficiency that is attained in gold mills (Yannopoulos, 1990). Cyanide has become a crucial part of the modern gold recovery process and it is therefore imperative to gain a basic understanding of the relationship between gold and cyanide.

1.2.2.1 Background

The general term "cyanide" refers to numerous compounds, both natural and man-made, having the chemical group CN (one atom of carbon and one atom of nitrogen). The acidic form of cyanide is called hydrogen cyanide or hydrocyanic acid, HCN. Cyanogen, C_2N_2, is formed by the oxidation of cyanide ions whereas a simple cyanide (HCN, NaCN) is a compound that dissociates to the cyanide anion (CN^-) and a cation (H^+, Na^+). There are three categories of cyanide that mine operators must normally be concerned with: free cyanide, weak-acid-dissociable (WAD) cyanide or total cyanide. Often, regulators require monitoring for only one of these categories. The procedure called total cyanide does not determine all of the various forms of cyanide (http://www.mpi.org.au/reports/bob morans_cyanide_paper.html).

1.2.2.2 Free cyanide

The cyanide ion, CN^-, and hydrogen cyanide, HCN, are collectively called free cyanide and the relative amounts present are largely controlled by the solution pH. Cyanide ion, CN^-, is the predominant stable form of free cyanide above a pH of about 9.0 to 9.5, depending upon the dissolved solids concentration of the water. As the pH drops, increasing amounts of CN^- convert to hydrogen cyanide, HCN. Therefore, most free cyanide in natural waters is present as HCN since the natural pH range is between about 6.0 and 8.5 (http://www.mpi.org.au/reports/bob_morans_cyanide_paper.html). Molecular HCN has a low boiling point and a high vapour pressure and can be lost from solution, particularly where there is a water/air interface (Smith and Mudder, 1991). The reaction between cyanide ion and water is expressed by the following equation:

$$CN^- + HOH = HCN + OH^-$$

At any particular pH and temperature this system is in equilibrium. This system is important because in gold cyanide extraction processes that are operated at pH 10.3, most of the free cyanide in process slurry water will be as CN^-. Since the HCN/CN^- ratio is low in process fluids, the capacity for cyanide loss by volatilisation is limited.

Free cyanide forms readily react with other chemicals they contact, producing a wide variety of new compounds which are often put in the following groups: simple cyanide compounds; cyanide complexes and cyanide related compounds http://www.mpi.org.au/reports /bob_moran_cyanide_paper.html). Simple cyanide compounds can be defined as the salts of hydrocyanic acid (KCN and NaCN), which dissolve completely in solution producing free alkali earth cations and cyanide anions. It is these forms of cyanide which are initially employed in the cyanidation process.

1.2.2.3 Cyanide complexes

The chemistry of the cyano-metal complex is more involved that that of the simple cyanide compounds. The alkali-metal cyanide complex have the following general formula: $A_aM(CN)_b$, thus the formula $KAu(CN)_2$ for potassium aurocyanide (Smith and Mudder, 1991). When an alkali-metal cyanide dissolves in water, the transition metal and cyanide stay combined together as a complex radical anion. The stability of the metal cyanide complex anion is dependent on the metal cation with which it is associated with. In Table 1.1 the stability of some of these metal cyanide complexes are shown by Scott and Ingles (1987). Though under conventional leaching conditions (pH = 10-11), $Au(CN)_2^-$ is the most stable gold species (Wang and Forssberg, 1990).

Gold forms a large number of complexes with various ligands such as thiocyanate (gold I), cyanide (gold I), chloride (gold III) and thiosulphate (gold I). However, the interaction between activated carbon and the chloride and cyanide complexes of gold have received predominant attention in literature because of their significance in the hydrometallurgical recovery of gold (McDougall and Fleming, 1987). The ability of activated carbon to adsorb different gold complexes follows the following order:

$$AuCl_4^- > Au(CN)_2^- > Au(SCN)_2^- > Au[CS(NH_2)_2]_2^+ . Au(S_2O_3)_2^{3-}$$

Because of the strong complex formed between cyanide and gold as well as its solubility, relatively weak cyanide solutions can be used for the extraction of gold from ore. It should also be noted that at lower cyanide concentrations, although $Au(CN)_2^-$ is not the dominant gold species, it is the dominant stable cyanide species (Wang and Forssberg, 1990). It is for this reason, as well as the availability of cyanide, that a cyanide medium is used for gold ore processing. In gold mine or cyanidation solutions the cyanide compounds present include free cyanide, the alkali earth salts and the metal cyanide complexes formed with gold, mercury, zinc, cadmium, silver, copper, nickel iron and cobalt (Smith and Mudder, 1997). Gold dissolution in a cyanide medium occurs through the overall reaction known as Elsner's equation as follows:

$$4Au + 8NaCN + 2H_2O = 4NaAu(CN)_2 + 2NaOH$$

In spite of the relative specificity of the gold-cyanide reaction, other metals and inorganic constituents react both with cyanide and to a certain extent with hydroxide, which must be present to maintain cyanide in its ionic form. The following is an example of such a reaction:

$$Zn(CN)_2 + 2CN^- = Zn\,(CN)_4^{-2}$$

Hence, metal-cyanide complex ions form as the products of the reaction between the insoluble cyanide compound and excess cyanide ions.

1.2.3 Adsorption mechanisms for gold cyanide

Despite over 100 years of research and development with activated carbon, there is still not a complete agreement of the gold adsorption and desorption mechanism (McDougall and Hancock, 1981; McDougall 1991; Adams *et al*, 1987; Van der Merwe and van Deventer, 1988). The main reason for this being the fact that activated carbon can not be investigated by direct physical procedures such as Infra-red spectroscopy or X-ray diffraction, so that very little is known about the adsorbent itself. Presently, not even the identities of the oxygen-containing organic functional groups formed on the carbon during activation are known with certainty. The mechanisms proposed over the years can be simplified into one of the following three (McDougall and Hancock, 1981; Adams and Fleming, 1989; Wan and Miller, 1990; Yannopoulos, 1990; Lagerge *et al*, 1997):

- The $Au(CN)_2^-$ ion is adsorbed without undergoing chemical change, and held by electrostatic or Van der Waals forces,
- The gold compound is decomposed from $Au(CN)_2^-$ to AuCN and adsorbed as such,
- The aurocyanide is reduced to either gold metal or to a partially reduced state between gold(I) and gold(0).

The overriding agreement in these studies though, is that $Au(CN)_2^-$ does not undergo any change in structure in the adsorption step and that adsorption probably occurres by the mechanism which involves the extraction of ion pairs of the type $[M^{n+}][Au(CN)_2^-]_n$ where $M^{n+} = Na^+$, K^+, Ca^{2+}, Mg^{2+} etc., at high pH values , and where $M^{n+} = H^+$ in acidic solution (McDougall *et al*, 1980; Adams and Fleming, 1989).

In terms of the above mechanisms, gold is present on the carbon surface in one of the following forms (McDougall and Fleming, 1987):

1. Aurocyanide, $Au(CN)_2^-$ (gold valency 1)
2. Aurocyanide, AuCN (gold valency 1)
3. A cluster compound, $Au_x(CN)_y$ (gold valency 0-1)
4. Gold metal, Au (gold valency 0)

Recent investigations indicate that the graphite-like structure of activated carbon is the most important factor in the adsorption process. Jones *et al* (1989) proposed that gold cyanide resides on the plate faces of the graphite crystallites upon adsorption on activated carbon as the geometry of the graphitic plane provides an excellent match to the structure of the $Au(CN)_2^-$ ion as shown in Figure 1.4. These findings presented that oxygen-containing functional groups play a significantly smaller role than is commonly believed and that the graphitic plates of activated carbon play the most important role. This was confirmed by Ibrado (1992), although their findings gave no indication of how adsorbed gold cyanide interacts with the adsorbent surface. Jones *et al* (1989) also contradicted the theory of the formation of identifiable ion pairs $[M^{n+}][Au(CN)_2^-]_n$ on the carbon surface (McDougal *et al*, 1980) by stating that the cations in the system (Na^+, K^+) co-adsorb non-specifically at the carbon-solution interface.

1.2.4 Adsorption /Equilibrium Isotherm

1.2.4.1 Equilibrium

The practice in CIP technology is to avoid equilibrium conditions being attained, for effective gold adsorption in each stage of the adsorption process. During the establishment of equilibrium, gold cyanide is presumed to slowly diffuse into the carbon micropores and, as the cross-sectional area of the micropores approaches that of the aurocyanide ion, the resistance to mass transfer becomes infinite. The initial film diffusion controlled reaction, which presumably involves adsorption in the macropores and mesopores, results in the establishment of a pseudo-equilibrium in 4 to 48 hours. Gold cyanide will continue to adsorb slowly onto the carbon, diffusing into the micropores, until a true equilibrium is established which in practice can take up to several weeks. The aurocyanide-carbon interaction can therefore be considered to possess two thermodynamic reqimes: the macropore-mesopore equilibrium and the total equilibrium (McDougall and Fleming, 1987). Most plants use an average carbon residence time of about 24 hours per contactor and seldom exceed 48 hours. Hence, it is apparent that plants operate predominantly in the pseudo-equilibrium and that true equilibrium is never reached. The chemical environment and thermodynamics of the adsorption reaction influences this pseudo-equilibrium in the same way as a true equilibrium would be affected. An accurate estimation of the equilibrium conditions and information on the basic features of adsorption isotherms are therefore important requirements for modelling CIP plants. Adsorption efficiency decreases over time in the adsorption circuit and eventually activated carbon will need to be replaced or reactivated.

1.2.4.2 Equilibrium capacity

The equilibrium capacity is an important aspect of the efficiency of an adsorbent-adsorbate system. The rates and equilibrium loading of aurocyanide adsorption onto activated carbon depend upon the number of active sites available on the carbon. As the carbon becomes loaded it is slower to take up gold and the concentration of gold in equilibrium increases (Wan and Miller, 1990). The effect of factors which affects the carbon loading capacity will be discussed later in detail.

1.2.4.3 The isotherm relationship

Isotherms are empirical relations, which are used to predict how much solute can be adsorbed by activated carbon. Each granular activated carbon has its own isotherm curve and breakpoint characteristics. These help to predict the adsorptive capacity of particular activated carbons and give a design estimate for adsorptive life. Reactivation of the carbon becomes necessary once the breakpoint has been reached. The isotherm and breakpoint characteristics of a particular carbon are most often determined by modeling, testing, cost analyses, and pilot studies. The pilot studies ensure that the chosen carbon type effectively removes the desired substances for the particular raw aqueous source and allows the plant to reach desired levels of quality before treatment continues. Once a breakpoint of a particular carbon has been determined the plant operators know approximately how long the carbon will effectively function. As this time approaches the carbon must be changed to ensure adequate removal (http://www.activated-carbon.com/1-3.html).

1.2.4.4 Equilibrium expressions

As mass transport in microporous activated carbons is a function of the amount adsorbed, the description of the diffusion process depends on the choice of the adsorption isotherm equation (Linders *et al*, 1997).

(a) Monocomponent systems

The following three isotherms are generally used to describe single solute adsorption from aqueous solutions:

Linear isotherm

$$q_e = AC_e \tag{1.1}$$

Although this expression has been used by Nicol *et al.* (1984) to describe the adsorption of gold onto activated carbon, care should be taken, for it is only applicable at very low adsorbate concentrations.

Freundlich isotherm

$$q_e = AC_e^n \tag{1.2}$$

Most researchers that have studied the gold adsorption system (a single solute system) have used the Freundlich isotherm for describing equilibrium conditions. A disadvantage of using this expression is that it does not approach linearity at low equilibrium concentrations (Morris and Weber, 1962).

Langmuir Isotherm

$$q_e = \frac{AC_e}{B + C_e} \tag{1.3}$$

The Langmuir isotherm is based on the assumption that maximum adsorption occurs when a single layer of molecules covers the adsorbent surface and that the adsorption energy is constant (Morris and Weber, 1962). This isotherm reduces to a linear form at low concentrations.

(b) Multicomponent systems

The presence of multiple components in a solution creates the condition where the solid phase loading of a particular adsorbate is determined not only by its equilibrium liquid phase concentration, but also by the competitive effect of the other components. The equilibrium adsorption in multicomponent systems was first described by the accepted Langmuir competitive isotherm which is applicable only when each component in the system obeys a Langmuir behaviour in a monocomponent system. A simpler multicomponent isotherm which is based on the Freundlich isotherm was derived by Sheindorf *et al* (1981). This isotherm is derived on the assumption that each component individually obeys the Freundlich isotherm and that an exponential distribution of adsorption energies exists for each component (Sheindorf *et al*, 1981). This multicomponent Freundlich-type isotherm expressed in terms of weight of adsorbate is represented by the following equation:

$$q_{sj} = A_j C_{sj} \sum_{j=1}^{Comp} (b_{ij} C_{sj})^{nj-1} \tag{1.4}$$

The isotherm coefficients (A_j) can be determined from the monocomponent isotherm while the adsorption competition coefficient (b_{ij}) has to be determined experimentally.

1.2.4.5 Shifting equilibrium

The isotherm information used in the assessment of adsorption performance in the CIP plant is normally obtained from equilibrium tests involving the gold-bearing solution feeding the circuit and samples of the regenerated or fresh carbon used at the plant. The common practice is to use this single isotherm as a representative of the force driving the adsorption in each of the contactors in the plant. This creates a problem because the composition of the solution and of the carbon in each contactor is complex and changes down the adsorption train. These changes have an effect on the adsorption system and will subsequently affect the loading capacity of the carbon.

A change in loading capacity of carbon means a change in the equilibrium isotherm. The implication of this change, is that each contactor should be associated with a different isotherm (Woolacott and de Guzman, 1993a). The change in the isotherm from contactor to contactor is referred to as an 'isotherm shift'. The ideal would therefore be to expand the isotherm to incorporate changes in the operating parameters. Hence, many researchers have realised the need for expanding the models used in the simulation process.

The heterogeneity of the porosity of activated carbon makes the interpretation of the adsorption isotherm very difficult. Some researchers have attempted to prepare a new nonmicroporous carbon with a standard N_2 adsorption isotherm for characterization of activated carbons (Rodriquez-Reinoso *et al*, 1987).

A study on the adsorption of lead and chromium by activated carbon has shown to depend significantly on the pH, carbon dosage and initial adsorbate concentration. Langmuir and Freundlich expression were not able to describe adequately (the isotherm constants varied) the adsorption isotherms under the combined influence of initial adsorbate concentration and carbon dosage. Proposed empirical modifications to the two expressions in terms of mass ratio of carbon to initial amount of adsorbate in the solution were found to give good correlation of the experimental isotherms for the systems examined (Tan and Teo, 1987).

1.3. FACTORS INFLUENCING THE EQUILIBRIUM

The importance of the adsorption process and the ability of carbon to selectively adsorb gold cyanide have been discussed in detail in the previous sections. It was proposed that a change in operating conditions of the adsorption section could have an immense effect on the rate of gold loading and the equilibrium capacity. These factors/operating conditions will have the greatest effects on CIP performance where the loading of gold is allowed to approach the equilibrium or pseudo equilibrium value. As the loading in any stage approaches its equilibrium value, the rate of extraction decreases and therefore any factor that influences the equilibrium loading has a bearing on plant performance under these conditions (Fleming and Nicol, 1984).

Most researchers have investigated influences of these operating conditions individually, although certain parameters were combined in some studies (Fleming and Nicol, 1984; Petersen and Van Deventer, 1991; Adams, 1990a; Van der Merwe and Van Deventer, 1988; Tan and Teo, 1987; Woollacott and de Guzman, 1993). A discussion of the most important variables affecting the equilibrium follows.

1.3.1 Carbon Pore Structure

It has already been stated that the size of the pores in the carbon formed during activation has an important influence on adsorption behaviour because the pores act as a screen. Steam activated carbons have a high affinity for gold cyanide, while chemically activated carbons have virtually no affinity at all. The effect of the carbon pore structure on the adsorption process has been investigated by Voges (1996).

Different batches of a coconut shell carbon, produced by the same manufacturer, were used and subjected to the same conditions to ensure the surface chemistry of the carbon batches to be uniform for direct comparison of adsorption profiles. It was concluded that a change in pH does affect the adsorption in the pores of activated carbon. As this indicated a difference in the adsorption between the batches, it was suggested that the amount of available pores from batch to batch definitely differs. The carbon batch with the highest micropore area (determined through BET analyses) produced the highest equilibrium loading during equilibrium tests. The effect of the different micropore structures of the different batches could also be seen from the way the presence of potassium chloride affected gold adsorption. An increase of 48% in gold adsorption was observed for one batch, while only a 37% increase was observed for another under the same conditions. Adsorption tests that were conducted under conditions of competitive metal cyanides indicated no clear distinction between the individual batches with respect to gold adsorption and the relevant pore size distributions.

1.3.2 pH and ionic strength

In general, the rate and the loading capacity of gold adsorption both improve with increasing acidity or ionic strength, but the effect on the capacity is far greater than the kinetic effect

(McDougall *et al*, 1980; Fleming and Nicol, 1984; McDougall and Fleming, 1987; Van Deventer, 1986a). The adsorption of aurocyanide from neutral solutions, is normally accompanied by a shift in pH. For this reason a mechanism is suggested in which both $HAu(CN)_2$ and $M^{n+}[Au(CN)_2^-]_n$ are adsorbed simultaneously over a fairly wide pH range (Adams and Fleming, 1989). The drop in adsorption rate with increasing pH can be explained by the competition of hydroxide and aurocyanide ions for active sites on the carbon (Davidson, 1974).

The pH concentration on modern CIP plants are normally raised to about 10.5 to 11, by the addition of lime. The required potential for gold to dissolve in alkaline cyanide solution is much lower than in acidic solutions. In early CIP research Davidson *et al* (1979) suggested an acidified adsorption circuit (pH 4 to 5), as the results of tests on a plant solution and a synthetic solution of high ionic strength and low pH indicated a sharp increase in capacity constant while the adsorption of gold from alkaline solutions entailed relatively slow adsorption kinetics resulting in low carbon loadings together with calcium carbonate fouling. From more recent studies it was deducted that although the increased hydroxide ions has a decreasing effect on gold adsorption, the calcium cations enhances the gold adsorption, which results in the assumption that lime addition has very little effect on gold adsorption (Yannopoulos, 1990).

The control of pH as an operational parameter is important in view of the effect it has on other parameters. Fleming and Nicol (1984) explained that conditions of low pH and low concentrations of free cyanide could enhance the loading of copper significantly, which would decrease the equilibrium loading of gold. Lower pH levels also account for a significant loss in cyanide concentration which in return also effect gold loadings.

1.3.3 Cyanide concentration

The free cyanide concentration has a large effect on the selectivity of the carbon for gold adsorption. The decreasing effect of free cyanide concentrations on equilibrium loading has been well established (Davidson *et al*, 1979; Fleming and Nicol, 1984). It is generally understood that the effect of an increase in cyanide concentration is more detrimental at low cyanide concentrations than at high cyanide concentrations. However, it was noted by

Davidson *et al* (1982) that this effect only occurred when the oxygen concentration was above 5.5 ppm. It was reported by Davidson *et al* (1982) that the equilibrium parameter (A) changes significantly with a change in cyanide concentration in the range of 0 to 25 ppm (free cyanide), while Woollacott (1993b) reported this range to be between 0 to 100 ppm. It is therefore crucial to identify the factors which could affect the free cyanide concentration in solution.

- *Activated carbon* present in a cyanide solution will have a marked effect on the rate of cyanide loss, while the rate is very slow in the absence of carbon. In the absence of activated carbon the cyanide is lost by hydrolysis to hydrogen cyanide at room temperature. In the presence of activated carbon the catalytic oxidation of cyanide to cyanate is the primary mechanism for the loss of cyanide. The carbon also acts as a catalyst for decomposition of the cyanate. In addition, the carbon adsorbs some of the cyanide and cyanate. (Adams, 1990a). At high temperatures the cyanide loss in the presence of activated carbon are enhanced.

- *The importance of pH concentration* begins in the leaching section of the CIP circuit. High alkalinity in leaching is required to prevent the loss of cyanide from hydrolysis. Davidson (1986) suggested that the destruction of cyanide at lower pH levels could be explained by the increased loading of copper on the carbon as copper promotes the hydrolyses of cyanates to bicarbonate and ammonia. Adams (1990a) also concluded that the pH has a definite effect on the cyanide stability. In the absence of activated carbon much higher rates of cyanide loss are observed below pH 9,39 (pK_a), while only a slight amount of cyanide is lost at the natural pH of cyanide solutions (about 10,2). A similar effect of pH dependence was observed when activated carbon was present, although higher rates were obtained.

- *Free Oxygen content:* The direct oxidation of CN^- requires a mineralogical, bacteriological, or photochemical (sunlight) catalyst and produces cyanate ions:

$$2CN^- + O_2 + \textit{catalyst} = 2CNO^-$$

In the absence of activated carbon, the concentration of oxygen in the solution has no effect on the rate of cyanide loss. However, in the presence of a catalyst like activated carbon, oxygen in its molecular form acts as an oxidant for the oxidation of cyanide to cyanate. Within the heap environment, HCNO and CNO^- readily hydrolyse to form ammonia and carbon dioxide, which evolve from the system as gases. In this manner, oxidation of HCN or CN^- (as a result of higher oxygen concentrations in the solution) lowers the overall cyanide content of the system.

1.3.4 Oxygen concentration

Previous researchers have investigated the effect of oxygen in two ways. In the first instance pre-treated activated carbon, which is referred to as oxygen saturated carbon, was compared with untreated carbon or de-oxygenated carbon. The observation made by Tsuchida and Muir (1986) was confirmed by Petersen and van Deventer (1991) that de-oxygenated carbon adsorbed less $Au(CN)_2^-$ and $Ag(CN)_2^-$ than oxygen-saturated carbon. They concluded that oxygen indeed had an effect on the loading of gold cyanide, but only when oxygen–poor carbon was used. Tsuchida and Muir (1986) proposed that the role of oxygen is probably to oxidize the carbon surface to form a functional group that can ion exchange with $Au(CN)_2^-$. However, Jones *et al* (1989) suggested that surface oxides are not involved in the adsorption process.

In other studies oxygen and nitrogen were respectively bubbled through the solution for testing the effect of high and low concentrations of dissolved oxygen in the solution on the adsorption capacity of carbon for gold cyanide. Adams (1990a,b) showed that bubbling oxygen through a solution enhances the gold loading, but only under conditions of low ionic strength.

