A SOLUTION CONCENTRATION MODEL FOR CIP SIMULATION

BY

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ABSTRACT

Carbon-in-pulp technology is used extensively in the mining industry to recover metal cyanides from solution. Also, this technology has found increasing application in the gold mining sector, replacing the less efficient zinc precipitation procedure. The extensive use of carbon in such processes have prompted many researchers to investigate the mechanism of metal cyanide adsorption. Not only has this provided many viable theories in the understanding of the mechanism, but has also led to an improved understanding of the effects of the various operating conditions on the CIP circuit.

Also, the modelling of this process has resulted in proposed rate equations, of which the famous "kn" model is the most widely used in design. This is a single rate equation that could result in significant errors and hence, a dual resistance model was developed. However, this model is mathematically complex. Recently, in an attempt to overcome the shortcomings of previous models, empirical calculations to accurately describe adsorption kinetics were developed at the Cape Technikon.

These correlations were derived using batch experimental data. In this study the focus was on modeling the adsorption process on a continuous scale using a laboratory scale cascade system. This study utilized the fact that solution concentration is the main driving force for aurocyanide adsorption onto activated carbon and that carbon loading has an indirect effect on adsorption kinetics. The metal was ultimately tested against actual plant data and provided very accurate results.

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CONTENTS

PAGES
ABSTACT i
ACKNOWLEDGEMENTS ii
CONTENTS iii
LIST OF TABLES vi
LIST OF FIGURES vii

1. INTRODUCTION AND LITERATURE STUDY 1

1.1 ACTIVATED CARBON 2
1.1.1 Raw Materials 2
1.1.2 Physical manufacture 3
1.1.3 Chemical Manufacture 4
1.1.4 Physical Structure of Activated Carbon 4
1.1.5 Chemical Properties of Activated Carbon 5

1.2 THE CARBON-IN-PULP (CIP) PROCESS 6

1.2.1 Adsorption 7
1.2.2 Adsorption tanks 7
1.2.3 Mixing 8
1.2.4 Interstage screening 8
1.2.5 Carbon transfer 9
1.2.6 Elution 9
1.2.7 Carbon regeneration 10
1.2.8 Electrowinning 11
1.2.9 Mechanism for Gold Cyanide Adsorption 12
1.2.10 Modelling 13

1.3 SIGNIFICANCE OF THE LITERATURE STUDY 19

1.4 OBJECTIVES OF STUDY 19

2. EXPERIMENTAL 26

2.1 Experimental material 26
2.2 Experimental set-up 27
2.3 Minimum stirring speed 27
2.4 Adsorption rate 27

3. PLANT LAYOUT AND COMMISIONING 29

3.1 Design of cascade system 29
3.1.1 Tanks in cascade 29
3.1.2 Feed and waste tank 30
3.1.3 Pumps 30
3.1.4 Motors 30
3.1.5 Materials of construction 31
3.2 Preparation of feed slurry 31
3.2.1 Washing of sand 32
3.2.2 Make up of slurry 33
3.3 Construction of cascade system 34
3.3.1 Tanks 34
3.3.2 Channels 34
3.3.2.1 Testing for suitability of channels and feed pump 34
3.3.3 Framework, agitator, motor and associated construction 36
3.4 Commissioning of CIP plant 37
3.4.1 Feed tank agitation 37
3.4.2 Feed pump 38
3.4.3 Cascade belts and pulleys 38
3.4.4 Fixed cascade tank impellers 38
3.4.5 Calibration of speed controller revolution counter 39
3.4.6 Performance of screens 39
3.5 Final note 39

4. MODEL DEVELOPMENT 40

4.1 Batch adsorption 41
4.2 Hypothesis 41

5. COMPUTER PROGRAM OVERVIEW 43

5.1 General 43
5.2 Optimum determination 44

6. RESULTS AND DISCUSSION 46

7. CONCLUSSIONS AND RECOMENDATIONS 59

REFERENCES 60

APPENDIX A C++PROGRAM FOR SIMULATION OF GOLD ADSORPTION ONTO ACTIVATED CARBON 65

LIST OF TABLES

		PAGE
Table 1.1	The various types of elution processes available, along with their advantages and disadvantages	20
Table 1.2	The various types of electrowinning cells available	21
Table 3.1	Pumps utilised in pilot plant	30
Table 3.2	Motors utilised in pilot plant	30
Table 3.3	Materials of construction	31
Table 6.1	Tabulated results of experimental run	47
Table 6.2	Tabulated results received from anglogold	48
Table 6.3	k and n values calculated from the kn model	51
Table 6.4	k and K values calculated from the updated kn model	53
Table 6.5	k_c, k_d and K values calculated from the solution concentration model	55