Van der Merwe and Van Deventer (1988) proposed two ways in which metal cyanides such as gold and silver cyanide are adsorbed onto activated carbon: (1) where oxygen is consumed during adsorption and (2) where the adsorption takes place without the use of oxygen. However, the existence of oxygen levels (approximately 9 mg O_2/l) above which the equilibrium loading of metal cyanide showed no further increase, could not be explained.

Oxygen concentrations above 9 mg O_2/l even caused a decrease in silver loading on one carbon sample.

Similar results were obtained by Voges (1996), where lower equilibrium capacities were obtained for oxygen enrichment tests for clear gold adsorption tests. The negative result of gold adsorption found in these tests were also thought to be as a result of the combined effect of high oxygen concentration and low concentration of free cyanide.

Considering previous research findings the influence of dissolved oxygen on gold adsorption isotherms may be summarised as follows (Woollacott, 1993b):

a) Increasing the oxygen concentration increases the equilibrium loading.

b) The effect is more significant with solutions of low ionic strength than solutions with high ionic strength.

c) Changes in the oxygen concentration affect the equilibrium loading significantly only when the oxygen concentration is low.

1.3.5 Competitive adsorption

CIP plant solutions contains additional metallic elements other than gold and silver which are found in the gold bearing ores in the form of oxides, sulphides, arsenides or antimonides. The elements commonly found in such solutions are copper, nickel, zinc, cobalt and iron. In spite of the relative specificity of the gold-cyanide reaction these metals and other inorganic constituents react with cyanide during the cyanidation process. Although activated carbon is generally very selective for gold cyanide, these metal-cyanide complexes may create a problem when a noticeable reduction in the adsorption of gold takes place by a competitive adsorption process (McDougall and Fleming, 1987). This problem resulted in numerous studies to determine the extent to which competing ions in the solution affects gold adsorption.

The effect of oxygen on competitive adsorption between gold and silver was found to be negligible through studies conducted by Van der Merwe and van Deventer, (1988). The presence of competitive metal cyanides was found to have a profound effect on adsorption of aurocyanide when compared to adsorption tests conducted in clear gold cyanide solution (Voges, 1996). The results from these tests showed that copper affected gold adsorption more negatively than nickel, while nickel in return had a more negative effect than iron.

Fleming and Nicol (1984) concluded that with the exception of copper, and to a lesser extent nickel, metal-cyanide complexes have little effect on gold extraction efficiency as they are present in very low concentrations. The loading of copper in the adsorption process is controlled by the pH value and free cyanide concentration of the solution. At low pH values and free cyanide concentrations the predominant copper complex present is $Cu(CN)_2^-$ which loads very well onto carbon. At high free cyanide concentration, the predominant copper complexes are $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$, which do not load onto activated carbon.

1.3.6 Organic solvents

Activated carbon becomes easily fouled by organics and finely divided clays or shale minerals which are encountered on CIP plants. It was found that for species such as hematite and organics that are insoluble in water, the mechanism of poisoning is most likely by means of a physical blocking of the carbon macropores rather than by a competitive adsorption at the active sites on the carbon surface (Fleming and Nicol, 1984; McDougall and Fleming, 1987). In a study with organic foulants present, such as phenol, xanthate and benzene, it was found that the extraction efficiency of carbon was decreased in two ways (Petersen and van Deventer, 1991). A decrease in intraparticle diffusivity was associated with pore blocking at low organic loading (therefore a kinetic influence), while at high organic loadings on the carbon, the equilibrium loading of gold cyanide was influenced as well.

1.4 OBJECTIVES OF THIS STUDY

The importance of the adsorption section in a CIP circuit is due to the fact that the efficiency of the adsorption of gold not only determines the amount of soluble gold lost in the residues, but also the function of the other processes in the plant. A number of kinetic models have been developed to describe the adsorption of gold onto activated carbon, for predicting and assessing the efficiency of a CIP adsorption circuit. These methods are commonly referred to as the simulation approach. As confidence has increased in the reliability of the predictions of the rate of gold adsorption, it has become important to acquire knowledge of the equilibrium condition that is driving this process. The literature review showed the significance to focus on different operating conditions in the adsorption circuit, which might have an effect on the adsorption process. In this study, the combined influence of such factors on the adsorption equilibrium will be investigated. The specific objectives were:

- To identify operating conditions, which could be practically measured on a continuous plant, that will have a significant effect on the equilibrium isotherm.
- To express the effect of changes in these operating conditions on the equilibrium isotherm in terms of the influence on the equilibrium A parameter.
- To develop a modified A parameter which incorporates the sensitivity of these variables, hence, modifying the existing isotherm.
- To test this modified isotherm in a surface diffusion/film diffusion model in order to comment on the fit and to validate the model.

This study will be conducted under conditions of a synthetic batch adsorption system and the results would therefore not directly apply to a large-scale CIP plant. Nevertheless, a shift in the equilibrium isotherm in a batch reactor will give a relative indication of changes to be expected in a real plant solution.

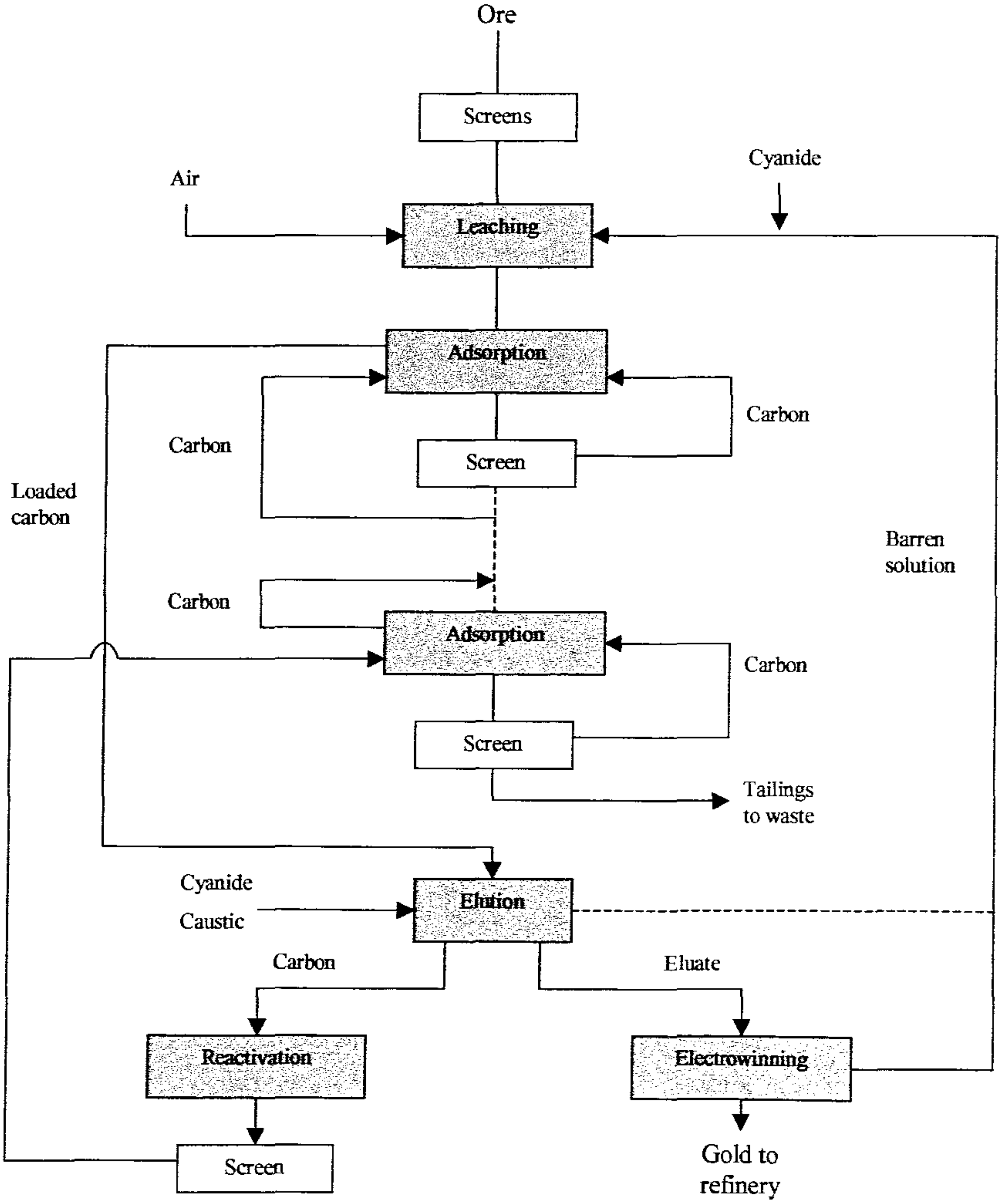

FIGURE 1.1 A flowsheet which represent a typical Carbon-in-Pulp circuit.

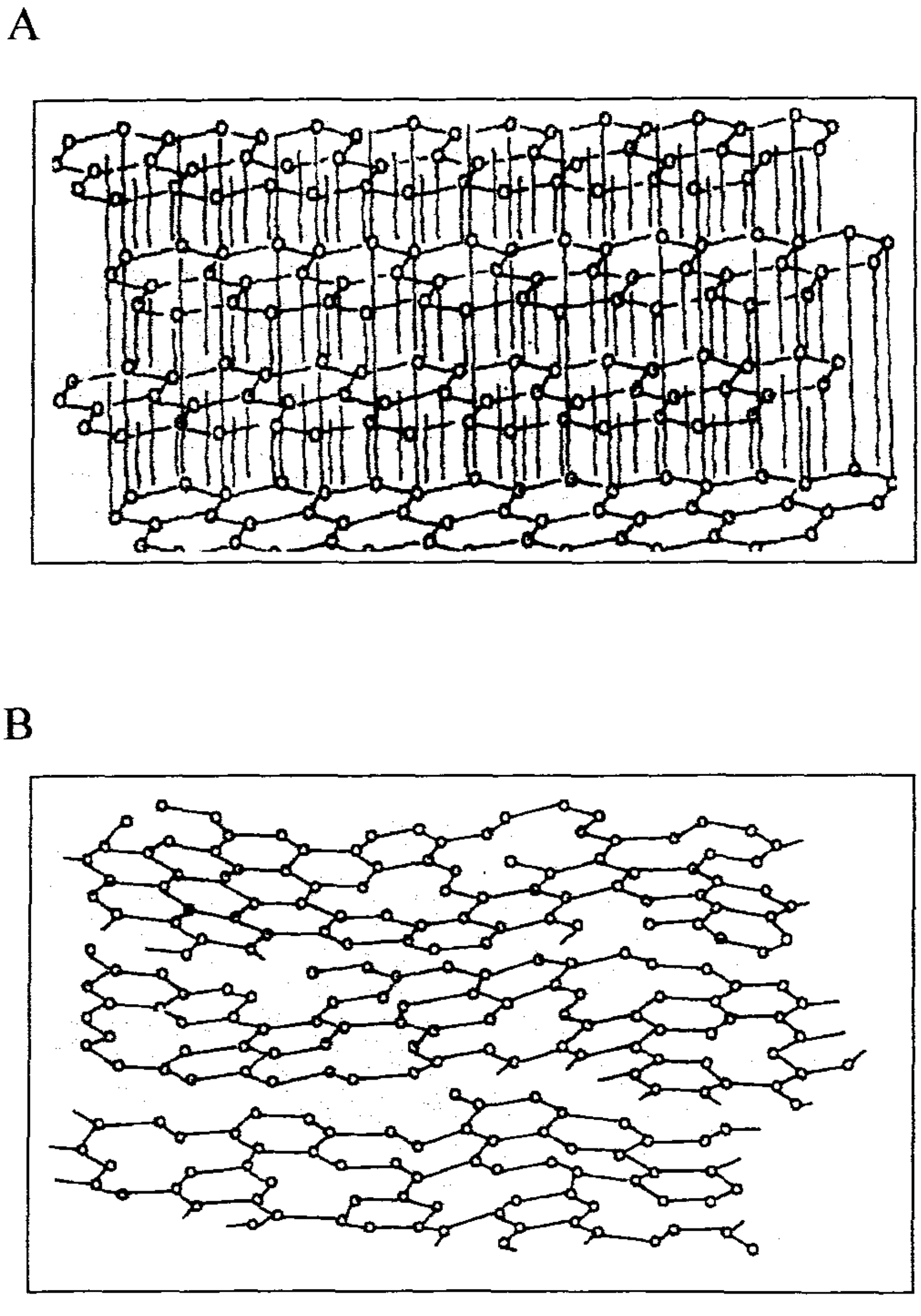

FIGURE 1.2 A schematic representation of the structure of (A) graphite and (B) the proposed structure of activated carbon. The circles denote the positions of carbon atoms, while the horizontal lines represent carbon-to-carbon bonds.

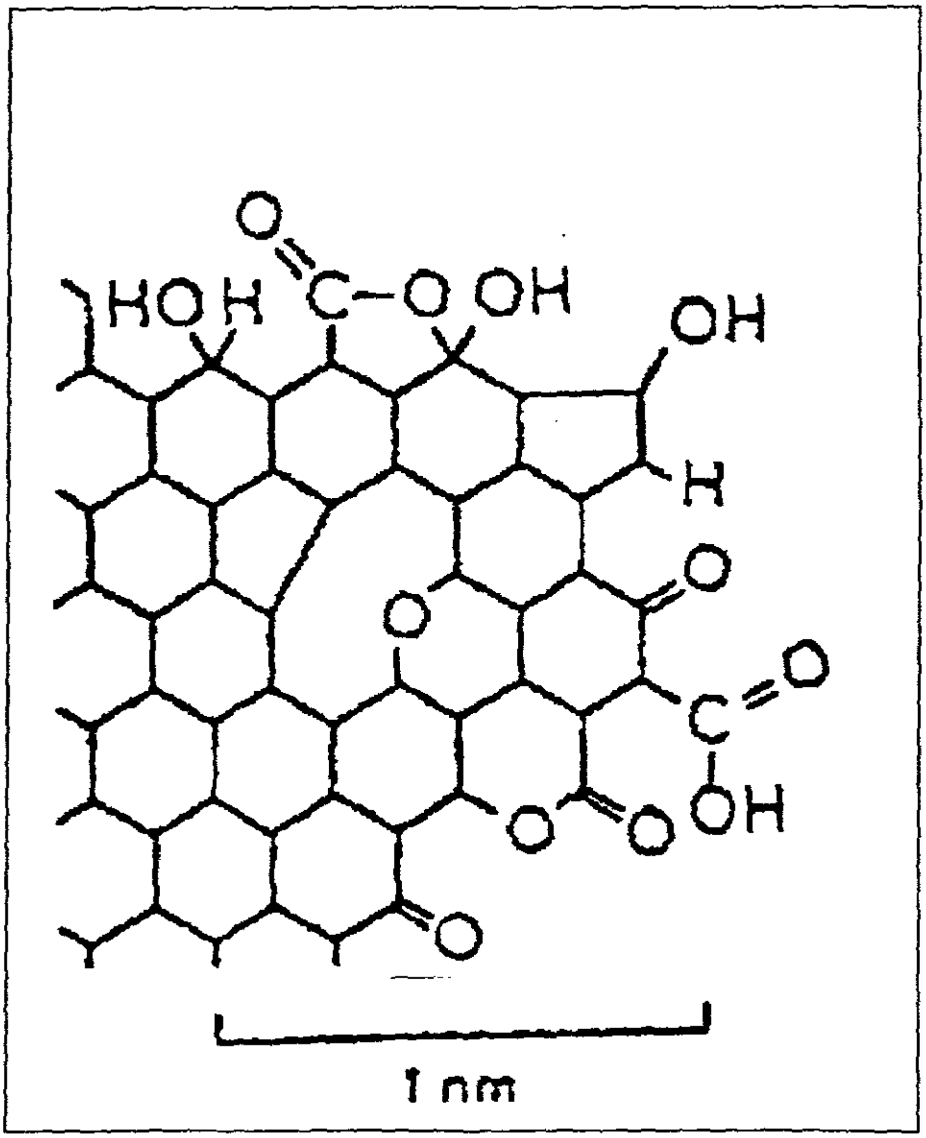

FIGURE 1.3 The structure of a basal plane in a steam activated carbon. Oxygen containing functional groups are located at the edges of broken graphitic rings.

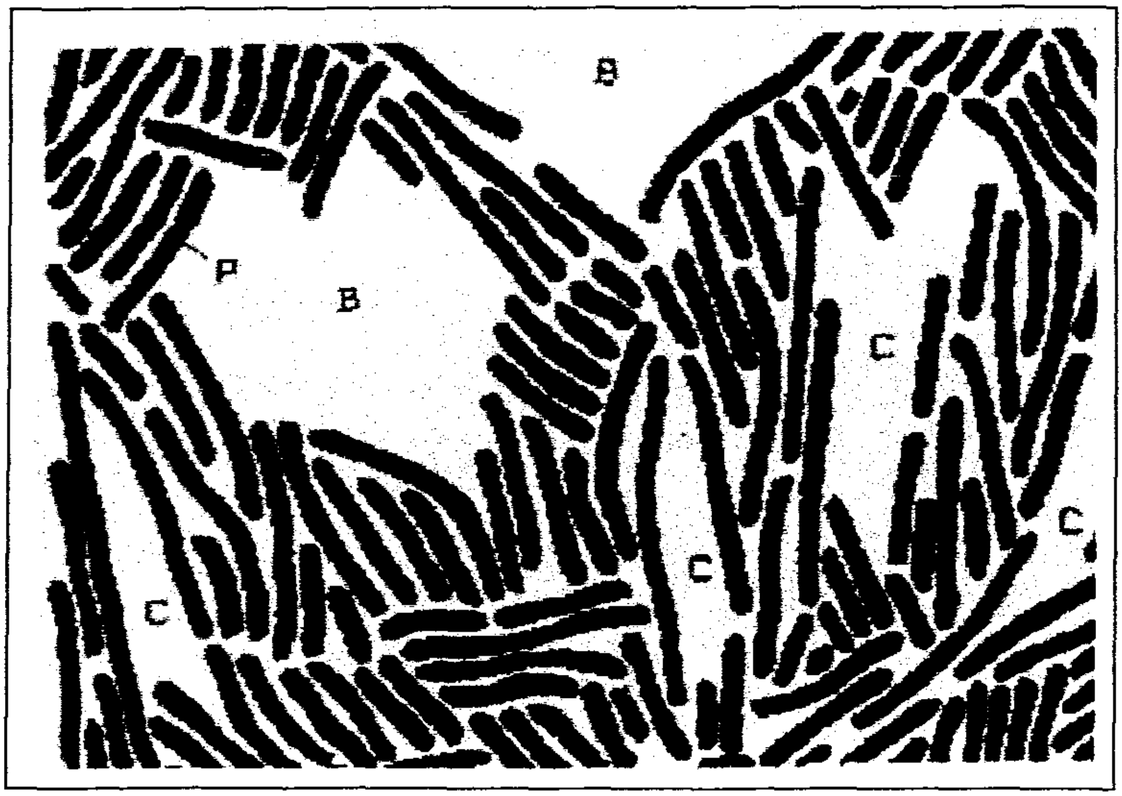

FIGURE 1.4 A crossectional view of micro- and mesopores

- P: basal planes
- B: mesopores
- C: micropores

TABLE 1.1 The classification of cyanide compounds in cyanidation solutions on the basis of stability.

CLASSIFICATION	CYANIDE COMPOUND
1. Free Cyanide	CN^-, HCN
2. Simple Compounds (a) readily soluble (b) neutral insoluble salts	 NaCN, KCN, $Ca(CN)_2$, $Hg(CN)_2$ $Zn(CN)_2$, $Cd(CN)_2$, CuCN, $Ni(CN)_2$,AgCN
3. Weak Complexes	$Zn(CN)_4^{-2}$,$Cd(CN)_3^{-1}$,$Cd(CN)_4^{-2}$
4. Moderately Strong Complexes	$Cu(CN)_2^{-1}$, $Cu(CN)_2^{-1}$, $Ni(CN)_4^{-2}$, $(CN)_2^{-1}$
5. Strong Complexes	$Fe(CN)_6^{-4}$, $Co(CN)_6^{-4}$, $Au(CN)_2^{-1}$, $Fe(CN)_6^{-3}$

CHAPTER 2

THEORY

2.1 MODEL FORMULATION

This chapter deals with a model for gold adsorption onto activated carbon, which has been used by numerous authors (Van Deventer, 1986, Petersen and Van Deventer, 1991). Kinetic models are normally classified as empirical, mechanistic or a combination of the two. The rate of adsorption of an adsorbate onto activated carbon, from a mechanistic point of view, can be described by one of the following series of transport mechanisms (Le Roux *et al*, 1991):

(a) film diffusion i.e. diffusion from the bulk liquid phase through a hypothetical hydrodynamic boundary layer or film surrounding the particle;
(b) pore diffusion; i.e. diffusion within the pore fluid of the particle;
(c) surface diffusion, i.e. migration of adsorbed molecules along the internal pore wall.
(d) adsorption onto the internal surface of the carbon.

The model used in this study is based on the assumption of initial film-transfer dominance, eventual surface-diffusion dominance, and a transition period during which both mechanisms influence the adsorption rate. The effects of intraparticle diffusion are combined by means of an effective surface-diffusion coefficient, which can be viewed as a measure of intraparticle diffusion (Le Roux *et al*, 1991). The result is a dual resistance model or generally referred to as a surface diffusion/intraparticle diffusion model. This model is based on further assumptions as summarised below:

- A spherical-particle geometry is assumed for the carbon particles.

- Pore diffusion is assumed to be negligible.

- Adsorption is considered to take place under isothermal conditions.
- Intraparticle diffusion is assumed to be instantaneous.
- The concentration of the liquid phase at the particle-liquid interface is assumed to be in equilibrium with the concentration of the solid adsorbate at the interface, and can therefore be described by an appropriate isotherm model.
- The macro- and micropores are distributed homogeneously through the carbon particles.
- The macro- and micropores are not interconnected, and both the pore types extend from the particle surface to the centre of the particle.
- The macro- and micropore diameters are taken to be weighted average diameter of all pores within the certain pore size range.

2.2 THE MATHEMATICAL MODEL

It was found that rate mechanisms are studied more easily by the use of agitated batch adsorption systems (Le Roux *et al*, 1991). This method was also employed for the purpose of this study. In the early stages of a batch adsorption experiment, film transfer can be assumed to determine the adsorption rate. The surface diffusion/intraparticle diffusion model accounts for accumulation into two types of pores (macropores and micropores). The micropore mass balance will be excluded from the model.