LIST OF FIGURES

		PAGE
Figure 1.1	A schematic representation of the structure of graphite.	22
Figure 1.2	A schematic representation of the proposed structure of activated carbon.	23
Figure 1.3	An illustration of the pore structure of activated carbon.	24
Figure 1.4	A flow diagram representing the Carbon-in-pulp circuit.	25
Figure 2.1	The apparatus for experiments performed in 5L reactors.	28
Figure 6.1	Graphical representation of rate vs C_1	49
Figure 6.2	Sectional graphical representation of rate vs C_{s1}	49
Figure 6.3	Sectional graphical representation of rate vs C_{s1}	50
Figure 6.4	Graphical representation of the actual and the predicted C_{s1} results	51
Figure 6.5	Graphical representation of k values	52
Figure 6.6	Graphical representation of n values	52
Figure 6.7	Graphical representation of the actual and the predicted C_{s1} results	53
Figure 6.8	Graphical representation of the k values	54
Figure 6.9	Graphical representation of the K values	54
Figure 6.10	Graphical representation of the actual and the predicted C_{s1}	55
Figure 6.11	Graphical representation of the k_c values	56
Figure 6.12	Graphical representation of the k_3 values	56
Figure 6.13	Graphical representation of the K values	57

CHAPTER 1

INTRODUCTION AND LITERATURE STUDY

Gold is a word that has become as famous as wildlife when reference is made to South Africa. For years, revenue from gold production has been the dominating factor in the South African gross domestic product. Although this dominance is expected to reduce in magnitude as is already experienced. revenue from this noble metal will still play a vital role in the local economy in that it remains the largest single industry employer.

Research in the field of gold mining has grown enormously since the late 1950's. This is hardly surprising given the large revenue generated by this single local industry. Not only has advances in technology been experience in the mining division. An example of metallurgical technology advancement can be seen in the replacement of the zinc precipitation procedure by the use of activated carbon via the carbon-in-pulp (CIP) process to recover aurocyanide from solution after cyanidation. This CIP process was selected as focus point of this study.

The difficulty in CIP modeling and plant design stems from the fact that gold adsorption onto activated carbon follows a dual kinetic rate. In the initial stages of adsorption film diffusion is the rate controlling factor whereas intra-particle diffusion limits the reaction rate once the carbon reaches 60-70% of its equilibrium loading value *[Johns, 1987]*.

However, most kinetic models for CIP simulation do not take this dual kinetic rate into consideration. This simplification inevitably leads to significant errors. These methods are described in full detail later in the chapter. Methods to address this shortcoming have been proposed [Van Deventer, 1984]. However, these are mathematically complex and difficult to apply to a continuous process.

This study focuses on this modeling procedure, attempting to eliminate the shortcomings of the single rate models, but at the same time removing the mathematical complexity of those models attempting to describe dual rate kinetics.

1.1 ACTIVATED CARBON

Charcoal is a strange and interesting substance. The fact that it has the power to abstract gold and silver from cyanide solutions to the extent of 7 percent of its weight in gold or 3 percent of its weight in silver without showing the slightest change in appearance, even under the microscope, clothes it with a mystery that has long interested metallurgists. Even now, with the mass of data made available by various investigators, much remains to be learned *[Gross and Scott, 1927]*.

1.1.1 Raw Materials

Activated carbon can be manufactured from wood, nut shells, coal, petroleum coke, and a variety of organic products *[McDougall, 1991; Bhuppa, 1990]*. The choice of material along with the method of production, has a large effect on the structure and properties of the product *[van Dam, 1995]*. Coconut shell carbon, however, is the preferred brand with commendable durability and high adsorption capability for gold and silver cyanides *[Bhuppa, 1990]*. There are basically two forms of activated carbon:

1) powdered and

2) granular.

The powder form is usually used on a throw-away basis and the granular form is generally re-used after regeneration. The use of granular carbon is therefore more cost effective and more extensively used.