2.2.1 Mass balance equations

A mass balance over the batch reactor yields:

$$q_s = \frac{(C_i - C)V}{M} \tag{2.1}$$

The liquid phase material balance yields the following equation, which demonstrates the change in the solution concentration in a batch reactor governed by film-diffusion.

$$\frac{dC}{dt} = \frac{6k_f M}{d_p V \rho_c}(C_s - C) \tag{2.2}$$

The mass balance over the pores of the carbon can be represented by the following ordinary differential equation:

$$\frac{dq}{dt} = \frac{60D}{d_p^{\,2}}\left(\frac{q_s^{\,2} - q^2}{2q}\right) \tag{2.3}$$

With no accumulation of gold cyanide at the external surface of the carbon, the following boundary condition is yielded:

$$\frac{d_q}{d_r}\bigg|_{r=R} = \frac{k_f}{\rho_c D}(C - C_s) \tag{2.4}$$

2.2.2 Equilibrium Isotherm equation

The concentration of the liquid phase at the particle-liquid interface is assumed to be in equilibrium with the concentration of the solid adsorbate at the interface, and can therefore be described by an appropriate equilibrium relationship (Le Roux *et al*, 1991).

The equilibrium isotherm should have the following characteristics:

- It should accurately describe the data for a particular system.
- It should be applicable for the widest possible range of equilibrium concentration values.
- It should, if possible, have some theoretical foundation.

In the present study, the Freundlich isotherm was found to adequately describe the experimental equilibrium data which has the following form:

$$q_s = AC_s^n \tag{2.5}$$

In this equation, C_S represents the concentration of the gold in the solution and is measured in milligrams gold per litre of solution. The concentration of the gold on the carbon is measured in milligram gold per gram of carbon and can be determined through the following calculation:

$$q_s = \frac{(C_i - C_s)Volume_{reactor}}{Mass_{carbon}} \tag{2.6}$$

The equilibrium parameters, A and n, can be determined experimentally by a plot of log of q_s vs. C_S, which will represent the linearized form of the Freundlich isotherm.

Equation (2.5) will be substituted by the following equation for a multicomponent system:

$$q_{sj} = A_j C_{sj} \sum_{(j-1)}^{comp} (b_{ij} C_{sj})^{nj-1} \tag{2.7}$$

Equations (2.2), (2.3), (2.4) and (2.5) were solved with a forth order Runga-Kutta to produce the decay curve for gold cyanide in a batch reactor.

2.2.3 External mass transfer coefficient

A linear concentration gradient is postulated from the bulk liquid to the adsorbent particle surface, as it is assumed that film mass transfer determines the initial rate of gold loading onto the activated carbon. The adsorbate concentration on the surface of the adsorbent (C_s) is assumed to be negligibly small as compared to the adsorbate concentration in the bulk liquid. An adsorption profile can be established by plotting the concentration or dimensionless concentration versus time. The slope at time zero of a plot of $\ln(C_o/C)$ versus time can be used to compute the value of the external mass transfer coefficient, k_f.

2.2.4 Intraparticle diffusivity

The surface diffusion coefficient, D, in the homogeneous surface diffusion model is in fact a lumped intraparticle diffusion coefficient and can be estimated by using the Runga-Kutta solution for the batch kinetics of a single solute in a Powell least squares regression routine.

2.3 DEPENDENCY OF THE ISOTHERM

The model chosen in the previous section was formulated to create a quantitative understanding of the carbon-based gold extraction system. This model is used for satisfactory predictions of the performance of a gold adsorption system. In practice this surface diffusion/film diffusion model is applied to a gold adsorption system with non-ideal conditions, which in effect influences the kinetics and equilibrium of adsorption. Through the years researchers have identified many factors (operating conditions) influencing the changing of equilibrium, which eventually influences the gold extraction performance (Fleming and Nicol, 1984; Petersen and Van Deventer, 1991; Adams, 1990a&b; Van der Merwe and Van Deventer, 1988; Tan and Teo, 1987; Woollacott and de Guzman, 1993a&b). The operating conditions considered in this study are the concentration of cyanide and oxygen, competing ions, ionic strength and the pH of the gold bearing solution.

The assumption is made that the equilibrium isotherm for gold adsorption is dependent on changes in the conditions of the adsorption system. In the Freundlich isotherm, numerous authors have indicated that the exponential parameter, n, has little influence on the overall capacity of gold adsorption. Therefore, changes in the equilibrium will be reflected in the parameter, A. Hence,

$$A_j = f\,([CN^-];\ [O_2];\ pH;\ \text{Ionic strength};\ \text{Competing ions}) \qquad (2.8)$$

where j = 1 for a single-component system.

Equation (2.8) could then be back-substituted into Equations (2.4) and (2.5) and used in the surface diffusion/film diffusion model to predict the gold adsorption profile under conditions of a shifting equilibrium.

CHAPTER 3

EXPERIMENTAL

The experimental conditions, procedures and analytical techniques of the work conducted for this thesis, are explained in this chapter. In order to investigate the combined influence of certain factors on the adsorption isotherm, equilibrium tests were conducted in batch reactors using synthetic solutions and fresh activated carbon.

3.1 FACTORIAL DESIGN

A method of factorial design was used to create a set of tests in which the critical operating conditions were changed to determine the effect on the equilibrium isotherm.

The effect of more than one variable on a certain response is normally determined by a series of simple comparative experiments. With a one-factor-at-a-time procedure, a total of 24 samples would be required when the effect of three different variables has to be tested. With a single matrix-design experiment, all the variables could be included to permit a valid experiment to be made with a total of only eight samples, resulting in a saving of 67 percent in direct sample preparation and testing costs and time. A further advantage is that the information obtained from the matrix-design experiment would be greater than would be obtained by a series of comparative experiments (Diamond, 1981).

The experimental condition found in this work is referred to as a two-level, three-variable experiment. Each variable has a high level and a low level that are being investigated in the experiment. This factorial design is generated from an eight-trial Hadamard Matrix which allows the mean effects of all three variables and all their interactions to be determined (Diamond, 1981). The eight trials cover all combinations of the two levels and three variables. If a single sample is made at each of the eight treatment combinations specified, the effect of each variable has been measured four times. The experiment was replicated though to give two results at each treatment combination, from which an estimate of the variance could be obtained with one degree of freedom at each treatment combination. The procedure for the design can be found in Appendix 1.

3.2 EXPERIMENTAL MATERIAL

The adsorbent used in this study was coconut shell activated carbon, ANK 11, supplied by Norit and National Chemical Products Ltd in South Africa. This granular activated carbon has an average particle size of 2mm. In general it takes about three weeks for equilibrium to be reached, which is a very time consuming process. The carbon was therefore milled between 425μm and 500μm in size in order to reduce the contact time that was needed to approach equilibrium.

Before the milled activated carbon could be used in any of the experiments, it was first washed in order to remove any fine particles and air trapped within the carbon pores. This was achieved by rinsing the carbon several times in clean distilled water. The carbon was then left to dry in an oven for two days at a temperature of 40°C and stored afterwards in a dessicator to avoid adsorption of moisture from the atmosphere.

The adsorbate used in this study was potassium dicyanoaurate, $KAu(CN)_2$, supplied by Johnson Matthey. A standard solution of 1000 ppm Au in the form of $Au(CN)_2^-$ was used to make up the solutions used in all the experiments. A mass of 1.493 g of the $KAu(CN)_2$ was weighed off and made up in a 1 L volumetric flask using distilled water to produce this standard solution. A standard solution of the other salt, potassium nickel(II)cyanide ($K_2Ni(CN)_4.xH_2O$), used in the competitive adsorption experiments were prepared through the same method.

A stock solution of 1000 ppm free cyanide, CN^-, as KCN was used in experiments with a higher free cyanide content. This solution was prepared with 2.5 g potassium cyanide weighed off and made up to 1 litre with distilled water. The pH and ionic strength were adjusted by the addition of a 10 molar sodium hydroxide solution (NaOH) or concentrated hydrochloric acid (HCl). The 10 molar NaOH solution was also used as the ionic strength adjuster (ISA) in the free cyanide analyses. The preparation of this solution was done in a fume cupboard, as the reaction is highly exothermic. A mass of 400 g NaOH pellets was slowly added to a 1000 ml beaker with approximately 900 ml of distilled water in it. Once the solid NaOH had dissolved and the solution was cooled down, it was transferred to a 1 litre volumetric flask and made up to a litre with distilled water.

The reagents used throughout the experimental work were of analytical grade and made up with distilled water.

3.3 EXPERIMENTAL SET-UP

In this study the effect of change in the experimental conditions on the equilibrium loading were investigated in batch reactors. The experiments were performed in 1 litre batch reactors made of perspex. Three evenly spaced baffles with a width of 1 cm each were fitted inside the reactors with an internal diameter of 11 cm and height of 15 cm. Each reactor was covered by a perspex lid to minimise loss of sample by spillage or evaporation.

Agitation was provided through mechanical stirring as this simulates plant conditions (Van Deventer, 1986; Davidson, 1986). The stirring speed was kept at 300 rpm to ensure that all the carbon was kept in suspension. Woollacott and de Guzman (1993b) have used the rolling bottle technique as they found that mechanical stirring caused destruction of cyanide in solution (Van Deventer, 1986; McDougall *et al*, 1980; Adams and Fleming, 1989). A flat blade impeller (width 6cm and height 5cm) was driven by an electric motor at a constant speed of 300 rpm. A sketch of the apparatus is shown in Figure 3.1.

3.4 EQUILIBRIUM TESTS

The aim of the experiments conducted in this study was to create a series of equilibrium isotherm results obtained under different experimental conditions. A batch technique was used in these tests. A known mass of activated carbon (0.2 g) was agitated in a 1 litre solution with known amount of dissolved gold cyanide complex, which varied from 10 to 40 mg/l gold. Equilibrium conditions are normally determined over a period of three weeks. For the purpose of this study each test was performed over a period of 48 hours assuming *pseudo-equilibrium conditions.*

Through factorial design a set of tests were conducted where the solution pH, concentration of free cyanide and other metal cyanides in solution were changed. The influence of pH on the equilibrium loading was tested at pH levels of 9.5 and 11.5. The free cyanide concentrations of the solutions were varied between 20 ppm and 100 ppm. The effect of competitive ions was investigated by the addition of 50 ppm of potassium nickel (II) cyanide to the gold solutions.

The solutions were analysed for gold at the beginning and at the end of each experiment. From this concentration the carbon loading for each sample was determined. The equilibrium isotherm of the carbon was then determined using the Freundlich equation where the gold loading of the carbon (mg Au/mg carbon) was plotted against the concentration of gold in solution (mg Au/L of solution). The equilibrium constant, A, was then obtained for the gold loading on the carbon in equilibrium with gold in solution. Free cyanide concentrations were also measured at the end of the experiments.

3.5 ANALYTICAL METHODS AND PROCEDURES

3.5.1 Metal complex analyses

The metal concentration in solution was measured using an Inductively Coupled Plasma (ICP) to ensure accurate readings.

3.5.2 Free cyanide (CN^-) analyses

Many methods exist for the determination of cyanide in solution (Smith and Mudder, 1991; http://www.mpi.org.au/reports/bob_morans_cyanide_paper.html, *Cyanide in mining*). A quick, simple and accurate method was chosen which makes use of the cyanide ion selective electrode, for determining the free cyanide only in solution. This method involves the direct measurement, using an expanded scale pH or voltmeter, of the response of the electrode to the cyanide in solution against a reference electrode, which is recommended for low level measurements. An ionic strength adjuster (ISA) was added to all samples, standards and the blank solution to obtain a 0.01 Molar solution and a pH of between 11 and 13. The solution requires stirring throughout the analyses.

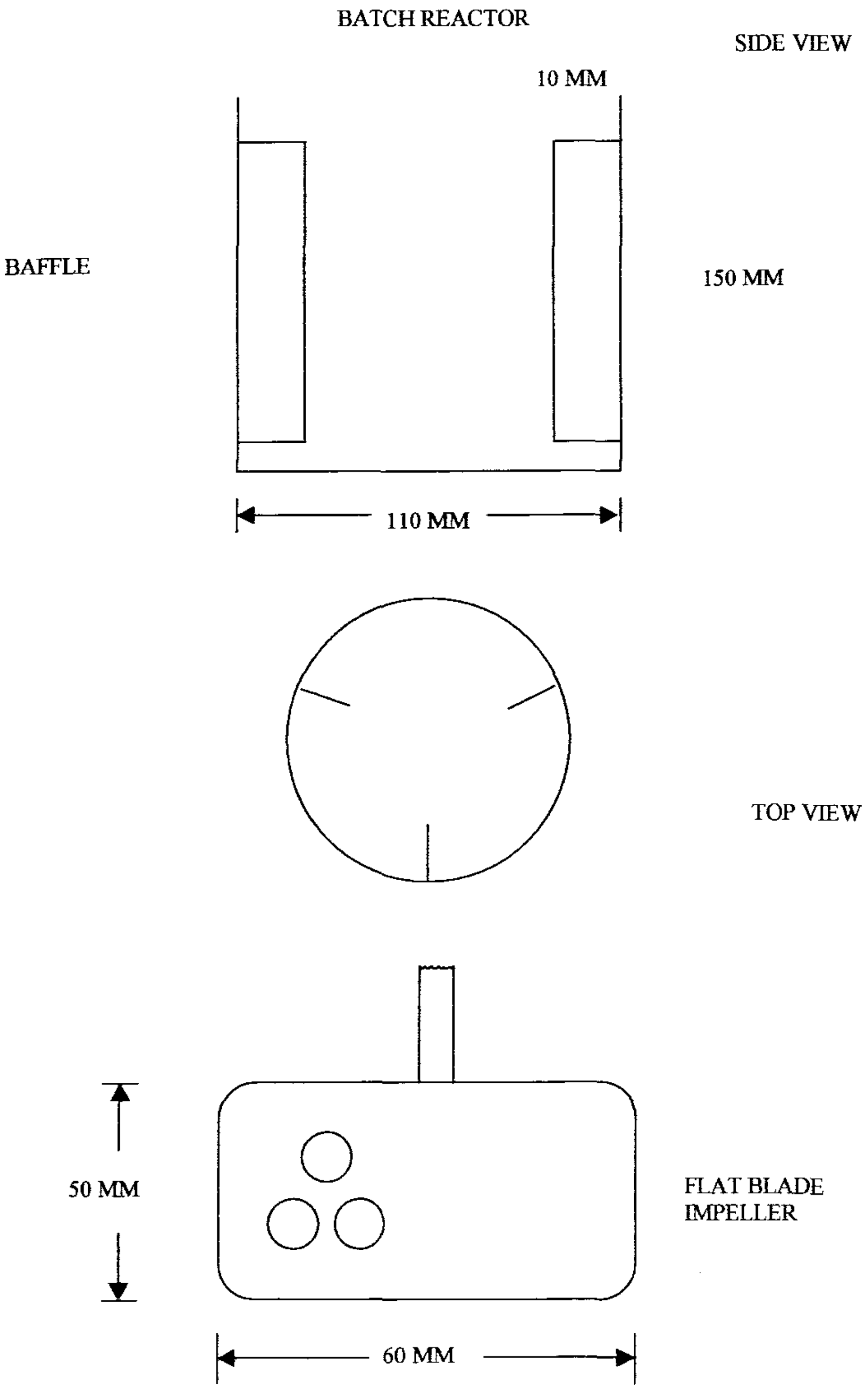

FIGURE 3.1 The experimental apparatus used in the equilibrium and adsorption tests

CHAPTER 4

DETERMINING SIGNIFICANT FACTORS CAUSING AN EQUILIBRIUM SHIFT

The factors typically affecting the performance of the gold adsorption system such as pH, ionic strength, cyanide and oxygen concentration, fouling and competitive adsorption have been identified and discussed in Chapter 1. Operators on CIP plants are well aware of the change of these operating variables but are challenged by the difficulty of control and measurability of some of these operating conditions. The aim with this work was therefore to identify the most realistic factors causing an isotherm shift, which can be measured easily. In this chapter the results of previous research and preliminary tests were used to determine the most sensitive factors and to eliminate some of the variables.

Figure 4.1 and Table 4.1 shows the equilibrium result and the isotherm (linearized Freundlich isotherm) determined for a batch adsorption test with a clear synthetic gold solution, which can be used as standard for comparison with the other experiments. From a plot of log q_s vs. log C_s, the A and n parameters were determined. The results were obtained by contacting a range of different concentrations of gold solutions, with a mass of 2.0 g of activated carbon at a pH of 10.5. Potassium cyanide was added to the solutions in the beginning of the tests to obtain a free cyanide concentration of 20 ppm.

4.1 FACTORS ELIMINATED

4.1.1 The effect of ionic strength

Fleming and Nicol (1984) determined equilibrium loadings from solutions with variable ionic strength. The increasing effect on the loading capacity with an increase in ionic strength, was found to be much greater than the loading rate. Adams (1990a) explained the interrelating effect of ionic strength and oxygen, and the pH shift which occurs upon adsorption, by a dual adsorption mechanism that becomes more dominant under conditions of low ionic strength. It was concluded from this work that adsorption under conditions of high ionic strength, involves an ion-pair mechanism whereas, under conditions of low ionic strength, a portion of the gold is adsorbed by electrostatic interaction with ion-exchange sites formed through oxidation of the carbon surface by molecular oxygen.

Woollacott and de Guzman (1993a) investigated several commercial CIP plants and found that the ionic strength of the solutions were very high and are not likely to change appreciably down the adsorption train. It can therefore be concluded that a change in the ionic strength would only cause a noticeable shift of the equilibrium at low ionic strength, and because plants operate mainly at high ionic strength conditions, this factor could therefore be ignored.

Hence, in all the experiments conducted in this work, the ionic strength was adjusted to 0.01 Molar in the beginning of each experiment, representing an intermediate ionic strength concentration. The introduction of other ions in the solution was avoided and therefore sodium hydroxide was used as an ionic strength adjuster instead of potassium chloride. It was determined that the ions already in solution contributed by the potassium gold cyanide and potassium cyanide, would have an effect of less than 1% on the ionic strength obtained by the addition of sodium hydroxide.

4.1.2 The effect of oxygen concentration

The general opinion is that the capacity of carbon for gold cyanide is greater in an aerated or oxygenated solution than in a solution through which nitrogen is bubbled (McDougal and Fleming, 1987).

In the previous section the proposed mechanisms for aurocyanide adsorption by Adams (1990a) were referred to. It was suggested that under conditions of low ionic strength two mechanisms takes place where: (1) the adsorption of $[M^{n+}][Au(CN)_2]_n$ ion pairs occurs to a greater extent in the absence of oxygen; and (2) where ion-exchange sites are formed that coordinate aurocyanide adsorption by simple electrostatic ion-exchange; this mechanism occurs to a greater extent in the presence of oxygen. It was concluded from this research that the ion pair is adsorbed onto the carbon without chemical change under conditions of high ionic strength. Therefore, under all practical plant conditions (high ionic strength) it can be assumed that oxygen concentration has no significant effect on gold adsorption. Adams (1990) suggested that the oxygen effects associated with the operation of CIP plants can therefore be contributed to the catalytic oxidation of free cyanide (as discussed previously) which results in more favourable conditions for gold adsorption.

The extent to which changes in the oxygen concentration affect the loading capacity of the carbon was also investigated by Woollacott and de Guzman (1993b) and divided into three regions. An oxygen-sensitive region was identified in solutions low in oxygen (<3.6 ppm), where the equilibrium isotherm are likely to be very sensitive to changes in oxygen levels.

A moderate to high oxygen concentration (>5,5 ppm) combined with low free cyanide levels (<100 ppm) is referred to as a sensitive region, where changes in the concentration of either component (oxygen or cyanide) will affect the loading capacity. Tests on plant systems suggest that the boundary is much lower, probably between 10 and 50 ppm. Figure 4.2 illustrates the effects of bubbling respectively oxygen and nitrogen through synthetic gold solutions. The results correspond with Woollacott's findings that oxygen enrichment under conditions of low cyanide concentrations (20 ppm free cyanide), will have a significant effect on the loading capacity (see Table 4.1).

The third, insensitive region was identified in solutions with moderate to high oxygen concentrations (>3.6 ppm) and high free cyanide levels (>100 ppm), where the effect of change in either component will have in insignificant effect on the loading capacity. Although the oxygen concentration on CIP plants decreases from one contactor to the next, it was found from measurements made on three South African plants that the oxygen levels seldom reaches concentrations lower that 3.6 ppm (Woollacott and de Guzman,1993a).

Hence, it can be concluded from these research findings that a change in oxygen concentrations will have a negligible effect on the equilibrium isotherm; under conditions of high ionic strength, high cyanide concentrations and at oxygen levels higher that 3.6 ppm. As these are conditions typically found on CIP plants, it was decided to ignore the effect of oxygen as a factor causing an isotherm shift.

4.1.3 The effect of organic fouling

Activated carbon becomes easily fouled by organics and clayey minerals which therefore reduce the carbon's activity for gold. At higher organic loadings on the carbon, the influence on the equilibrium is larger (Petersen and van Deventer, 1991). The organic content of South African ore is relatively low, which result in organic fouling only affecting the kinetics of adsorption. Changes in the degree of fouling and other species down a cascade of adsorption tanks, makes it impossible to consider the fouling effect of each individual species. Therefore, the influence of fouling on the adsorption capacity can be incorporated with the effect of competing ions in a combined competition coefficient (Liebenberg and van Deventer, 1997).

4.2 SELECTING KEY FACTORS

Considering the conclusions made in the previous section, the most significant factors causing an isotherm shift can be minimised to the following three, namely pH, free cyanide concentration and competitive adsorption. In this study a synthetic batch adsorption system were used to investigate the effect of change in these variables on the loading capacity of gold cyanide onto activated carbon. The influence of these factors will be quantified in terms of their influence on the equilibrium parameter (A) in the Freundlich isotherm. It was noticed that the value of n (isotherm parameter) is insensitive to changes in these factors and could therefore be ignored. This was confirmed by research done by Woollacott and de Guzman (1993b).

A method of factorial design, which can be found in Appendix 2, was used to create a series of tests in order to determine the impact of changes of these operating variables on the equilibrium isotherm in a batch reactor. The results were fitted to the Freundlich isotherm expression and graphically illustrated in Figures 4.3 to 4.10. The A values obtained are recorded in Table 4.2 which gives the layout of the experiment with eight trials in which all the combinations of the three variables were tested. The results of the hypotheses drawn from the variables are shown in Appendix 2. The effect of each variable has been measured four times.