1.1.2 Physical Manufacture

Gaseous pyrolysis at lower temperature (300 to 600 ^{0}C) of the raw material to drive off the volatile matter (H, O, traces of S and N), leaving a product consisting of approximately 90% carbon *[de Jong, 1991; Mattson, 1971]*. The product is a hydrophobic skeleton which is made up of an irregular crystalline structure with free fissures remaining between the crystallites *[Bailey, 1987]*. Decomposition and deposition of disorganised carbon results in filling and blocking of these pores. The activation step is therefore necessary to enhance the low adsorption capacity of the carbon *[Balci et al., 1994]*. Heating of the material at temperatures in the range of 700 to 1000 ^{0}C are used to facilitate a controlled dehydration and devolatilization of parts of the carbon *[Bailey, 1971; Hassler, 1974; McDougal, 1991]*. The reactive oxygen burns away part of the carbon skeleton as carbon monoxide and carbon dioxide, thereby increasing the internal surface area of the carbon *[Bailey, 1987]*. As a result of the low affinity of dicyanoaurate for chemically produced products, the thermal manufacture of activated carbon has become the preferred route for the production of products suitable for use in the gold-recovery process *[McDougall, 1991]*.

1.1.3 Chemical Manufacture

Chemical activation is used mainly for uncarbonized cellulose materials, primarily wood *[McDougall, 1991]*. The raw material is first mixed with a dehydrating agent and dried at temperatures of 200 to 650 ^{0}C resulting in the carbon skeleton. Next the activating agents are added and the mixture heated to 350-650 ^{0}C *[McDougall, 1991]*. Lower temperatures than in physical activation results in smaller crystallites being formed which promote the development of the pore structure *[de Jong, 1991]*.

1.1.4 Physical Structure of Activated Carbon

The most significant physical properties of activated carbon are the number and size distribution of the pores, bulk density, dry impact hardness, wet abrasion resistance and particle size distribution *[McDougall, 1991]*. During activation the carbon develops a porous graphitic structure of molecular dimensions with an extraordinarily large internal surface area on which adsorption may take place. X-ray studies show activated carbon to have a structure similar to that of *graphite [Hassler, 1974; Mattson, 1971; Mc Dougall, 1991]* As can be seen in figure 1.1, graphite consists of fused hexagonal rings forming layers which are held approximately 3.35 Å apart by Van der Waals forces *[Mc Dougall, 1991]*.Thermally activated carbons are believed to be made up of tiny graphite-like platelets only a few carbon atoms thick and 20 to 100 Å in diameter(see figure 1.2) Walls of open cavities or pore structures are formed. The overall structure is very disorganized as the hexagonal rings are randomly arranged and many have undergone cleavage. The separation between the layers is also greater than that of graphite, ie. 3.6 Å *[de Jong, 1991; Mc Dougall, 1991]*. Raw materials which have dense cellular structures produce hard brittle products and therefore carbons made from coconut shell are used almost exclusively in the gold mining industry *[Bailey, 1987]*. Pore sizes may exert a screening effect which prevents molecules from being adsorbed, or it promotes adsorption when pore diameters are of optimum size. In cross-section the pores in activated carbons could be circular or rectangular, or a variety of irregular shapes. The pores can be classified according to three distinct groups based on their pore diameter *[de Jong, 1991; Mc Dougall, 1991]*:

- Macropores (>25nm), are channels which are determined by the cell structure of the original carbon material. They provide rapid access to the meso and micropores where actual adsorption takes place.
- Mesopores or transitional (1-25nm and account for 5 % of the internal surface area), are situated between graphite-like micro-crystallites which are also formed by activation perpendicular to the plates.
- Micropores (<1nm and account for 95 % of .he internal surface area), are developed during activation, when graphite-like micro-crystallites are affected.

[Figure 1.3 gives an illustrated representation of the pore structure of activated carbon]

1.1.5 Chemical Properties of Activated Carbon

As a result of structural imperfections there are many opportunities for reactions with carbon atoms forming on the edges of the planar layers. These reactions cause the formation of oxygen-containing functional groups on the surface of the carbon *[Mattson, 1971; Mc Dougall, 1991]*. Although a large number of these groups have been identified (carboxyl, penolic hydroxyl, quinon-type carboxyl, normal lactones, fluorescein, carboxylic acid anhydrides and cyclic peroxides), carbon remains unamendable to infrared spectroscopy, leaving doubts as to the nature of unidentified groups *[Mc Dougall, 1980]*. It is known however that the nature of the su face groups are dependent on the conditions during and after manufacture *[Mattson, 1971; Mc Dougall, 1991]*.