4.2.1 The effect of pH

The pH concentration on a CIP plant is normally raised to about 10.5 to 11 by the addition of lime. A pH shift is typically observed with the adsorption of aurocyanide onto activated carbon. In order to test the effect of pH through factorial design, a pH of 11.5 was chosen as the present level found in real plant solutions (low level) and pH 9.5 as the alternative level (high level). The pH value was increased to 11.5 by adding small amounts of sodium hydroxide (NaOH) and decreased to a value of 9.5 by the slight addition of hydrochloric acid (HCl) to the solutions.

The general conclusion from the results in Table 4.2 confirms that an increase in pH has a decreasing effect on the A parameter (McDougall *et al,* 1980; Fleming and Nicol, 1984; Van Deventer, 1986). This effect is specifically demonstrated by comparing trials 3 and 4, as well as trials 2 and 6. Petersen and van Deventer (1991) observed the same effect with silver adsorption onto activated carbon and deduced that a lower pH seems to make the carbon surface more acceptable for adsorption of metal cyanide.

The first two trials give an indication of the influence of a low pH on the A parameter at different cyanide levels with competing ions in solution. The A value increased with 20 % when a lower cyanide level was used at the same pH value of 9.5. A similar trend was observed at pH 11.5 (Trials 6 and 8) although the absolute values of A were lower, once again as a result of the influence of pH. It should also be noted that only an 18 % increase in the A value is observed which indicates that the effect of cyanide concentration is higher at low pH levels than at high pH levels.

4.2.2 The effect of free cyanide concentration

4.2.2.1 Free cyanide degradation

As previously discussed, Woollacott and de Guzman (1993b) identified certain regions in which the loading capacity is sensitive to changes in oxygen and cyanide concentrations. The free cyanide-sensitive region was determined in solutions with oxygen levels higher than 5.5 ppm and cyanide levels lower than 100 ppm. The average free cyanide concentrations in the feed solutions (first stage) of a CIP plant are normally in the range from 80 to 130 ppm (sometimes even higher). This concentration will slowly decrease from one contactor to the next as cyanide destruction occurs through the catalytic oxidation of CN^- to cyanate ions. The stability of free cyanide levels is influenced by the pH of the solution. At pH levels higher than 11.5 the cyanide destruction catalysed by activated carbon is relatively low, while a significant decrease in cyanide is found at low pH levels. From investigations carried out by Woollacott and de Guzman (1993a) on three South African CIP plants, it was found that the cyanide levels could drop by up to 60 % in the first contactor and a further 10 % from one contactor to the next in the rest of the circuit. Table 4.3 shows the cyanide concentrations measured in the beginning and at the end of each trial experiment (trials 1 to 8) carried out in this work. A similar trend in the decrease of cyanide levels was found at high and low pH levels.

The work done by Woollacott and de Guzman (1993a) was utilised to establish a relationship between the cyanide profile in the adsorption circuit and the initial cyanide concentration. A first order decay in cyanide is illustrated in Figure 4.11, from which the following relationship was calculated:

$$[CN^-]_{decay} = [CN^-]_{initial}(stage+1)^{-6.02+0.502*pH} \qquad (4.1)$$

The initial pH and cyanide concentration can be obtained through physical measurements or experimental data. This means that the cyanide decay concentration can be calculated at any given time in a contactor at practical measurable pH and cyanide concentrations. At a pH higher than 12, no degradation of cyanide will take place.

4.2.2.2 The influence of cyanide decay on the equilibrium

Therefore, in the factorial design, the high (present level) and low levels (alternative level) of free cyanide was chosen as 100 ppm and 20 ppm to illustrate the effect of the above mentioned change in cyanide on the equilibrium. The different concentrations of free cyanide in the solutions were obtained by the addition of potassium cyanide.

The equilibrium parameter (A) increases significantly with a change in free cyanide concentration from 100 to 20 ppm as seen in trials 5 and 3, as well as trials 7 and 4. This confirms the sensitive range reported by Woollacott and de Guzman (1993b) and the decreasing effect of free cyanide on gold equilibrium loading (Davidson *et al*, 1982; Fleming and Nicol, 1984).

A comparison between trials 3 and 5 illustrates an important occurrence. The equilibrium A parameter for a solution with free cyanide content of 100 ppm at a pH of 9.5 will be relatively low as a result of the detrimental effect of high cyanide concentration. It is most likely, though that the free cyanide concentration will decrease in a real plant solution as the result of low pH. A change in cyanide concentration from 100 ppm to 20 ppm will then result in a 64 % increase in the equilibrium A parameter, which indicates a significant equilibrium shift.

Furthermore, Trial 8 versus trial 6 shows that the detrimental effect of a high cyanide concentration is more prominent than the effect of competing ions in the solution.

4.2.3 *The interaction between pH and free cyanide concentration*

The outcome of the factorial design is to determine the nature of the interaction between two variables (see Appendix 2). From the plot of this interaction, engineering decisions can be made.

A plot of the interaction between pH and free cyanide concentration showed that a linear relationship was found (Figure 4.12). Within the operating range of pH and free cyanide concentration investigated, the isotherm parameter, A, changed in value from 12.9 to 36, an average change of 64 %.

The effect of a pH change from 11.5 to 9.5 at a free cyanide concentration of 20 ppm, resulted in a 42% increase in the A parameter. However, at a high cyanide concentration, a change in pH had little effect on the equilibrium parameter.

A decrease in the free cyanide concentration from 100 ppm to 20 ppm will increase the A parameter with 47% at a pH of 9.5, while the same decrease in cyanide concentration at a pH of 11.5 will only result in a 32% increase in the A value. It can therefore be concluded that the effect of a change in the free cyanide content on the equilibrium A parameter is larger at a low pH than at a high pH. From these conclusions the effect of the free cyanide concentration on the A parameter at a solution pH of 10.5 could be illustrated by Figure 4.13. The arithmetical mean of the A value at pH 9.5 and 11.5 were used to determine the value of the A parameter at a high free cyanide concentration (100 ppm) due to unavailability of experimental results.

The linear relationship between the free cyanide content and the equilibrium A parameter at a standard pH of 10.5, yields the following equation:

$$A = 20.676 - 0.0628[CN^-] \tag{4.2}$$

This equation represents a pre-exponential A parameter. The cyanide decay concentration calculated in Equation (4.1) can be substituted into Equation (4.2), which yields a modified A parameter. This means that as the adsorption process takes place, a new value for the A parameter can be calculated and substituted in the Freundlich isotherm, incorporating changes in pH and free cyanide concentrations.

4.2.4 The effect of competing ions

Previous research on the competition effect of other metal-cyanides on gold loading showed that, with the exception of copper and nickel, these metal cyanide complexes have little effect on gold extraction efficiency (Fleming and Nicol, 1984). More recent research have established that with the changing conditions in CIP systems, it becomes difficult to account for all possible effects (Liebenberg and Van Deventer,1997). The adsorption of copper onto activated carbon is normally controlled by the pH and cyanide level of the solution. It was therefore decided to use nickel to represent the effect of competition. Through factorial design the adsorption behaviour was measured in a pure gold solution, 0 ppm nickel, for the high level; while 50 ppm nickel was added to the solution for the low level.

The negative effect of the adsorption of nickel onto activated carbon on gold loading is illustrated by trials 3 and 2 at pH 9.5 and trials 6 and 4 at pH 11.5. It is evident that the competitive effect is greater at a low pH than at a high pH. The observation was made in the previous section that the detrimental effect of a high cyanide concentration is more prominent than the effect of competing ions in the solution (trial 8 versus trial 6).

The effect of competitive adsorption was combined with the effect of fouling and accounted for by the lumping of these effects as a combined competition coefficient, by Liebenberg and Van Deventer (1997).

4.3 SUMMARY

Through a process of elimination the factors influencing the equilibrium isotherm were minimized to only three practical variables. The effect of ionic strength and oxygen concentration can be ignored, whereas the effect of fouling is lumped into a competition factor.

It was found that a change in the ionic strength would only cause a noticeable shift of the equilibrium at low ionic strength, and because plants operate mainly at high ionic strength conditions, this factor could therefore be eliminated. Measurements made on real plant solutions (Woollacott and de Guzman, 1993a) showed that oxygen concentrations seldom reaches levels below 3.6 ppm. At oxygen concentrations above this level, a change in oxygen concentration will have a negligible effect on the equilibrium isotherm, under conditions of high ionic strength and high cyanide concentrations typically found in CIP circuits.

Changes in the degree of fouling and other species down a cascade of adsorption tanks, makes it impossible to consider the effect of each individual species. Therefore the influence of fouling on the equilibrium capacity should be incorporated with the effect of competing ions in a combined competition coefficient.

A series of tests constructed through a factorial design matrix demonstrated the influence of pH, cyanide concentration, competing ions and their interactions with each other on the equilibrium isotherm. A decrease in pH from 11.5 to 9.5 can cause a considerable increase of 46 % in the equilibrium capacity in a clear gold solution (20 ppm free cyanide). It was shown that pH affects the stability of the free cyanide levels on a CIP plant. The effect of changes in the cyanide levels on the equilibrium was found to be higher at low pH levels than at high pH levels. A change in cyanide from 100 ppm to 20 ppm resulted in a 64 % increase in the equilibrium A parameter, which indicates a significant equilibrium shift. The detrimental effect of high cyanide concentrations was more prominent than the effect of competing ions. The negative effect of nickel adsorption on the gold loading was also affected by pH levels. The competitive effect was greater at pH 9.5 than 11.5.

A first order decay in cyanide concentration was established from previous work done by Woollacott and de Guzman (1993a), represented by Equation (4.1). At a solution pH of 10.5, a relationship between the cyanide concentration and the equilibrium A parameter was then postulated which resulted in a pre-exponential A parameter in Equation (4.2). A modified A parameter was obtained by substituting Equation (4.1) in Equation (4.2).

TABLE 4.1 Equilibrium parameters in a clear gold cyanide solution (pH 10.5, 20ppm free cyanide).

	A Parameter	n Parameter
Standard solution	19.482	0.221
Low oxygen	16.590	0.244
High oxygen	26.451	0.151

TABLE 4.2 The sensitivity of the equilibrium parameter, A, to pH, free cyanide concentration and competing ions in solution through a factorial design matrix.

Trial	pH	Cyanide (ppm)	Nickel cyanide (ppm)	A parameter Sample 1	A parameter Sample 2
1	9.5	100	50	20.687	19.362
2	9.5	20	50	25.920	26.094
3	9.5	20	0	35.989	34.457
4	11.5	20	0	19.275	19.590
5	9.5	100	0	12.381	11.473
6	11.5	20	50	16.683	14.610
7	11.5	100	0	11.160	12.933
8	11.5	100	50	13.356	11.999

TABLE 4.3 The effect of pH on the stability of the free cyanide content.

	pH	**Free $[CN^-]$ ppm beginning conc.**	**Free $[CN^-]$ ppm end conc.**
Trial 1	9.5	100	80
Trial 2	9.5	20	13
Trial 3	9.5	20	8
Trial 4	11.5	20	17
Trial 5	9.5	100	13
Trial 6	11.5	20	15
Trial 7	11.5	100	88
Trial 8	11.5	100	80

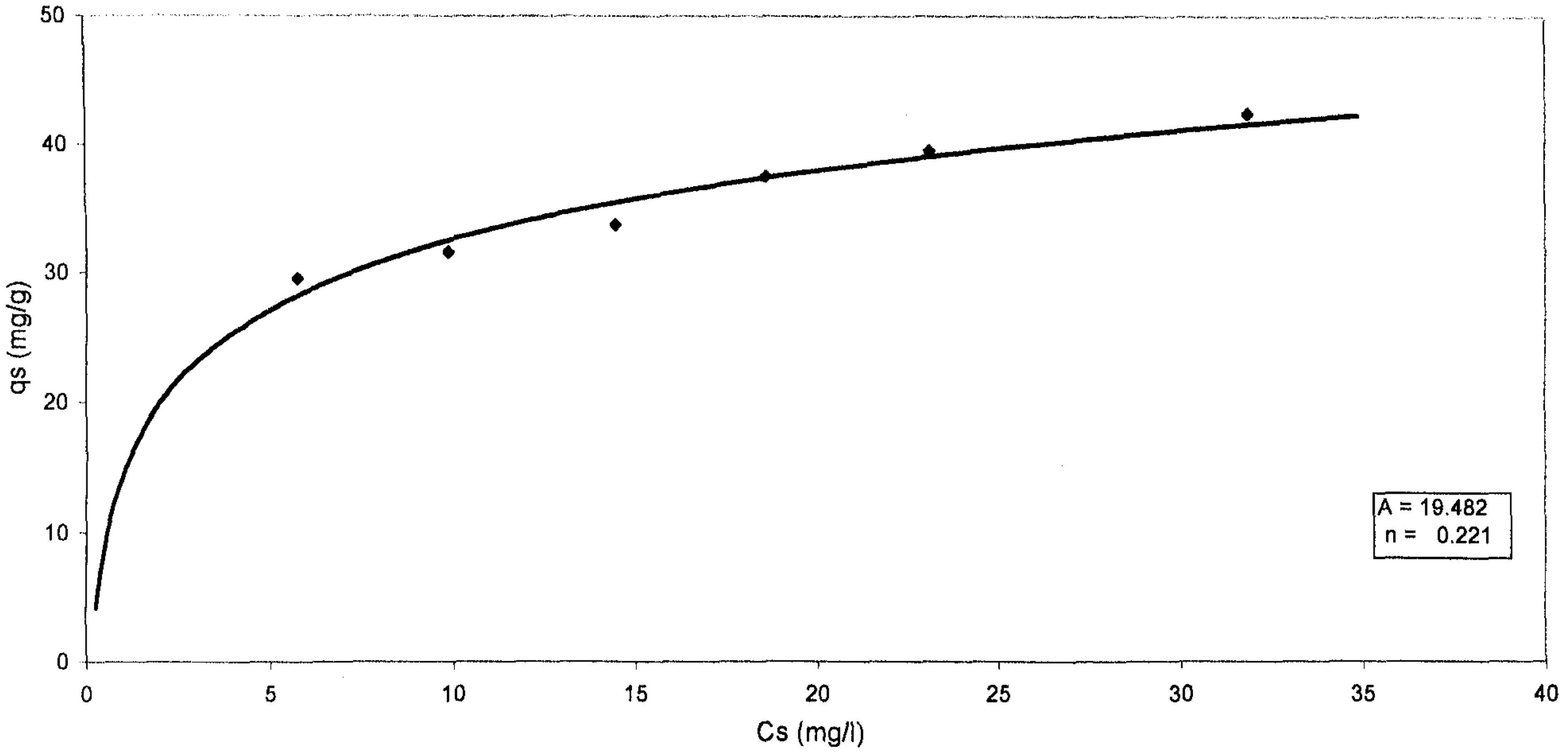

FIGURE 4.1 The equilibrium adsorption of gold cyanide from a clear solution on activated carbon, pH 10.5 (Experiment 1)

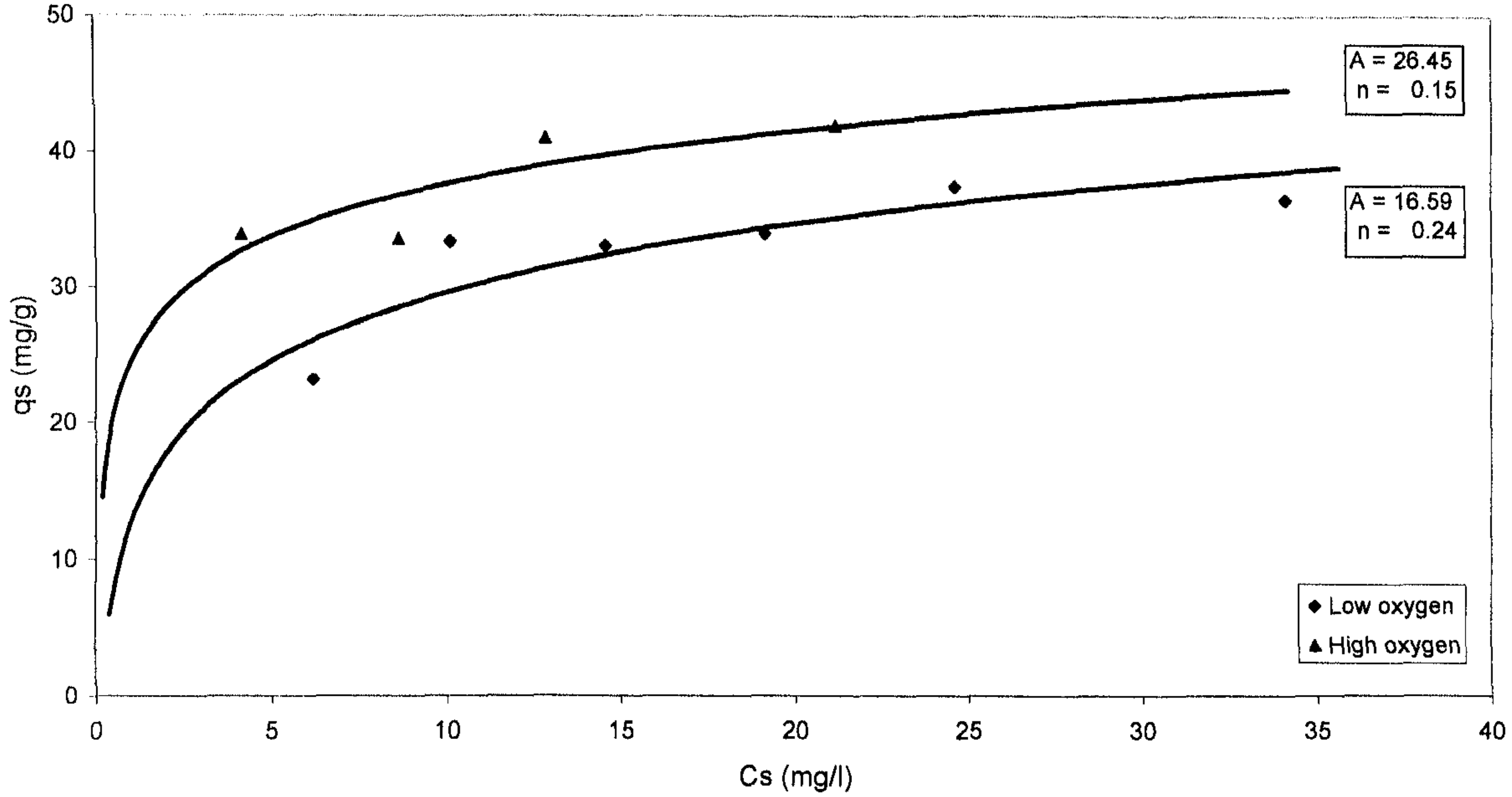

FIGURE 4.2 **The effect on the equilibrium with respectively bubbling oxygen and nitrogen through a clear gold solution. (Experiment 2)**

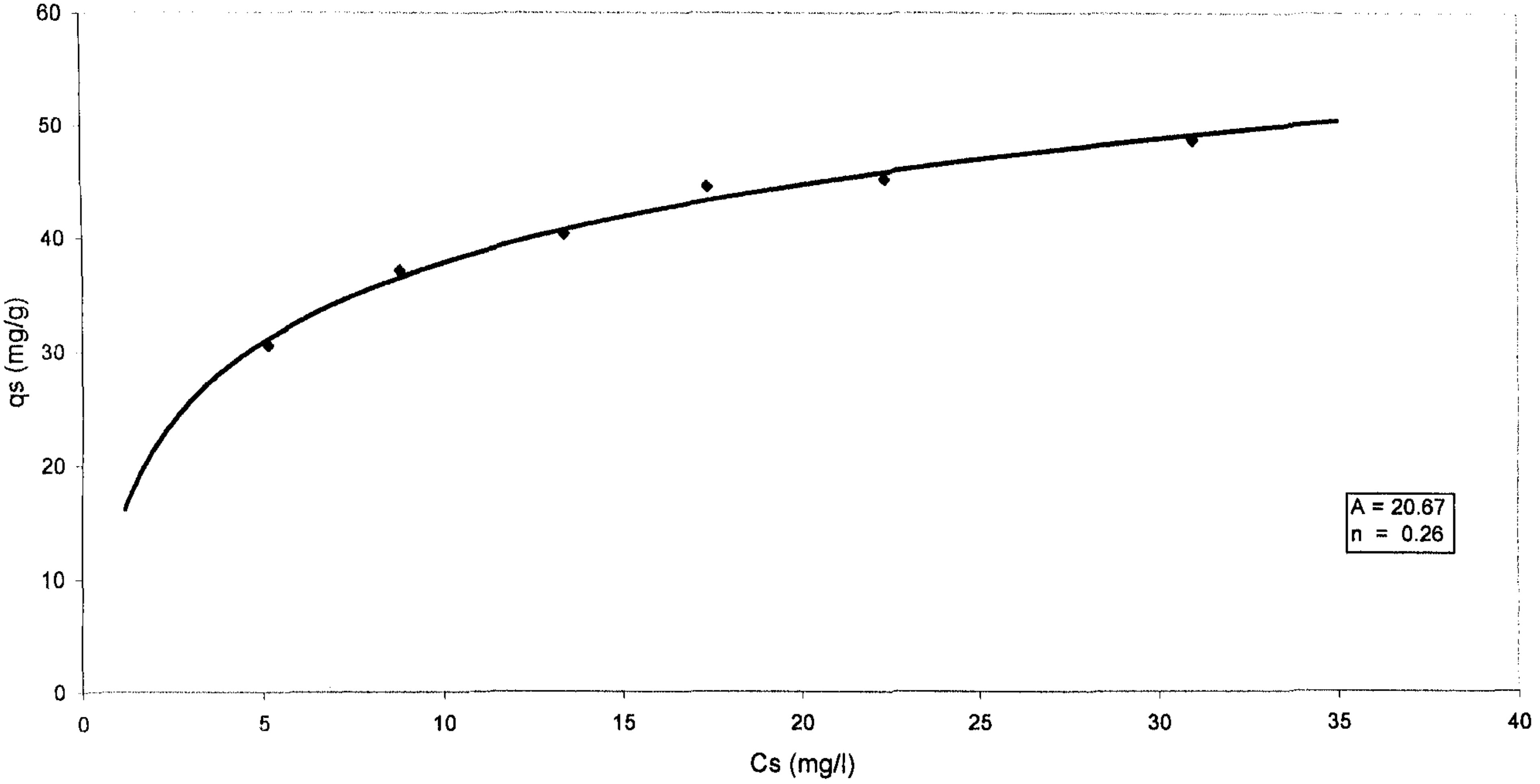

FIGURE 4.3 **Equilibrium adsorption of gold cyanide at pH 9.5, 100 ppm free CN, 50 ppm Ni. (Experiment 3, Trial 1)**