1.2 THE CARBON-IN-PULP (CIP) PROCESS

In the late seventeenth century the adsorptivity property of carbon was discovered. A century later, the gold adsorption from leached cyanide solution was reported. The carbon-in-pulp circuit was first employed on a small scale by the Carlton mills around 1951*[Fast, 1988]*. It was only in August 1973 that the process gained recognition when the first large scale CIP circuit was commissioned by the Homestake Mining Company *[Hall, 1974]*. The availability of hard carbon and the development of the Zadra method for gold elution made it more economical to use. The CIP circuit has since become the preferred route for gold recovery. Reasons for its popularity are *[Stanley, 1990]*.:

- Reduced capital expenditure

Economic evaluation has shown that the filtration/zinc precipitation process requires a capital expenditure significantly higher than the CIP process.

- Reduced operating costs

Estimation of operating cost for the CIP process indicated that they would be lower than those for the filtration /zinc precipitation route. Difference of 12% has bveen given by Gencor Group Mines.

- Improved gold recovery

The CIP gives a far better recovery of gold than the Resin-in-Pulp process as well as the filtration/zinc precipitation method.

- Reduced sensitivity of recovery to throughput rate
- Ability to handle shaley and clayey ore more efficiently than filtration. Ore containing clay particles is more difficult to filter and consequently increases gold losses. These material do not affect the CIP process significantly.

The mined ore first undergoes crushing and grinding to obtain a particle size of 80% under 75µm*[La Brooy et al. 1994]*. For economic reasons the pulp must be concentrated and thickeners are necessary to obtain the correct solid to liquid ratio prior to cyanidation

[Adamson, 1972; Bailey, 1987; Stanley, 1990; Yannopoulos, 1991]. During leaching the gold is adsorbed to form an aurocyanide solution.

$$4Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O(l) \longrightarrow 4Au(CN)^-_2(aq) + 4OH^-(aq)$$

The gold in the ore is oxidised and sodium cyanide and lime are added to form the aurocyanide complex.

1.2.1 Adsorption

After cyanidation the ore pulp is pre-screened at 710μm before it enters the CIP circuit. This facilitates the removal of wood chips or other oversized materials which may block the inters-stage screens *[Dahya, 1983; Laxen et al, 1994; Menne, 1982]*. The carbon-in-pulp (CIP) process recovers gold in solution from slurry streams by contacting carbon with the pulp and separating the two by screening. This occurs in a number of adsorption vessels in series. These tanks are arranged in a cascade to facilitate the use of gravity for continuous movement of pulp *[Bailey, 1987;Yannopoulos, 1990]*. The pulp flows continuously from the first tank to the last while the carbon is transferred counter-currently from the last tank to the first. The slurry flows through the adsorption system resulting in the decrease of gold in solution. while the concentration of gold increases on the carbon. The solution gold value therefore decreases down-stream *[Dahya, 1983; Laxen et al, 1994]*. For maintaining the pH of the pulp in the range of 10-11 lime is added *[Yannopoulos, 1990]*.

1.2.2 Adsorption Tanks

The size and number of adsorption tanks depend mainly on the feed gold concentrations *[Laxen et al, 1994]*. Tanks have a staggered layout to assist in the flow of pulp. Open launders or pipes are used to interconnect the tanks for the flow of the ore pulp.

1.2.3 Mixing

The rate of gold extraction is a sensitive function of mixing for hydrometallurgical operations. Incorrect design and operation can result in major gold losses, due to the prodution of carbon fines and the imperfect contacting of the carbon and the pulp mixture *[Dahya, 1983]*. Mechanical agitation remains the more popular choice as its adsorption kinetics are twice as high as air agitation *[Menne, 1982]*. The agitator which is decided upon must perform the following mixing principles:

i. Uniform suspension of solids and carbon
ii. Optimum mass transfer to carbon
iii. High volume efficiency
iv. Fast re-suspension after a power failure

1.2.4 Inter-stage Screening

Screens are used to separate the carbon from the pulp. The pulp is pre-screened to separate oversize material such as wood chips that cause inter-screen blockages. Pulp flow through the tanks of a carbon-in-pulp plant is continuous whereas the carbon is moved intermittently *[Dahya, 1983; Yannopoulos, 1990]*. A screening system is employed to allow the pulp to pass from one tank to the other but preventing the carbon from moving between tanks. There are two types of inter-stage screens used in industry *[Dahya, 1983; Yannopoulos, 1990]*, namely:

- Airswept static screens with the pulp airlifted onto external screens which allow the pulp to pass through while retaining the carbon and returning it to the same tank.
- Equalised-pressure air cleaned (EPAC) screens which are placed on the periphery of the tank. These provide minimal blockage as long as the pulp levels on either side of the screen are maintained as near equal as possible.

1.2.5 Carbon Transfer

Carbon transfer is effected by the use of airlifts or pumps. Pumps are used mainly for large-scale plants *[Laxen et al, 1994; Menne, 1982]*. Carbon transfer can be done on a continuous or intermittent basis *[Stange et al, 1990]*. When considering the duration of transfer times it should be noted that a single large transfer is more effective than a number of smaller transfers *[Bailey, 1987]*. The amount of carbon transferred daily is not constant and carbon transfer is not an instantaneous process. As a result of these variations steady-state is never reached *[Schubert et al, 1993; Stange et al, 1990]*.

1.2.6 Elution

Elution is a slow process, which, depending on the method employed, requires from 8 to 48 hours for completion even at elevated temperatures. This is due primarily to the slow diffusion of the aurocyanide ion within the micropores of the relatively large particles of activated carbon. Unlike the adsorption process which has received considerable attention in the past from both a kinetic modeling point of view, very little attention has been paid to the elution methodology other than publication of elution profiles under various conditions. Four elution techniques are commonly use in industry today. These are given along with their advantages and disadvantages in Table 1.1 *[Dahya et al, 1983, Laxen et al, 1982 and 1984; Stange, 1991; Wan et al, 1990; Yannopoulos, 1991]*.

All elution processes are based on Ficks first law:

$$J = \frac{-DC}{Rg} * \frac{d\mu}{dy}$$

Where mass transfer rate is a linear function of molar concentration gradient (high temperature) *[Coulson and Rchardson, 1990]*.

1.2.7 Carbon Regeneration

The rate at which the carbon removes the gold from the pulp in a carbon-in-pulp plant is the main criterion governing the process. During the period that the carbon is in contact with the pulp it becomes progressively poisoned and loses its activity *[Bailey, 1987; Dahya, 1983; Yannopoulos, 1991]*. It is essential that the carbon added to the circuit is as active as possible to counteract this loss. This can be achieved by discarding the carbon after elution but the most cost-effective system is to re-use the carbon after restoration of its activity. Various chemicals have been shown to be capable of restoring the activity of the carbon when single or defined adsorbates are loaded. Appropriate solvents or chemicals can be found specifically to desorb these adsorbates. However, if a carbon has been loaded with a heterogeneous mixture of adsorbates, as would be present in a gold plant process stream, only partial restoration of activity is usually achieved using chemical regeneration techniques. Thermal regeneration techniques are effective in restoring the activity of carbon loaded with organic adsorbates. Thermal regeneration involves three types of reactions corresponding to three types of adsorbates on the spent carbon *[van Vliet, 1985 b]*:

Type 1:
Thermal desorption of volatile organic compound initially adsorbed on the activated carbon, but not irreversibly bound to active surface sites;

Type 2:
Thermal decomposition (cracking) of organic compounds not sufficiently volatile for thermal desorption and / or which are tenaciously bound to surface sites;
Type 3:
Pyrolysis of the remaining compounds with the concomitant deposition of a carbonaceous residual. Compounds involved in this type of reaction are critical to

regeneration considerations, since the carbonaceous residual has to be removed selectively. In practice this is achieved by the use of endothermic stream or carbon dioxide oxidation at comparatively high temperatures. Within this temperature domain energy losses increase significantly, equipment specifications become more stringent (and costly), and base-activated carbon losses invariably occur, concurrent with the oxidation of pyrolysed adsorbate residuals.