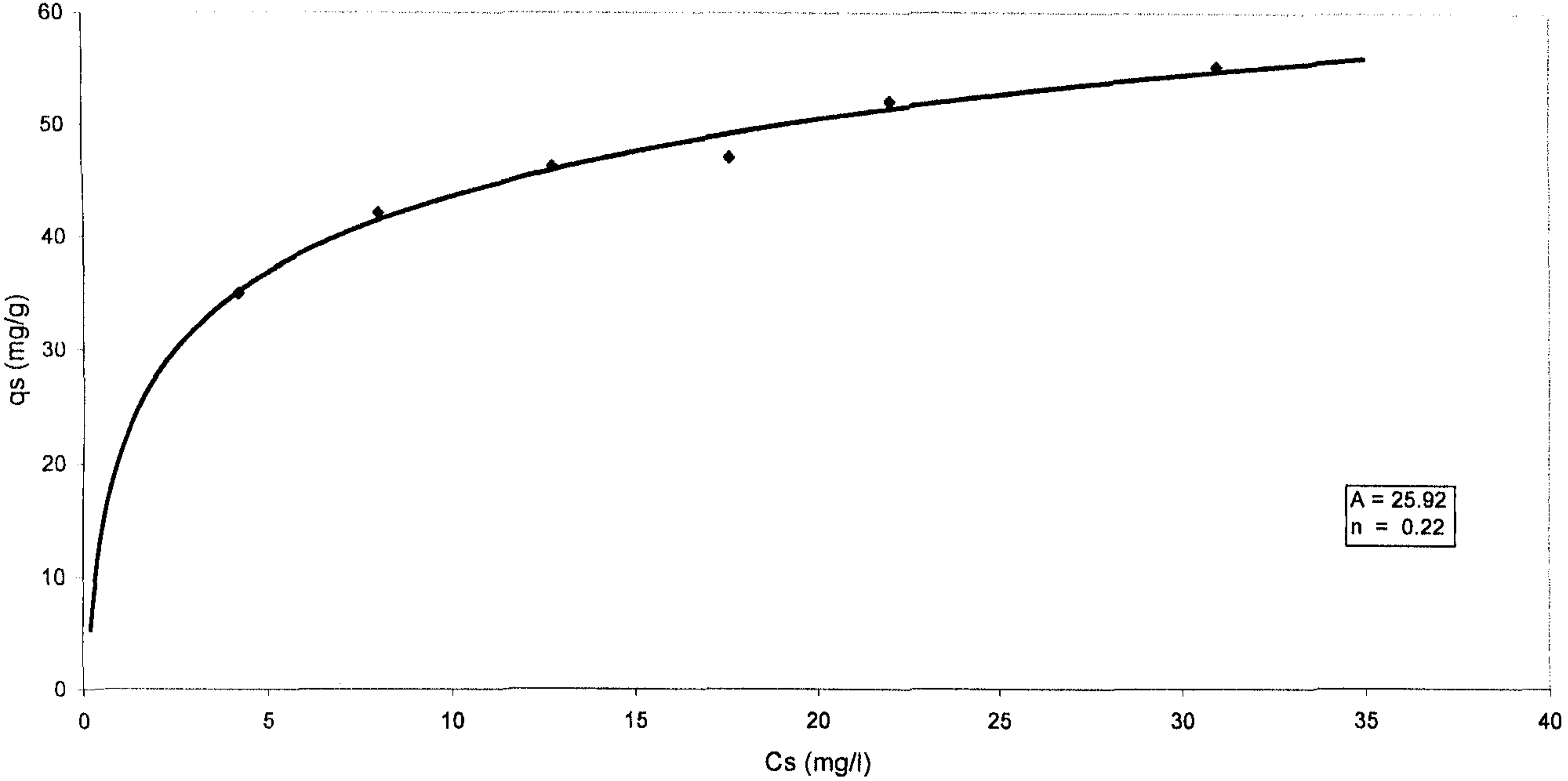

FIGURE 4.4 Equilibrium adsorption of gold cyanide at pH 9.5, 20 ppm free CN, 50 ppm Ni. (Experiment 4, Trial 2)

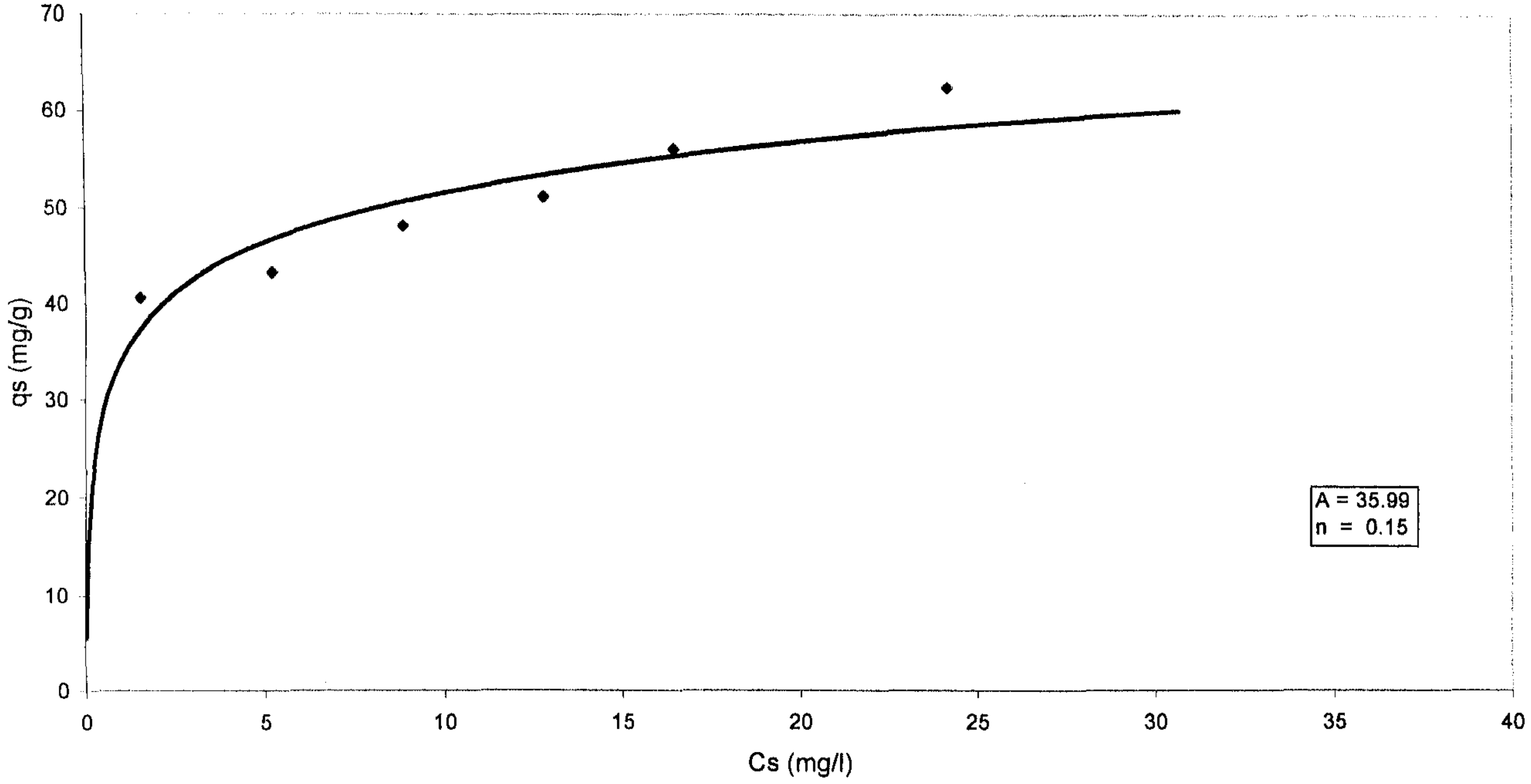

FIGURE 4.5 **Equilibrium adsorption of gold cyanide at pH 9.5, 20 ppm free CN, 0 ppm Ni. (Experiment 5, Trial 3)**

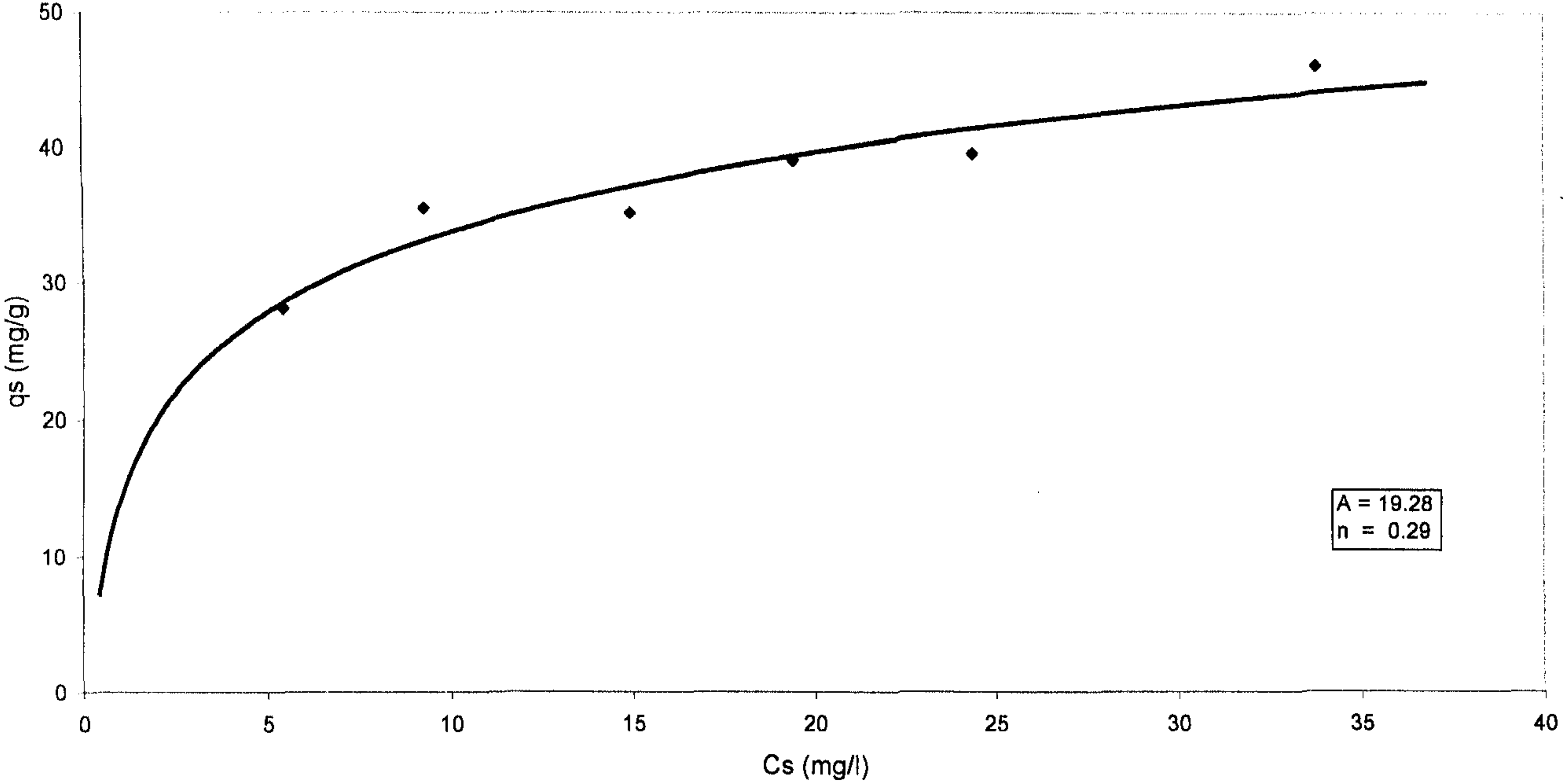

FIGURE 4.6 Equilibrium adsorption of gold cyanide at pH 11.5, 20 ppm free CN, 0 ppm Ni. (Experiment 6, Trial 4)

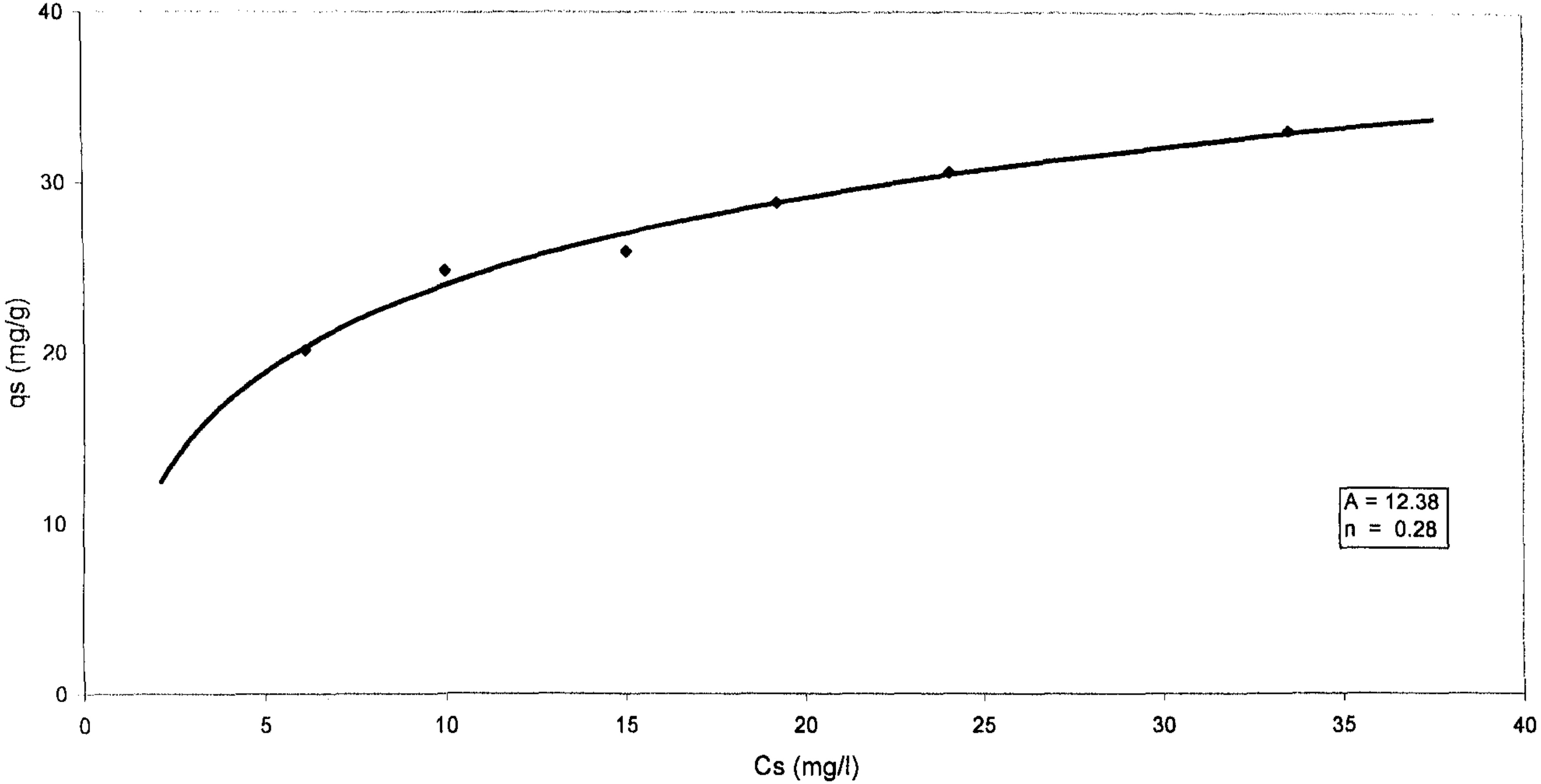

FIGURE 4.7 Equilibrium adsorption of gold cyanide at pH 9.5, 100 ppm free CN, 0 ppm Ni. (Experiment 7, Trial 5)

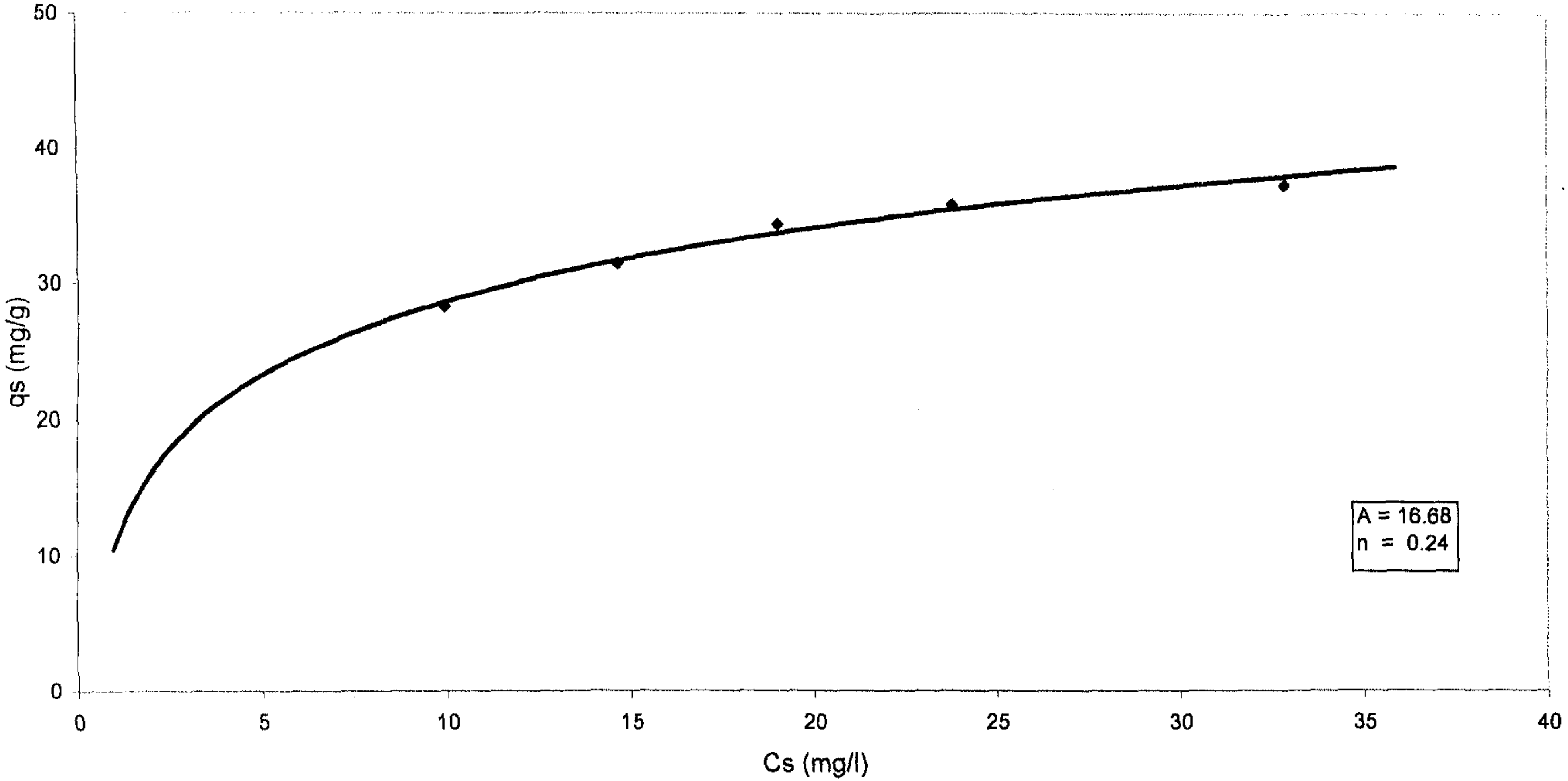

FIGURE 4.8 Equilibrium adsorption of gold cyanide at pH 11.5, 20 ppm CN, 50 ppm Ni. (Experiment 8, Trial 6)

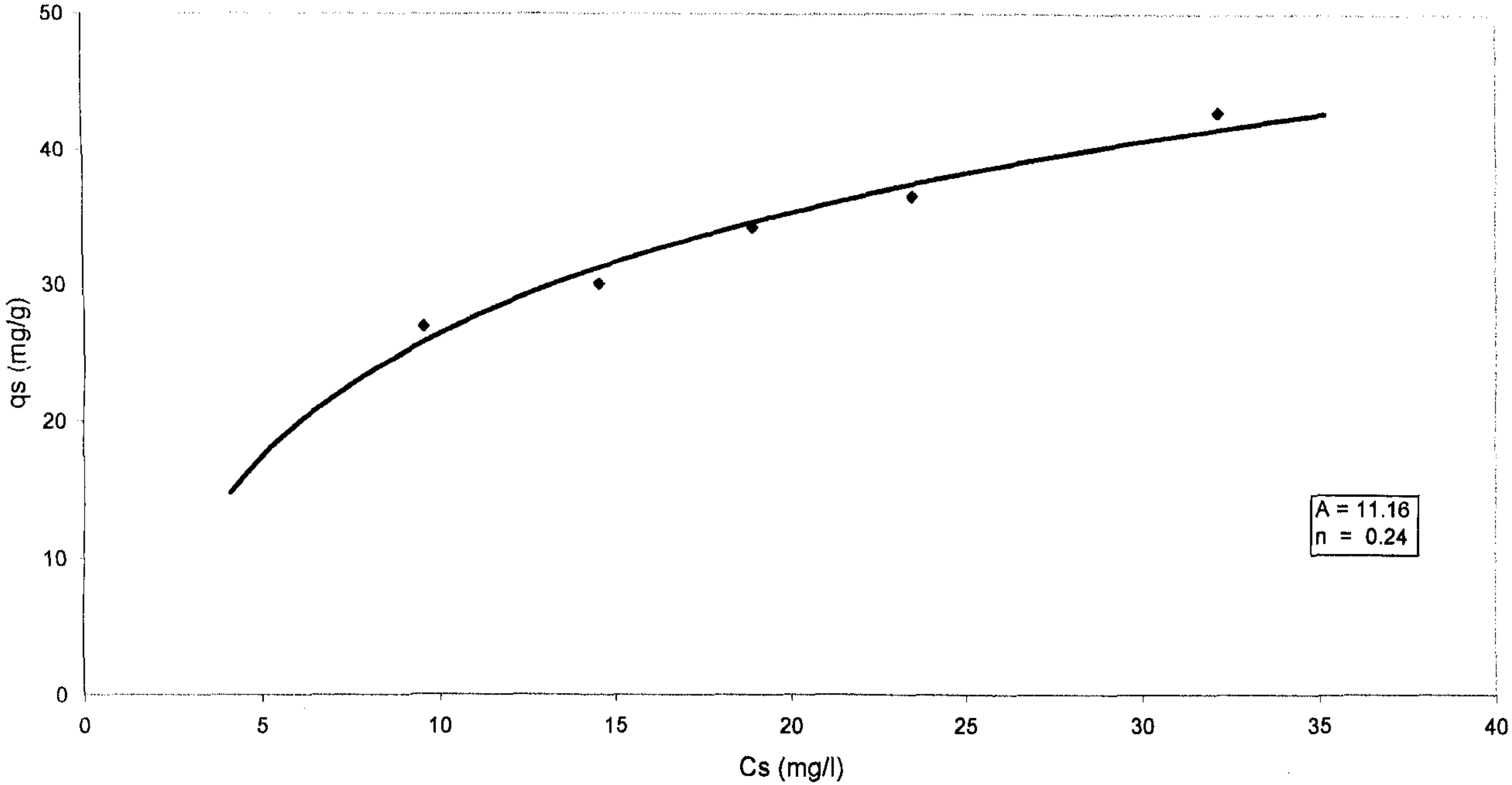

FIGURE 4.9 **Equilibrium adsorption of gold cyanide at pH 11.5, 100 ppm free CN, 0 ppm Ni. (Experiment 9, Trial 7)**