Thermal regeneration involves heating the carbon to 650 °C in the absence of air for 30 minutes *[Dahya, 1983; Laxen et al, 1994; Yannopoulos, 1991]*. Wet carbon is introduced into a rotary kiln, the feed end of which is sealed to force the stream generated to pass over the carbon bed. The steam is then exhausted from a flue pipe at the discharge end and so prevent air from entering the kiln *[Dahya 1983, Yannopoulos, 1991]*. However, regeneration results in the partial combustion of the carbon (carbon losses due to combustion increases with time and activation temperature) as expressed in equations below *[Dahya, 1983, Yannopoulos, 1991]*:

$$C + H_2O \longrightarrow CO + H_2$$

$$C + 2H_2O \longrightarrow CO_2 + 2H_2$$

Reactivated carbon is then air cooled in the cooling section of the kiln or in a hopper. The Re-activated carbon is then screened at 20 mesh to remove fines and conditioned with water before recycling to the adsorption circuit *[Dahya, 1983]*.

1.2.8 Electrowinning

The recovery of gold from cyanide leach solutions by electro-precipitation was practiced at the turn of the century but was abandoned in favor of the cementation by zinc. This was due to the poor efficiency and relatively low unit throughput rates that could be achieved at the low gold tenors. However recent developments involving intensive cyanidation of gravity concentrates and the use of activated carbon for the recovery of gold from solutions and pulps have resulted in the production of solutions containing in excess of 500 grams gold per ton of solution. Electorwinning becomes a viable alternative at these gold levels.

Table 1.2 describes a number of the cells which have been designed for the recovery of gold from eluted solutions *[Dahya, 1983]*. The majority of these cells contain a steel wool cathode. This is due to the large surface area it provides for electrolytic deposition of precious metals *[Dahya, 1983, Laxen et al, 1994]*. These cathodes are capable of loading 30 kg of gold and 6 kg of silver, after which they are removed and smelted with a flux (borax, nither and silica) to produce a high purity bullion *[Bhappu, 1990; Laxen et al, 1994]*. In some cases the removed cathodes are dissolved in hydrochloric acid and the residue is then smelted. This process reduces the consumption of flux during smelting *[Dahya, 1983]*.

1.2.9 Mechanism for Gold Cyanide Adsorption

The kinetics and thermodynamics of the adsorption of gold cyanide on activated coconut-shell carbon have been investigated *[Dixon, Cho and Pitt, 1976, Cho, Dixon and Pitt, 1979]*. Over the years a number of possible mechanisms have been suggested for the adsorption of dicyanoaurate onto activated carbon. However, no consensus has been reached and all possible mechanisms can be simplified into one of these basic forms:

- The $Au(CN)^{2-}$ ion is adsorbed without undergoing chemical change, and held by electostatic or van der Waals forces.
- The gold compounds is decomposed from $Au(CN)^{2-}$ to $Au(CN)$ and adsorbed as such.
- The aurocyanide is reduced to either gold metal or to a partially reduced state between gold(1) and gold(0).

[Adams et al.1989; Jones et al. 1989; Mc Dougall et al, 1980; Wan et al. 1990; Yannopoulos, 1990].

Doubts surrounding the mechanism for adsorption stem mainly from the fact that carbon is not amendable to infrared spectroscopy or any other technique of physical investigation *[Mc Dougall, 1980]*. This makes it difficult for investigators to know the true nature of the oxygen containing functional groups on carbon which play an important role during adsorption.

1.2.10 Modelling

- ***The 'kn' model***

This model developed by Fleming *et al* (1979) was the first South African model used. This model was developed using the results from the Fairview pilot plant and it was found that a common rate law was applicable in all the stages.

$$C_c - C_c(I) = k \times C_s \times t^{0.5}$$

Where: C_c = Carbon loading at time t [g/t]
C_s = Solution Au concentration at time t [g/t]
I = Incoming carbon
k = Rate constant [h^{-1}]

By utilising the above and combining it with a mass balance over the cascade system yields :

$$\frac{C_c(I)}{C_s(i)} = \left[1 + k\left(\frac{M_c}{F_c}\right)^{0.5} \times \frac{F_c}{F_s}\right]$$

Where: i = Stage number

M_c = Mass of carbon in stage [t]

F_c = Flow rate of carbon [t/h]

F_s = Flow rate of solution [t/h]

This rate expression was used at Grootvlei and resulted in an over design [Fleming and Nicol. 1981]. This phenomenon was ascribed to a difference in the order of the reaction. Hence, the rate equation was amended with the half order time dependency replaced by a variable, n.

By closer investigation it becomes apparent that the rate equation used in the 'kn' model is single rate dependent. Thus, no provision is made for the dual reaction rate that is present when carbon is used as adsorbent. This may account for significant errors, especially when certain stages are running closer to equilibrium.

- ***An updated 'kn' model***

This updated model includes an equilibrium parameter *[Nicol et al. 1984]*.

With constant gold concentration in solution the rate equation was found to be:

$r = k(KC_s - C_c)$

Where: r = Rate [$mg/m^3 h$]

K = Equilibrium constant

From a mass balance over the first stage in the train of cascading vessels the following is obtained:

$$C_c(1) = \frac{C_c(2) + KC_s(1)\,k\left(\frac{M_c}{F_c}\right)}{1 + k\left(\frac{M_c}{F_c}\right)}$$

Where: 1,2 = First and second stage respectively

This procedure is slightly more complex in nature since it involves a convergence step. The first step involves estimating the value of M_c/F_c and then solving for $C_c(1)$ and (2) as well as for the subsequent stages. The value of Cs(1) is compared to the desired value and the calculation repeated with new values of M_c/F_c until the desired value for $C_s(1)$ is obtained.

Although this procedure was well accepted it is still based on a single rate equation. Furthermore, the rate constant k is dependent on external particle variables such as agitation rate and pulp density. Therefore, prior knowledge of this value is limited if experimental conditions do not simulate actual plant conditions accurately.

- ***The Van Deventer Model***

In order to overcome the shortcomings of previous models which incorporated a single rate equation, a branched pore model was proposed *[van Deventer, 1984]*.

This model did not only acknowledge a dual reaction mechanism but also incorporated various types of intraparticle diffusion. The model is broken down into 4 steps.

a) Transfer of gold across the liquid boundary layer surrounding the particle

$$M_s r_s' = F_s\left(C_s(i-1) - C_s(i)\right) - \frac{6k_f}{d_p \rho_c} \sum_{j=1}^{n} \left(C_s(i) - C_s(i)^{(s,j)}\right) M_c$$

b) Adsorption at the solid-liquid interface

$$\frac{k_f}{\rho_c}\left(C_s(i) - C_s(i)^{(s,j)}\right) = km\left(\frac{C_c(i)^{(s,j)^2} - C_c(i)^{(m,j)^2}}{2C_c(i)^{(m,j)}}\right)$$

c) Transport of gold in the macropore network by a surface diffusion mechanism

$$\alpha r_c^{i(m,j)} = \frac{6km}{d_p}\left(\frac{C_c(i)^{(s,j)^2} - C_c(i)^{(m,j)^2}}{2C_c(i)^{m,j}}\right) - k_f\left(C_c(i)^{(m,j)} - C_c(i)^{(b,j)}\right)$$

d) Diffusion from the macropore to the micropore

$$(1-\alpha) r_c^{i(b,j)} = kb\left(C_c(i)^{m,j} - C_c(i)^{(b,j)}\right)$$

Where:

k_f = film transfer coefficient

km = macropore mass transfer coefficient

kb = micropore mass transfer coefficient

∝ = fractional number of total capacity available as macropores

n_i = number of probability density functions for carbon loading

r_s^i = rate constant for solution in stage i

r_c^i = rate constant for carbon in stage i

Superscripts in brackets:

s = surface of particle

m = macropore region

b = micropore region

j = carbon loading fraction

The Van Deventer model does describe the change in the gold loading mechanism which previous models ignore. However, the model is mathematically complex and requires a number of parameters that must be calculated or estimated *[Stanley 1987]*.