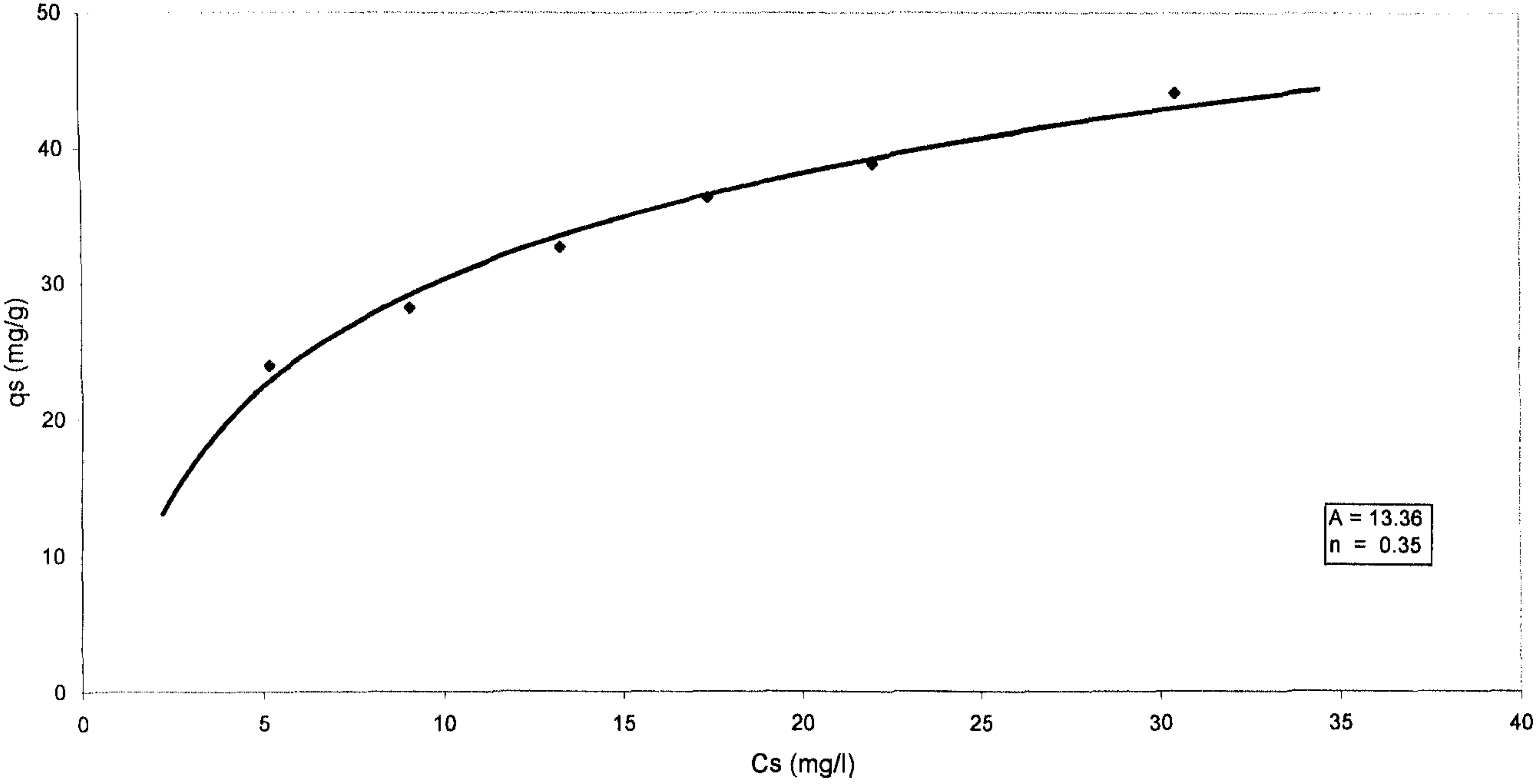

FIGURE 4.10 **Equilibrium adsorption of gold cyanide at pH 11.5, 100 ppm free CN, 50 ppm Ni. (Experiment 10, Trial 8)**

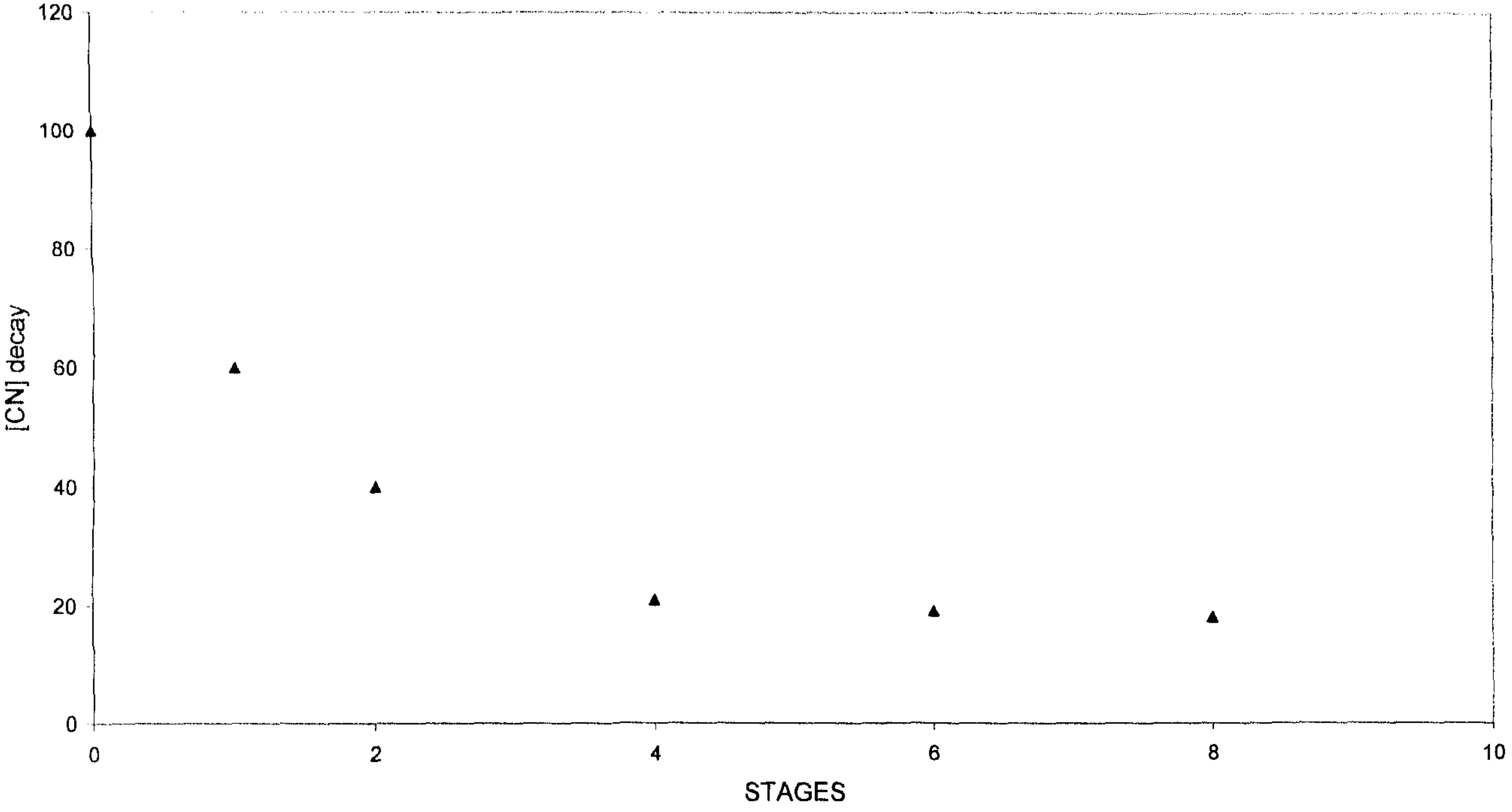

FIGURE 4.11 **A first order decay in free cyanide concentration.**

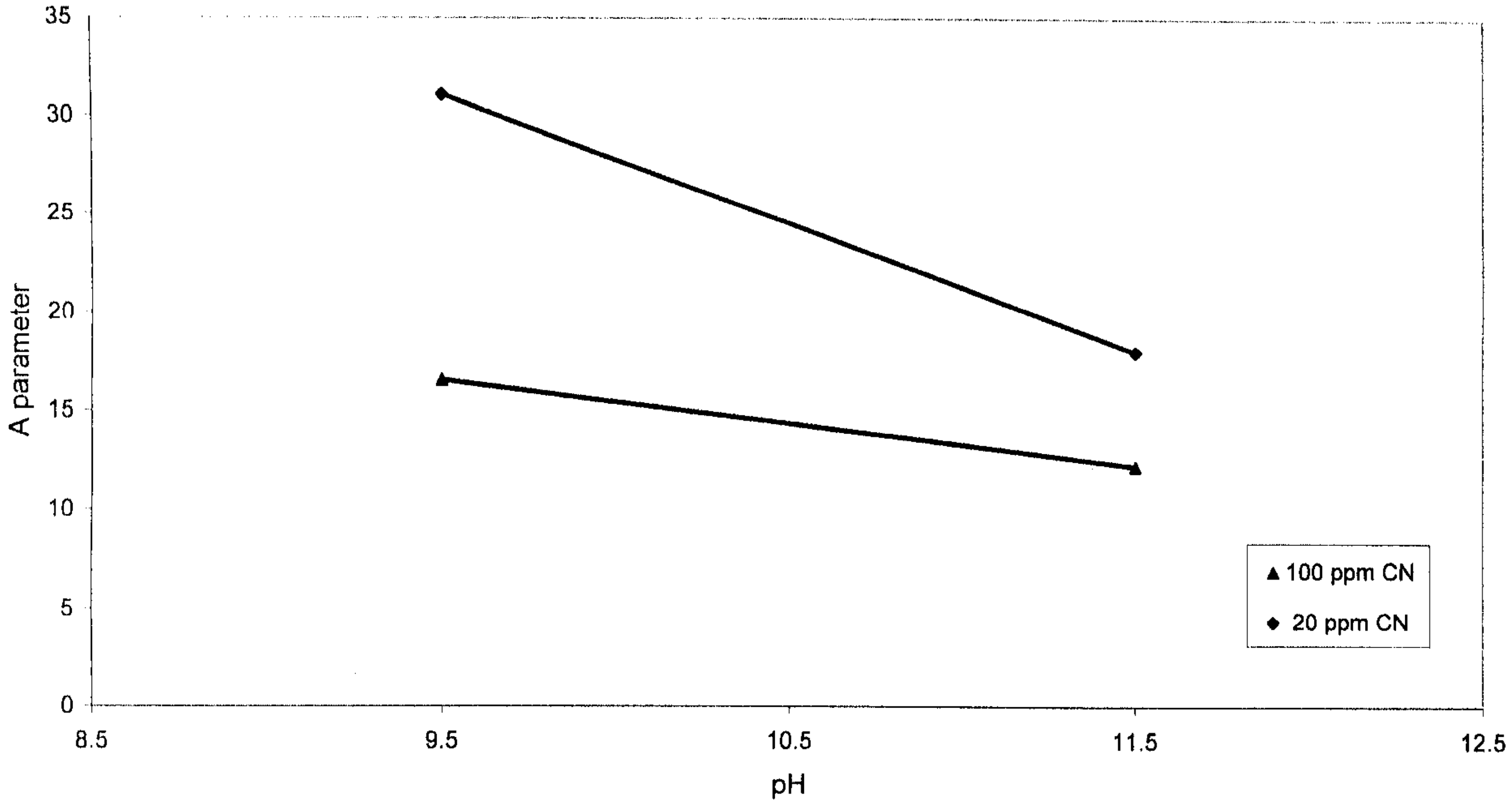

FIGURE 4.12 Plot of pH and free cyanide interaction.

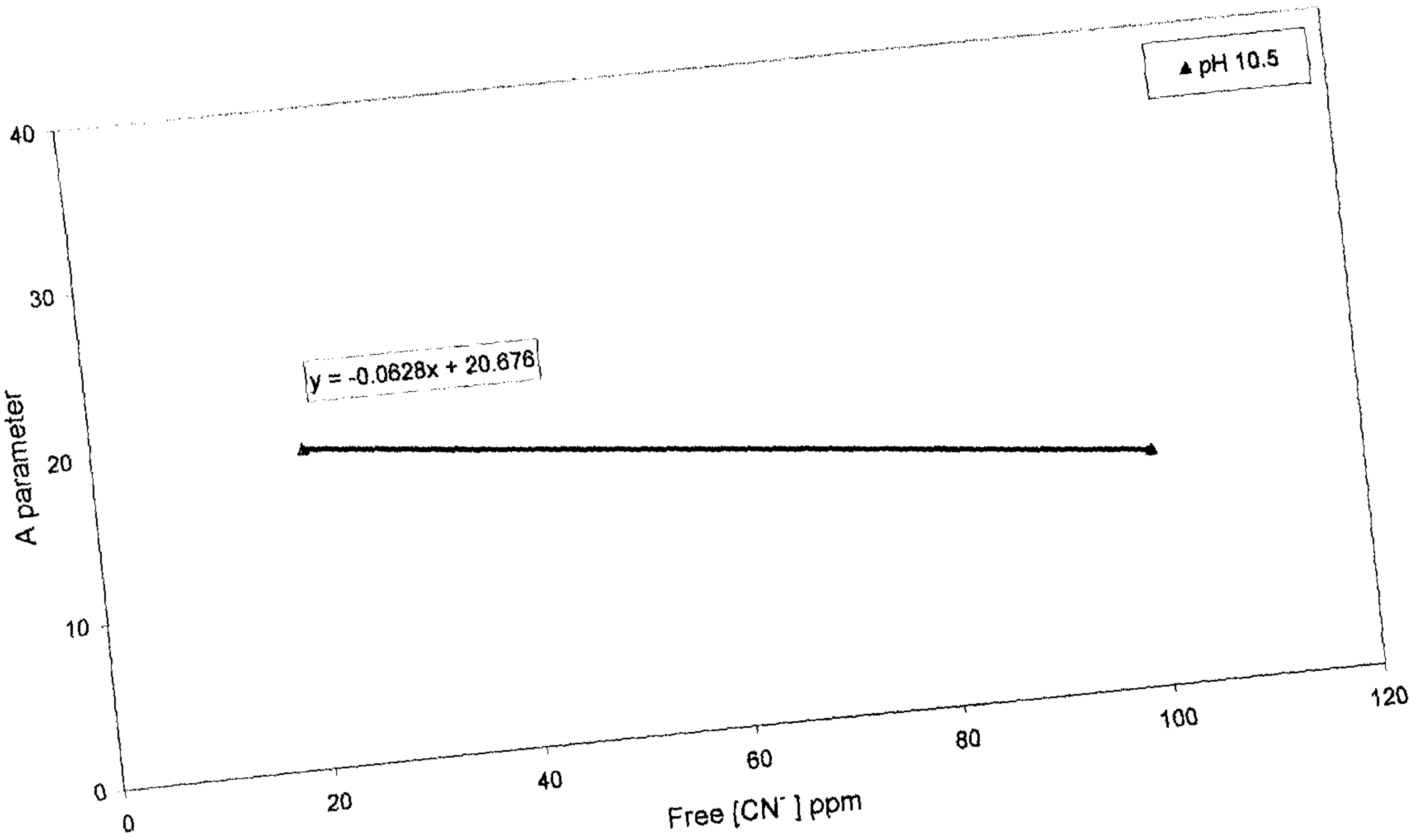

FIGURE 4.13 **Linear relationship between free cyanide and A parameter.**

CHAPTER 5

APPLICATION OF MODIFIED ISOTHERM

The logarithmic relationship between the solution concentration and the carbon loading is fundamentally important in the kinetic modelling of the gold adsorption system. This relationship is expressed in terms of the Freundlich isotherm as earlier explained. In the previous chapter the influence of three operating variables namely pH, free cyanide concentration and the concentration of nickel in solution were investigated and their influence on the equilibrium expression were established. The conditions of free cyanide concentration and pH are two parameters that can practically be measured on a real CIP plant. A correlation between pH and free cyanide in a batch reactor yielded a modified A parameter in the Freundlich isotherm that lumps the effect of these two factors together. It was attempted to account for the effect of competitive adsorption by determining the competition coefficients of gold and nickel. As a result of limited experimental data, the competition factor could not be determined and will therefore not be incorporated into the modified isotherm.

5.1 A SINGLE COMPONENT ISOTHERM

In practice a constant Freundlich isotherm is used in the kinetic model for the prediction of gold adsorption rates. The adsorption profile of a standard batch adsorption test of a clear gold solution was plotted graphically as illustrated in Figure 5.1. A mass of 0.2 g of activated carbon was contacted with 20 ppm clear gold cyanide solution at a pH of 10.5 with a free cyanide content of 20 ppm for a period of 24 hours. The external mass transfer coefficient, k_f, was obtained by using a curve fitting program while an estimated value was used for the surface diffusion coefficient, D_s. The kinetic and equilibrium parameters estimated is shown in Table 5.1 (Experiment 11).

A surface diffusion/film diffusion model was used for the estimation of the adsorption profile and was plotted against the actual results obtained as seen in Figure 5.1. This graphic representation shows that the model fits the actual experimental data with an accuracy of ±90%.

This error emphasises the importance of a method for predicting changes in adsorption behaviour. The typical changes in adsorption conditions that would most likely cause such a deviation can therefore be contributed to changes in pH and free cyanide concentrations. Figure 5.2 shows the difference in adsorption if the pH changes to 9.5 and the free cyanide content changes to 100 ppm respectively. This demonstrates the need to expand the model in order to describe the influence of operating variables on the extraction performance.

5.2 A MODIFIED ISOTHERM

A difference in the adsorption profile was observed with changing operating variables, hence the equilibrium expression should also be influenced. The influence of certain factors on the equilibrium isotherm was thoroughly investigated and ascribed as an effect on the equilibrium A parameter which resulted in a modified isotherm. Previous work showed that the changing conditions of a solution have a negligible effect on the n parameter in the isotherm, hence it was assumed that it stayed constant.

In order to obtain an acceptable fit for the model, the A parameter is the only parameter that could be changed if it is understood that the values of k_f and D_s stay constant. A modified A parameter was proposed in the previous chapter, which accounts for changes in pH and free cyanide concentration. If this modified A parameter is incorporated in the model the error in the fit to the experimental data is much smaller as seen in Figure 5.3. The value of the A parameter, hence the fit of the model was improved with 51 %. It can be assumed that if such an error were found in a single batch reactor, the error would even be larger if the same conditions were applied to a cascade system.

It should be noted that the investigation in the previous chapter proved the significant effect of competing ions and that this factor should be incorporated in the modified isotherm. As a result of limited experimental data, the competition factor could not be determined and will therefore not be incorporated into the isotherm at this stage. It is assumed that if this additional effect were added to the model, an even greater improvement in the fit would be obtained.

TABLE 5.1 The kinetic and equilibrium parameters estimated in a clear gold cyanide solution at pH 10.5 and free cyanide concentration of 20 ppm.

Parameter	Single isotherm	Modified isotherm
k_f	3.75×10^{-4}	3.75×10^{-4}
D_s	1.3×10^{-12}	1.3×10^{-12}
A	19.48	20.08
n	0.221	0.221

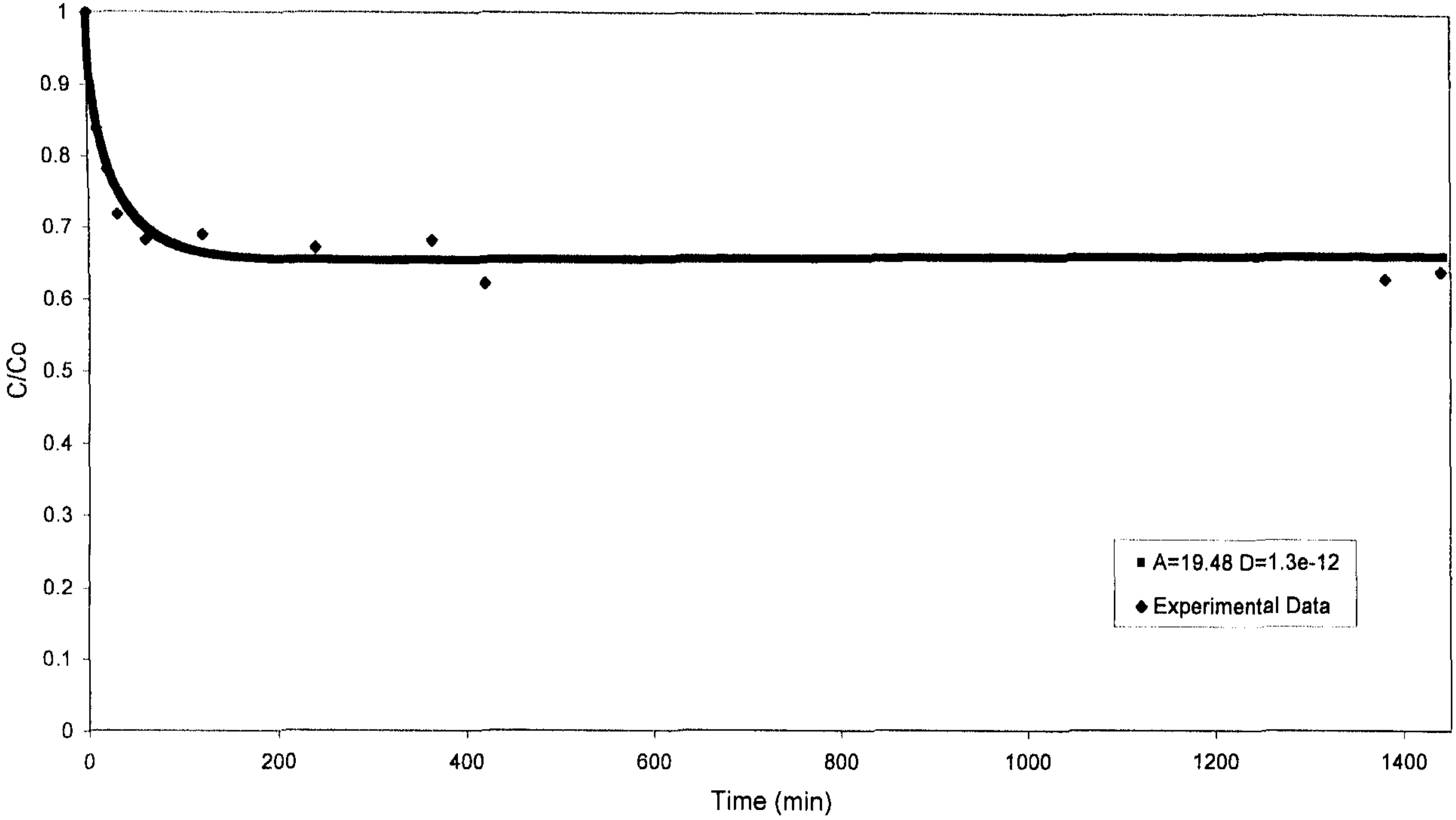

FIGURE 5.1 Adsorption profile for a clear gold solution fitted with model. (Experiment 11)

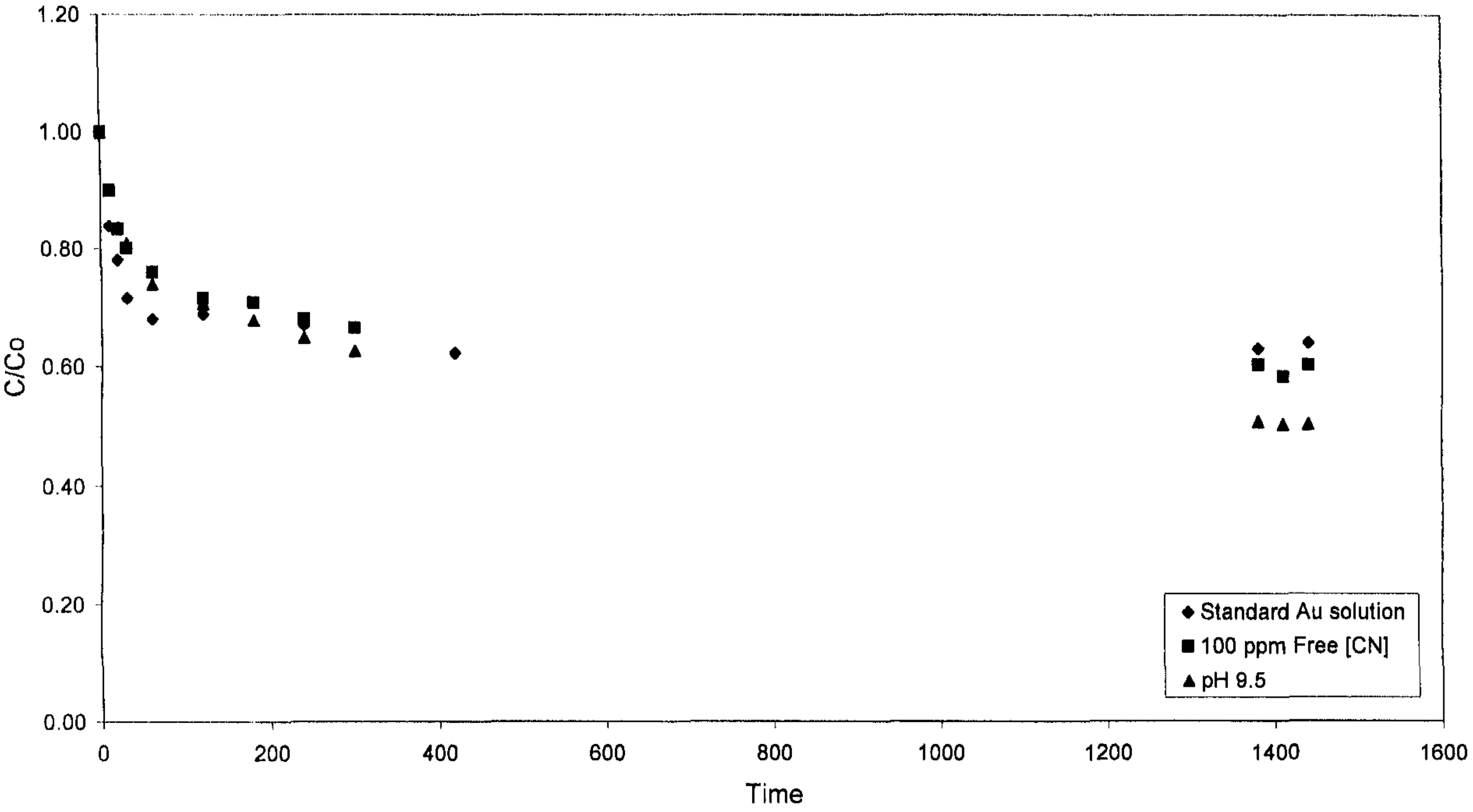

FIGURE 5.2 **The effect of a change in pH and free cyanide concentration alternatively on the adsorption profile of a clear gold solution. (Experiments 11, 12, 13)**

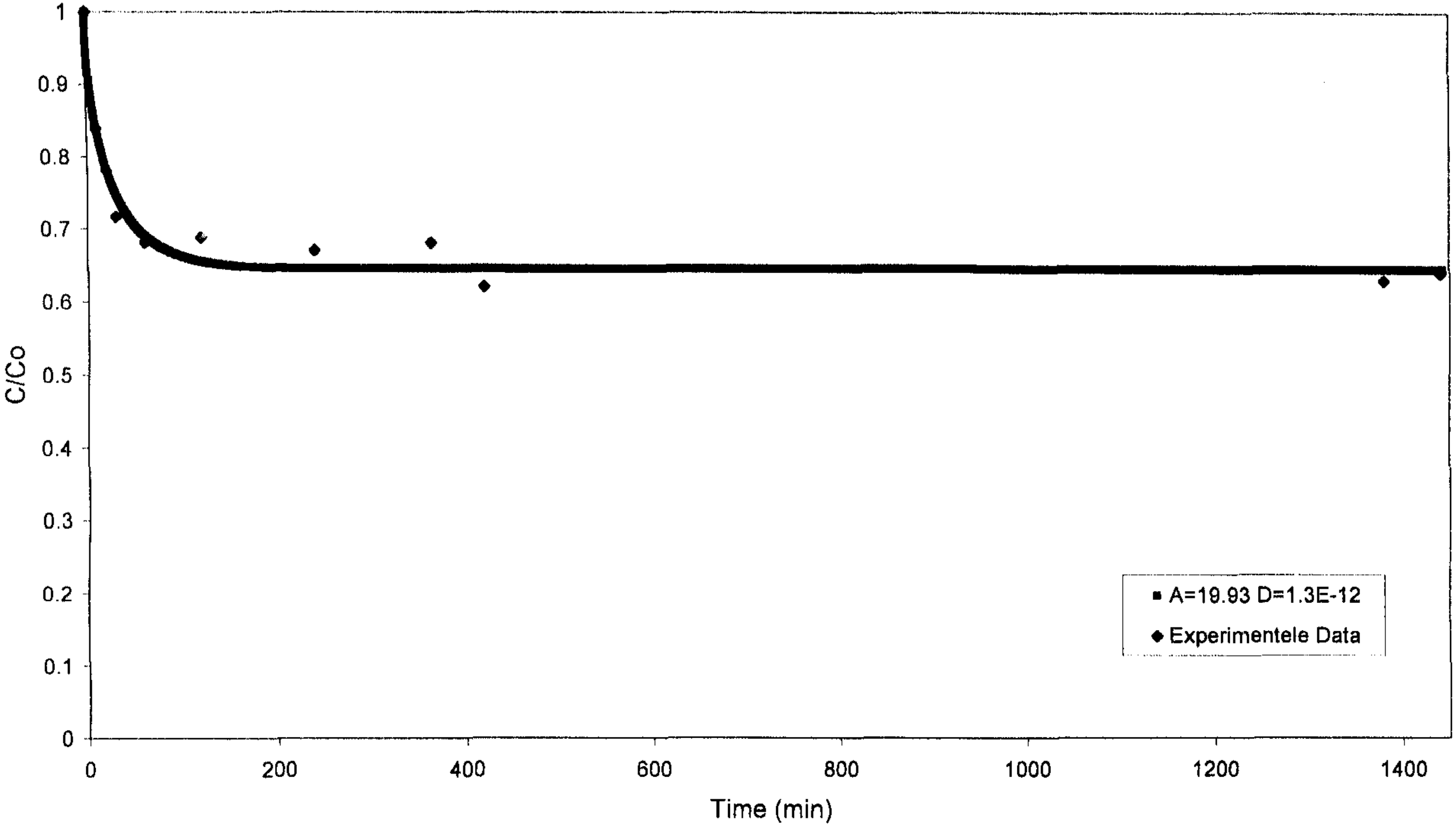

FIGURE 5.3 **Adsorption profile for a clear gold solution fitted with modified model.**

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions could be made on the basis of the research performed in this thesis:

- The main objective of this study was to identify operating conditions, which could be practically measured on a CIP plant; that will cause an isotherm shift. CIP circuits generally operate under conditions of high ionic strength and free cyanide content and at oxygen levels above 3 ppm. It was found that a change in either ionic strength or oxygen concentration under these conditions would not significantly affect the adsorption equilibrium of gold and that the influence of these variables could be ignored.

- Vast changes in the degree of fouling of organics and other minerals are found within a cascade of adsorption tanks and also between different plants. This makes it impossible to measure the effect of each individual species on the equilibrium. The influence of fouling as an operating parameter can therefore be lumped with the effect of competing ions in a combined competitive coefficient.

- The most significant factors causing an isotherm shift were minimised to pH, free cyanide concentration and competing ions in solution. It was concluded that pH as an operational parameter is important in view of the effect it has on other operating parameters. A pH shift between 11.5 and 9.5 may result in a 46 % change in the equilibrium loading. It is known that the adsorption of aurocyanide is accompanied by a pH shift. For this reason it is obvious that the pH should be monitored and adjusted regularly to avoid a shift in equilibrium.

- It was found that the stability of free cyanide concentration is to a large extent controlled by the pH of the solution. Low pH levels results in a significant decrease in cyanide concentration. A relationship was postulated between the cyanide profile in the adsorption circuit and the initial cyanide concentration, which yielded a first order decay in cyanide represented by the following expression:

$$[CN^-]_{decay} = [CN^-]_{initial}(stage+1)^{-6.02+0.502*pH}$$

- The effect of a change in free cyanide concentration is significant in the range from 100 ppm to 20 ppm free cyanide. The experimental results showed an increase of 64 % in the equilibrium A parameter if such a decrease should occur. The detrimental effect of high cyanide concentration was also found to be more prominent than the effect of competing ions. It can be concluded from the interacting effect between free cyanide and pH, that the influence of a change in free cyanide content on the equilibrium is larger at a low pH than at a high pH. A linear relationship was formed at a pH of 10.5 between the free cyanide concentration and the equilibrium A parameter, which is represented by the following equation:

$$A = 20.676 - 0.0628[CN^-]$$

- This work resulted in a modified A parameter when the two proposed expressions were combined. The modified A parameter can be substituted in the existing Freundlich isotherm which will modify the isotherm.

- A surface diffusion/film diffusion model was fitted to the experimental data to estimate the adsorption profile. The modified A parameter was incorporated into the model and it proved that a better fit (51 % improvement) could be obtained when a change in pH and free cyanide concentration was accounted for.

- As a result of limited experimental data the competition factor for gold and nickel could not be determined. It is suggested that future work should include the effect of competing ions, in order to include this factor in the modified Freundlich isotherm. It is assumed that if this additional effect were added to the model, an even greater fit of the model predictions would be obtained.

CHAPTER 7

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APPENDIX 1

A factorial design for determining the impact of changes of operating variables on the equilibrium isotherm in a batch reactor.

A. STATE THE OBJECT OF THE EXPERIMENT

A high and a low level are normally designated to each variable. The value of the variable that is expected to be best is usually designated as the high level. In this design the aim is to determine the effects of a change in the variables and not the best condition of the variable. The two levels therefore chosen for each variable are first the level of the variable presently found on CIP plants (low level) and secondly an alternative level or a change in the level (high level).

$(H_o)_1$: $\mu_{9.5} = \mu_{11.5}$

$(H_a)_1$: $\mu_{9.5} > \mu_{11.5}$

$(H_o)_2$: $\mu_{20} = \mu_{100}$

$(H_a)_2$: $\mu_{20} > \mu_{100}$

$(H_o)_3$: $\mu_{0} = \mu_{50}$

$(H_a)_3$: $\mu_{0} \neq \mu_{50}$

$(H_0)_4$: $\mu_{AB \text{ interaction}} = 0$

$(H_a)_4$: $\mu_{AB \text{ interaction}} > 0$

$(H_0)_5$: $\mu_{BC \text{ interaction}} = 0$

$(H_a)_5$: $\mu_{BC \text{ interaction}} > 0$

$(H_0)_6$: $\mu_{AC \text{ interaction}} = 0$

$(H_a)_6$: $\mu_{AC \text{ interaction}} > 0$

$(H_0)_7$: $\mu_{ABC \text{ interaction}} = 0$

$(H_a)_7$: $\mu_{ABC \text{ interaction}} > 0$

		LOW LEVEL	HIGH LEVEL
A	pH	11.5	9.5
B	Free Cyanide (ppm)	100	20
C	Nickel cyanide (ppm)	50	0

B. CHOOSE THE VALUES FOR α, β, δ

$\alpha = 0.05$
$\beta = 0.1$
$\delta = 2.5\sigma$
σ^2 = unknown

C. COMPUTE *N*

N refers to the number of comparisons that are to be obtained, not to the number of samples in each treatment combination. When one of the alternative hypotheses is double-sided, the size of *N* must be computed using table 2 (double-sided) for U_α and table 4 (double-sided) for t_α. Table 1 is used for U_β and table 3 is used for t_β.

$$N = 2(U_\alpha + U_\beta)^2 \frac{\sigma^2}{\delta^2} = 2(1{,}96 + 1{,}282)^2 \frac{\sigma^2}{2{,}5\sigma^2} = 3{,}36$$

$$N_{high} = N_{low} = 2(t_\alpha + t_\beta)^2 \frac{\sigma^2}{\delta^2} = 2(2{,}78 + 1{,}53)^x \frac{\sigma^2}{(2.5\sigma)^2} = 5{,}9$$

If the 8 x 8 Hadamard matrix is used, $N_{high} = N_{low} = 4$. The required sample size above, 5.9, is approximately equal to the sample size 4, therefore the 8 x 8 Hadamard matrix is the correct matrix.

D. LABEL THE 8 X 8 HADAMARD MATRIX

The matrix should be labelled properly and the eight treatment combinations should be labelled. The low level of a variable is represented by a minus sign (-), the number 1 or the absence of a letter. The high level of a variable is represented by a plus sign (+), or a letter "a" in the case of the high level of variable A, the letter "b" to represent the high level of variable B, and the letter "c" for the high level of variable C.

		A	B	C	-AB	-BC	ABC	-AC	Treatment Combinations
Trial	0	1	2	3	4	5	6	7	
1	+	+	–	–	+	–	+	+	a
2	+	+	+	–	–	+	–	+	ab
3	+	+	+	+	–	–	+	–	abc
4	+	–	+	+	+	–	–	+	bc
5	+	+	–	+	+	+	–	–	ac
6	+	–	+	–	+	+	+	–	b
7	+	–	–	+	–	+	+	+	c
8	+	–	–	–	–	–	–	–	(1)

E. DETERMINE THE A VALUE UNDER THE pH, CYANIDE CONCENTRATION AND NICKEL CYANIDE CONCENTRATION SPECIFIED IN EACH TRIAL.

Trial	pH	Cyanide (ppm)	Nickel cyanide (ppm)	A parameter Sample 1	Sample 2
1	9.5	100	50	20.687	19.362
2	9.5	20	50	25.920	26.094
3	9.5	20	0	35.989	34.457
4	11.5	20	0	19.275	19.590
5	9.5	100	0	12.381	11.473
6	11.5	20	50	16.683	14.610
7	11.5	100	0	11.160	12.933
8	11.5	100	50	13.356	11.999

F. DETERMINE THE EFFECT OF THE VARIABLES AND INTERACTION

The effect of the variables and interactions is determined by using the sings in the columns with the results obtained. The sum of each column is calculated.

Therefore $\Sigma X_{high} - \Sigma X_{low}$ = Total of each column

A	B	C	-AB	-BC	ABC	-AC
+20.687	-20.687	-20.687	+20.687	-20.687	+20.687	+20.687
+25.920	+25.920	-25.920	-25.920	+25.920	-25.920	+25.920
+35.989	+35.989	+35.989	-35.989	-35.989	+35.989	-35.989
-19.275	+19.275	+19.275	+19.275	-19.275	-19.275	+19.275
+12.381	-12.381	+12.381	+12.381	+12.381	-12.381	-12.381
-16.683	+16.683	-16.683	+16.683	+16.683	+16.683	-16.683
-11.160	-11.160	+11.160	-11.160	+11.160	+11.160	+11.160
-13.356	-13.356	-13.356	-13.356	-13.356	-13.356	-13.356
34.503	**40.283**	**2.159**	**-17.399**	**-23.163**	**13.587**	**-1.367**

G. ESTIMATE THE VARIANCE

The entire experiment was replicated twice. This gave two results at each treatment combination, from which an estimate of the variance could be obtained with one degree of freedom at each treatment combination.

A Parameter Sample 1	A Parameter Sample 2	S^2 (Variance)
20.687	19.362	0.878
25.920	26.094	0.015
35.989	34.457	1.174
19.275	19.590	0.050
12.381	11.473	0.412
16.683	14.610	2.146
11.160	12.933	1.572
13.356	11.999	0.921

$S^2_{average}$ = 0.896 (with 8 degrees of freedom)

S = 0.947

H. DETERMINE THE TEST CRITERION

$$\left|\overline{X}_{high} - \overline{X}_{low}\right|^* = t_a S \sqrt{\frac{1}{N_{high}} + \frac{1}{N_{low}}}$$

For the double-sided alternative hypothesis use Table 4:

$$\left|\overline{X}_{high} - \overline{X}_{low}\right|^* = (2{,}4)(0{,}947)\sqrt{\frac{1}{4}+\frac{1}{4}} = 1{,}607$$

For the single-sided alternative hypothesis use Table 3:

$$\left|\overline{X}_{high} - \overline{X}_{low}\right|^* = (1{,}86)(0{,}947)\sqrt{\frac{1}{4}+\frac{1}{4}} = 1{,}246$$

I. APPLY THE TEST CRITERION, AND MAKE THE DECISION.

$$\left(\left|\overline{X}_{9,5} - \overline{X}_{11,5}\right| = 8{,}626\right) > \left(\left|\overline{X}_{high} - \overline{X}_{low}\right|^* = 1{,}246\right)$$

Therefore, accept $(H_a)_1$: $\mu_{9.5} > \mu_{11.5}$ with at least 95% confidence (H_a was single-sided)

$$\left(\left|\overline{X}_{20\,ppm} - \overline{X}_{100\,ppm}\right| = 10{,}07\right) > \left(\left|\overline{X}_{high} - \overline{X}_{low}\right|^* = 1{,}246\right)$$

Therefore, accept $(H_a)_2$: $\mu_{20} > \mu_{100}$ with at least 95% confidence (H_a was single-sided)

$$\left(\left|\overline{X}_{0\,ppm} - \overline{X}_{50\,ppm}\right| = 0{,}539\right) < \left(\left|\overline{X}_{high} - \overline{X}_{low}\right|^* = 1{,}607\right)$$

Therefore, accept $(H_a)_3$: $\mu_0 < \mu_{50}$ with at least 97.5% confidence (H_a was double-sided)

$$\left(\left|\overline{X}_{+AB} - \overline{X}_{-AB}\right| = 4{,}350\right) > \left(\left|\overline{X}_{high} - \overline{X}_{low}\right|^* = 1{,}246\right)$$

Therefore, accept $(H_a)_4$: $\mu_{AB\ \text{interaction}} > 0$ with at least 95% confidence (H_a was single-sided)

$$\left(\left|\overline{X}_{+BC} - \overline{X}_{-BC}\right| = 5{,}790\right) > \left(\left|\overline{X}_{high} - \overline{X}_{low}\right|^* = 1{,}246\right)$$

Therefore, accept $(H_a)_5$: $\mu_{BC\ \text{interaction}} > 0$ with at least 95% confidence (H_a was single-sided)

$$\left(\left|\overline{X}_{+AC} - \overline{X}_{-AC}\right| = 0{,}342\right) < \left(\left|\overline{X}_{high} - \overline{X}_{low}\right|^* = 1{,}246\right)$$

Therefore, accept $(H_a)_6$: $\mu_{AC\ \text{interaction}} < 0$ with at least 95% confidence (H_a was single-sided)
A two interaction will not be drawn between AC, as the AC interaction effect is smaller than the criterion.

$$\left(\left|\overline{X}_{+ABC} - \overline{X}_{-ABC}\right| = 3{,}397\right) > \left(\left|\overline{X}_{high} - \overline{X}_{low}\right|^* = 1{,}246\right)$$

Therefore, accept $(H_a)_7$: $\mu_{ABC\ \mathrm{interaction}} > 0$ with at least 95% confidence (H_a was single-sided)

J. DETERMINE THE NATURE OF THE INTERACTION

A two-way chart is drawn of the AB interaction:

	1	**b**
1	11.160 13.356 Avg = 12.258	19.275 16.683 Avg = 17.979
a	12.381 20.687 Avg = 16.538	26.920 35.989 Avg = 31.04

The AB interaction is graphically plot.

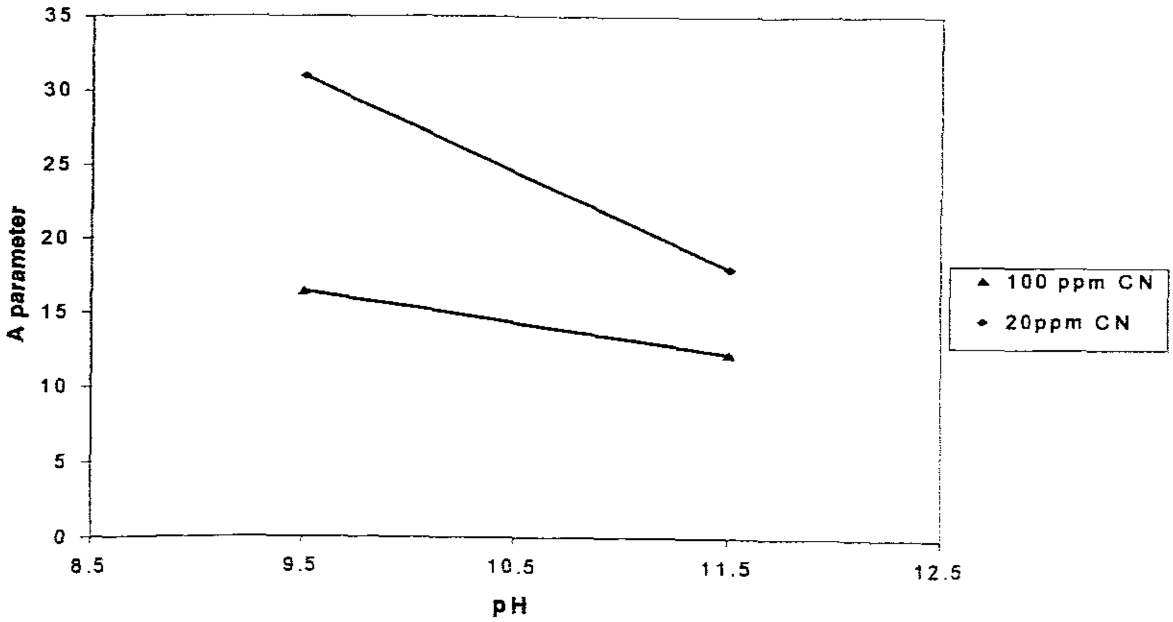

Table 1 Probability points of the normal distribution: single-sided; σ^2 known.

ρ (α or β)	U
0.001	3.090
0.005	2.576
0.010	2.326
0.015	2.170
0.020	2.054
0.025	1.960
0.050	1.645
0.100	1.282
0.150	1.036
0.200	0.842
0.300	0.524
0.400	0.253
0.500	0.000
0.600	0.253

Table 2 Probability points of the normal distribution: double-sided; σ^2 known.

ρ (α only)	U
0.001	3.291
0.005	2.807
0.010	2.576
0.015	2.432
0.020	2.326
0.025	2.241
0.050	1.960
0.100	1.645
0.150	1.440
0.200	1.282
0.300	1.036
0.400	0.842
0.500	0.675
0.600	0.524

Table 3 Probability points of t-distribution:
Single-sided, σ^2 unknown

	ρ						
ϕ	0.005	0.01	0.025	0.05	0.10	0.20	0.30
1	63.66	31.82	12.71	6.31	3.08	1.38	0.73
2	9.93	6.97	4.30	2.92	1.89	1.06	0.62
3	5.84	4.54	3.18	2.35	1.64	0.98	0.58
4	4.60	3.75	2.78	2.13	1.53	0.94	0.57
5	4.03	3.37	2.57	2.02	1.48	0.92	0.56
6	3.71	3.14	2.45	1.94	1.44	0.91	0.56
7	3.50	3.00	2.37	1.90	1.42	0.90	0.55
8	3.36	2.90	2.31	1.86	1.40	0.90	0.55
9	3.25	2.82	2.26	1.83	1.38	0.89	0.54
10	3.17	2.76	2.23	1.81	1.37	0.89	0.54
15	2.95	2.60	2.13	1.75	1.34	0.87	0.54
20	2.85	2.53	2.09	1.73	1.33	0.86	0.53
25	2.79	2.49	2.06	1.71	1.32	0.86	0.53
30	2.75	2.46	2.04	1.70	1.31	0.85	0.53
60	2.66	2.39	2.00	1.67	1.30	0.85	0.53
120	2.62	2.36	1.98	1.66	1.29	0.85	0.53
∞	2.58	2.33	1.96	1.65	1.28	0.84	0.52

Table 4 Probability points of t-distribution:
double-sided, σ^2 unknown.

	ρ						
ϕ	0.005	0.01	0.02	0.05	0.10	0.20	0.30
1	127.00	63.70	31.82	12.71	6.31	3.08	1.96
2	14.10	9.93	6.97	4.30	2.92	1.89	1.3
3	7.45	5.84	4.54	3.18	2.35	1.64	1.25
4	5.60	4.60	3.75	2.78	2.13	1.53	1.19
5	4.77	4.03	3.37	2.57	2.02	1.48	1.16
10	3.58	3.17	2.76	2.23	1.81	1.37	1.09
15	3.29	2.95	2.60	2.13	1.75	1.34	1.07
20	3.15	2.85	2.53	2.09	1.73	1.33	1.06
25	3.08	2.79	2.49	2.06	1.71	1.32	1.06
30	3.03	2.75	2.46	2.04	1.70	1.31	1.05
60	2.91	2.66	2.39	2.00	1.67	1.30	1.05
120	2.86	2.62	2.36	1.98	1.66	1.29	1.05
∞	2.81	2.58	2.33	1.96	1.65	1.28	1.04

APPENDIX 2

Tabulation of experimental results

Experiment 1 : Standard equilibrium test

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm
pH	10.5					
Free CN	20ppm (KCN)					
Ni	0ppm (Nickel cyanide)					
Ionic strength	0.01molar (NaOH)					
Carbon mass	0.2 g					
Stirring speed	300 rpm					

Sample	Co	Ce	Qe	ln Ce	Ln Qe
A	11.686	5.767	29.448	1.752	3.383
B	16.218	9.899	30.675	2.292	3.423
C	21.239	14.503	33.680	2.674	3.517
D	26.137	18.634	37.515	2.925	3.625
E	31.036	23.120	39.580	3.141	3.678
F	40.343	31.855	42.440	3.461	3.748

From linearized isotherm Ln A = 2.970 A = 19.492 n = 0.221

Experiment 2 : Low Oxygen

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm
pH	11.5					
Free CN	20ppm (KCN)					
Oxygen	2ppm (bubbling nitrogen through)					
Ionic strength	0.01molar (NaOH)					
Carbon mass	0.2 g					
Stirring speed	300 rpm					

Sample	Co	Ce	Qe	In Ce	Ln Qe
A	10.850	6.196	23.154	1.824	3.142
B	17.029	10.162	33.335	2.319	3.507
C	21.218	14.615	33.015	2.682	3.497
D	25.961	19.179	33.910	2.954	3.524
E	32.111	24.628	37.415	3.204	3.622
F	41.609	34.123	36.517	3.530	3.598

From linearized isotherm Ln A = 2.809 A = 16.590 n = 0.244

Experiment 2 : High Oxygen

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm
pH	11.5					
Free CN	20ppm (KCN)					
Oxygen	16ppm (bubbling pure oxygen through)					
Ionic strength	0.01molar (NaOH)					
Carbon mass	0.2 g					
Stirring speed	300 rpm					

Sample	Co	Ce	Qe	In Ce	Ln Qe
A	10.974	4.173	33.836	1.429	3.522
B	15.428	8.680	32.757	2.161	3.489
C	21.100	12.898	41.010	2.557	3.714
D	29.586	21.195	41.955	3.054	3.737

From linearized isotherm Ln A = 3.275 A = 26.443 n = 0.151

Experiment 3 : Trial 1
Sample 1

Gold conc.	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm

pH 9.5
Free CN 100ppm (KCN)
Ni 50PPM (Nickel cyanide)
Ionic strength 0.01molar (NaOH)
Carbon mass 0.2 g
Stirring speed 300 rpm

Sample	Co	Ce	Qe	In Ce	Ln Qe
A	11.314	5.163	30.602	1.642	3.421
B	16.489	8.832	37.170	2.178	3.615
C	21.485	13.406	40.395	2.596	3.699
D	26.338	17.403	44.675	2.857	3.799
E	31.445	22.379	45.330	3.108	3.814
F	40.992	30.995	48.766	3.434	3.887

From linearized isotherm Ln A = 3.030 A = 20.687 n = 0.257

Experiment 3 : Trial 1
Sample 2

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm

pH 9.5
Free CN 100ppm (KCN)
Ni 50PPM (Nickel cyanide)
Ionic strength 0.01molar (NaOH)
Carbon mass 0.2 g
Stirring speed 300 rpm

Sample	Co	Ce	Qe	In Ce	Ln Qe
A	11.332	4.669	33.149	1.541	3.501
B	16.165	9.460	32.549	2.247	3.483
C	21.549	13.346	41.015	2.591	3.714
D	26.764	17.681	45.415	2.872	3.816
E	43.759	32.279	57.400	3.474	4.050

From linearized isotherm Ln A = 2.963 A = 19.362 n = 0.257

Experiment 4 : Trial 2
Sample 1

Gold cyanide 10ppm 15ppm 20ppm 25ppm 30ppm 40ppm
pH 9.5
Free CN 20ppm (KCN)
Ni 50PPM (Nickel cyanide)
Ionic strength 0.01molar (NaOH)
Carbon mass 0.2 g
Stirring speed 300 rpm

Sample	Co	Ce	Qe	ln Ce	Ln Qe
A	11.247	4.204	35.040	1.436	3.556
B	16.724	8.031	42.199	2.083	3.742
C	22.099	12.813	46.430	2.550	3.838
D	27.085	17.636	47.245	2.870	3.855
E	32.436	22.007	52.145	3.091	3.954
F	42.299	30.960	55.312	3.433	4.013

From linearized isotherm Ln A = 3.255 A = 25.920 n = 0.222

Experiment 4 : Trial 2
Sample 2

Gold cyanide 10ppm 15ppm 20ppm 25ppm 30ppm 40ppm
pH 9.5
Free CN 20ppm (KCN)
Ni 50PPM (Nickel cyanide)
Ionic strength 0.01molar (NaOH)
Carbon mass 0.2 g
Stirring speed 300 rpm

Sample	Co	Ce	Qe	ln Ce	Ln Qe
A	10.462	3.678	33.751	1.302	3.519
B	15.942	8.215	37.510	2.106	3.625
C	20.669	13.046	38.115	2.568	3.641
D	25.596	16.352	46.220	2.794	3.833
E	30.383	21.268	45.575	3.057	3.819
F	40.401	30.474	49.635	3.417	3.905

From linearized isotherm Ln A = 3.262 A = 26.094 n = 0.180

Experiment 5 : Trial 3
Sample 1

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm
pH	9.5					
Free CN	20ppm (KCN)					
Ni	0PPM (Nickel cyanide)					
Ionic strength	0.01molar (NaOH)					
Carbon mass	0.2 g					
Stirring speed	300 rpm					

Sample	Co	Ce	Qe	ln Ce	Ln Qe
A	9.698	1.527	40.652	0.423	3.705
B	14.105	5.200	43.228	1.649	3.766
C	18.531	8.900	48.155	2.186	3.874
D	23.101	12.850	51.255	2.553	3.937
E	27.714	16.496	56.090	2.803	4.027
F	36.973	24.173	64.000	3.185	4.159

From linearized isotherm Ln A = 3.583 A = 35.989 n = 0.152

Experiment 5 : Trial 3
Sample 2

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm
pH	9.5					
Free CN	20ppm (KCN)					
Ni	0PPM (Nickel cyanide)					
Ionic strength	0.01molar (NaOH)					
Carbon mass	0.2 g					
Stirring speed	300 rpm					

Sample	Co	Ce	Qe	ln Ce	Ln Qe
A	9.636	1.988	38.050	0.687	3.639
B	14.202	6.001	39.811	1.792	3.684
C	18.084	9.225	44.295	2.222	3.791
D	22.399	13.638	43.805	2.613	3.780
E	27.323	18.528	43.975	2.919	3.784
F	35.901	25.257	53.220	3.229	3.974

From linearized isotherm Ln A = 3.540 A = 34.457 n = 0.103

Experiment 6 : Trial 4
Sample 1

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm
pH	11.5					
Free CN	20ppm (KCN)					
Ni	0PPM (Nickel cyanide)					
Ionic strength	0.01molar (NaOH)					
Carbon mass	0.2 g					
Stirring speed	300 rpm					

Sample	Co	Ce	Qe	ln Ce	Ln Qe
A	11.078	5.445	28.025	1.695	3.333
B	16.436	9.308	34.602	2.231	3.544
C	22.010	14.959	35.255	2.705	3.563
D	27.291	19.459	39.160	2.968	3.668
E	32.313	24.386	39.635	3.194	3.680
F	43.022	33.791	46.155	3.520	3.832

From linearized isotherm Ln A = 2.959 A = 19.275 n = 0.298

Experiment 6 : Trial 4
Sample 2

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm
pH	11.5					
Free CN	20ppm (KCN)					
Ni	0PPM (Nickel cyanide)					
Ionic strength	0.01molar (NaOH)					
Carbon mass	0.2 g					
Stirring speed	300 rpm					

Sample	Co	Ce	Qe	ln Ce	Ln Qe
A	10.706	4.953	28.622	1.600	3.354
B	15.464	9.378	29.544	2.238	3.386
C	20.221	12.808	37.065	2.550	3.613
D	25.200	17.234	39.830	2.847	3.685
E	29.737	22.102	38.175	3.096	3.642
F	39.252	28.630	53.110	3.354	3.972

From linearized isotherm Ln A = 2.975 A = 19.590 n = 0.230

Experiment 7 : Trial 5
Sample 1

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm

pH 9.5
Free CN 100ppm (KCN)
Ni 0PPM (Nickel cyanide)
Ionic strength 0.01molar (NaOH)
Carbon mass 0.2 g
Stirring speed 300 rpm

Sample	Co	Ce	Qe	In Ce	Ln Qe
A	10.261	6.103	20.687	1.809	3.029
B	15.137	10.020	24.840	2.305	3.212
C	20.252	15.067	25.925	2.713	3.255
D	25.037	19.264	28.865	2.958	3.363
E	30.181	24.054	30.635	3.180	3.422
F	40.294	33.509	33.098	3.512	3.499

From linearized isotherm Ln A = 2.516 A = 12.381 n = 0.282

Experiment 7 : Trial 5
Sample 2

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm

pH 9.5
Free CN 100ppm (KCN)
Ni 0PPM (Nickel cyanide)
Ionic strength 0.01molar (NaOH)
Carbon mass 0.2 g
Stirring speed 300 rpm

Sample	Co	Ce	Qe	In Ce	Ln Qe
B	15.105	10.190	23.859	2.321	3.172
C	20.281	15.010	26.355	2.709	3.272
D	25.302	19.739	27.815	2.983	3.326
E	30.448	24.278	30.850	3.190	3.429
F	40.500	33.442	34.429	3.510	3.539

From linearized isotherm Ln A = 2.440 A = 11.473 n = 0.300

Experiment 8 : Trial 6
Sample 1

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm
pH	11.5					
Free CN	20ppm (KCN)					
Ni	50PPM (Nickel cyanide)					
Ionic strength	0.01molar (NaOH)					
Carbon mass	0.2 g					
Stirring speed	300 rpm					

Sample	Co	Ce	Qe	ln Ce	Ln Qe
B	15.803	9.956	28.383	2.298	3.346
C	21.009	14.698	31.555	2.688	3.452
D	25.911	19.023	34.440	2.946	3.539
E	30.970	23.796	35.870	3.170	3.580
F	40.517	32.855	37.376	3.492	3.621

From linearized isotherm   Ln A = 2.814   A = 16.683   n = 0.238

Experiment 8 : Trial 6
Sample 2

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm
pH	11.5					
Free CN	20ppm (KCN)					
Ni	50PPM (Nickel cyanide)					
Ionic strength	0.01molar (NaOH)					
Carbon mass	0.2 g					
Stirring speed	300 rpm					

Sample	Co	Ce	Qe	ln Ce	Ln Qe
A	10.305	5.563	23.019	1.716	3.136
B	15.125	9.807	25.816	2.283	3.251
C	20.330	14.187	30.715	2.652	3.425
D	25.043	18.528	32.575	2.919	3.484
E	29.953	23.144	34.045	3.142	3.528
F	39.498	31.969	36.727	3.465	3.604

From linearized isotherm   Ln A = 2.682   A = 14.610   n = 0.268

Experiment 9 : Trial 7
Sample 1

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm
pH	11.5					
Free CN	100ppm (KCN)					
Ni	0PPM (Nickel cyanide)					
Ionic strength	0.01molar (NaOH)					
Carbon mass	0.2 g					
Stirring speed	300 rpm					

Sample	Co	Ce	Qe	ln Ce	Ln Qe
B	15.169	9.597	27.049	2.261	3.298
C	20.639	14.603	30.180	2.681	3.407
D	25.842	18.968	34.370	2.943	3.537
E	30.813	23.483	36.650	3.156	3.601
F	40.962	32.175	42.863	3.471	3.758

From linearized isotherm Ln A = 2.412 A = 11.160 n = 0.244

Experiment 9 : Trial 7
Sample 2

Gold cyanide	10ppm	15ppm	20ppm	25ppm	30ppm	40ppm
pH	11.5					
Free CN	100ppm (KCN)					
Ni	0PPM (Nickel cyanide)					
Ionic strength	0.01molar (NaOH)					
Carbon mass	0.2 g					
Stirring speed	300 rpm					

Sample	Co	Ce	Qe	ln Ce	Ln Qe
B	17.396	11.155	30.296	2.412	3.411
C	23.035	16.586	32.245	2.809	3.473
D	28.518	21.668	34.250	3.076	3.534
E	33.997	26.566	37.155	3.280	3.615
F	44.364	35.069	45.341	3.557	3.814

From linearized isotherm Ln A = 2.560 A = 12.933 n = 0.334

Experiment 10 : Trial 8
Sample 1

Gold cyanide	10ppm 15ppm 20ppm 25ppm 30ppm 40ppm
pH	11.5
Free CN	100ppm (KCN)
Ni	50PPM (Nickel cyanide)
Ionic strength	0.01molar (NaOH)
Carbon mass	0.2 g
Stirring speed	300 rpm

Sample	Co	Ce	Qe	In Ce	Ln Qe
A	10.037	5.208	23.442	1.650	3.155
B	14.927	9.100	28.286	2.208	3.342
C	19.833	13.294	32.695	2.587	3.487
D	24.675	17.394	36.405	2.856	3.595
E	29.787	21.998	38.945	3.091	3.662
F	39.494	30.450	44.117	3.416	3.787

From linearized isotherm Ln A = 2.592 A = 13.356 n = 0.348

Experiment 10 : Trial 8
Sample 2

Gold cyanide	10ppm 15ppm 20ppm 25ppm 30ppm 40ppm
pH	11.5
Free CN	100ppm (KCN)
Ni	50PPM (Nickel cyanide)
Ionic strength	0.01molar (NaOH)
Carbon mass	0.2 g
Stirring speed	300 rpm

Sample	Co	Ce	Qe	In Ce	Ln Qe
B	15.011	9.580	26.364	2.260	3.272
C	19.758	13.494	31.320	2.602	3.444
D	24.865	17.372	37.465	2.855	3.623
E	29.602	21.820	38.910	3.083	3.661
F	39.183	30.980	40.015	3.433	3.689

From linearized isotherm Ln A = 2.485 A = 11.999 n = 0.370

Experiment 11
Standard adsorption test

Gold cyanide	20ppm
pH	10.5
Free CN conc	20ppm (KCN)
Ionic strength	0.01molar (NaOH)
Carbon mass	0.2 g
Stirring speed	300 rpm
Running time	24 h

Time (min)	C (ppm)	C/Co (ppm)	ln(Co/C) ppm)
0	19.6542	1.00	0.000
10	16.4735	0.84	0.177
20	15.3628	0.78	0.246
30	14.1006	0.72	0.332
60	13.3938	0.68	0.384
120	13.5453	0.69	0.372
240	13.1919	0.67	0.399
420	12.2326	0.62	0.474
1380	12.3841	0.63	0.462
1440	12.5860	0.64	0.446

Experiment 12
Adsorption test with high cyanide concentration

Gold cyanide	20ppm
pH	10.5
Free CN conc	100ppm (KCN)
Ionic strength	0.01molar (NaOH)
Carbon mass	0.2 g
Stirring speed	300 rpm
Running time	24 h

Time (min)	C (ppm)	C/Co (ppm)	ln(Co/C) ppm)
0	21.2	1.00	0.000
10	19.094	0.90	0.105
20	17.661	0.83	0.183
30	16.981	0.80	0.222
60	16.12	0.76	0.274
120	15.213	0.72	0.332
180	15.056	0.71	0.342
240	14.439	0.68	0.384
300	14.132	0.67	0.406
1380	12.792	0.60	0.505
1410	12.373	0.58	0.538
1440	12.78	0.60	0.506

Experiment 13

Adsorption test with low pH

Gold cyanide	20ppm
pH	9.5
Free CN conc	20ppm (KCN)
Ionic strength	0.01molar (NaOH)
Carbon mass	0.2 g
Stirring speed	300 rpm
Running time	24 h

Time (min)	C (ppm)	C/Co (ppm)	ln(Co/C) (ppm)
0	20.655	1.00	0.000
10	18.578	0.90	0.106
20	17.261	0.84	0.180
30	16.702	0.81	0.212
60	15.306	0.74	0.300
120	14.614	0.71	0.346
180	14.045	0.68	0.386
240	13.403	0.65	0.432
300	12.927	0.63	0.469
1380	10.506	0.51	0.676
1410	10.414	0.50	0.685
1440	10.439	0.51	0.682

NOMENCLATURE

A	Parameter in Freundlich isotherm	
B	Parameter in isotherm expression	
C	Solute concentration	mg/l
d_p	Diameter of adsorbent particles	m
D	Diffusion coefficient	m^2/s
k_f	External film transfer coefficient	m/s
M	Mass of adsorbent	kg
n	Empirical constant in Freundlich isotherm	
q	Loading of solute onto adsorbent	mg/g
t	Time variable	s
V	Volume of liquid in reactor	m^3
ρ	Apparent density	g/m^3

Subscripts

c	Carbon
e	Equilibrium
i	Initial condition
j	A component in multicomponent system
s	Solution-adsorbent interface