- ***Through flow modelling***

A more recent development proposed by Menne, *[1995a]*. This aims to design plant expansions using existing plant data.

$$\boldsymbol{\delta Ya / \delta t = KaX[Y\max - Y]}$$

Where:

δYa = change in carbon loading, g Au/t

δt = change in time, hours

Ka = adsorption rate constant t solution/g Au.hour

Ymax = number of accessible adsorption sites on the carbon, g Au/t

Y = carbon loading, g Au/t

$$\delta Yd / \delta t = Kd Y$$

Where:

δYd = change in carbon loading due to desorption. g Au/t

δt = change in time. hours

Kd = desorption rate constant t solution/g Au.hour

Y = carbon loading, g Au/t

$$\delta Y / \delta t = \delta Ya / \delta t - \delta Yd / \delta t = Ka.X[Y\,\mathrm{max} - Y] - Kd.Y$$

Adsorption occurs if:

$\delta Ya/\delta t > \delta Yd/\delta t$

Elution occurs if:

$\delta Ya/\delta t < \delta Yd/\delta t$

The model preferably based on fundamental expressions becomes more complex as other processes occurring during adsorption are also mathematically combined to the model structure. Examples of processes incorporated into the through flow model are cyanide dissolution. carbon adsorption. carbon desorption etc.

Various other models as proposed by Vegter and Stange also exists. However. most of these are the property of various research laboratories and are not readily available. Also, it is believed that none of these are solely based on solution concentration as described in this study.

1.3 SIGNIFICANCE OF THE LITERATURE STUDY

- Much information is available on gold adsorption onto activated carbon which include the mechanism of adsorption and the CIP process
- Models for CIP simulation and design are either simplified by ignoring a dual kinetic rate or is mathematically complex when this dual rate is incorporated.

1.4 OBJECTIVES OF STUDY

- The development of a simple, yet accurate model for CIP simulation.

Name of process	Conditions under which process operates	Advantages and disadvantages
Zadra	• NaOH and 0.1% NaCN • 85-95°C • atmospheric pressure • 24-60 hours	Advantages : • relatively low capital cost Disadvantage: • long cycle time is a limiting factor on large scale plants
Anglo American (AARL)	• Preconditioning- ½ bed volume of 5% NaOH and 1% NaCN (½-1 hour) • 5 bed volumes hot water at 3 bed volumes per hour • 110°C • 50-100 kPa total cycle time 9 hours (including acid wash)	Advantages: • reduced reagent consumption • reduced carbon inventory • reduced size of stripping section Disadvantages: • use high temperatures and pressures • multiple streams increase circuit complexity
Alcohol Stripping	• 1% NaOH, 0.1% NaCN and 20% alcohol by volume (methanol) • 80°C • atmospheric pressure • 5-6 hours	Advantages: • reduced size of stripping section • less frequent carbon regeneration Disadvantages: • high fire risks associated with alcohol • high operating costs due to alcohol loss by volatilisation • number of safety features to minimise fire rises • effective vapour recovery system is essential to maintain economic balance
High Pressure Stripping	• 1% NaOH and 0.1% NaCN • 160°C • 350 kPa • 2-6 hours	Advantages: • reduced reagent consumption • reduced carbon inventory • reduced size of stripping section Disadvantages: • more costly equipment • effluent solution must be cooled before pressure reduction to avoid flashing

Table 1.1 The various types of elution processes available, along with their advantages and disadvantages

Type of cell	Cell design	Operation of the cell
Cylindrical Cell	• Consists of three concentric cylinders which rest inside one another. The cathode compartment, the overflow container and the outside container • Cathode: The inner container is perforated and serves as the cathode. It contains a feed tube, a current distributor and a quantity of steel wool • Anode: The anode is contained in the outside container and is made up of stainless steel screen	Pregnant electrolyte enters through a feed tube, and circulates upwards through the steel wool cathode. It then overflows into the outer container with the anode made of stainless steel screen. The solution is then recirculated back to the elution section
Rectangular Cell	• Consists of a rectangular tank with the anodes and cathodes positioned alternately along length • Cathode: Consist of steel wool in rectangular plastic baskets. They are connected electrically in parallel by bus bars provided on the top of the cell on both sides. • Anodes: Consist of stainless steel sheets. They are connected the same as the cathodes	The pregnant solution is fed to one side on the cell . It passes through the cell and overflows on the other side, where it is recirculated to the elution section.
Anglo American Cell (AARL)	• Consists of a cylindrical annular design. The cell is divided into anode and cathode compartments by a cation permeable membrane. • Cathode: Consists of stainless steel wool in a sock shape. • Anode: The anode is stainless steel. A strong, alkaline solution in circulated through the anode compartment.	The electrolyte solution is circulated through the cathode compartment, after which it is recirculated to the elution section.

Table 1.2 The various types of electrowinning cells available

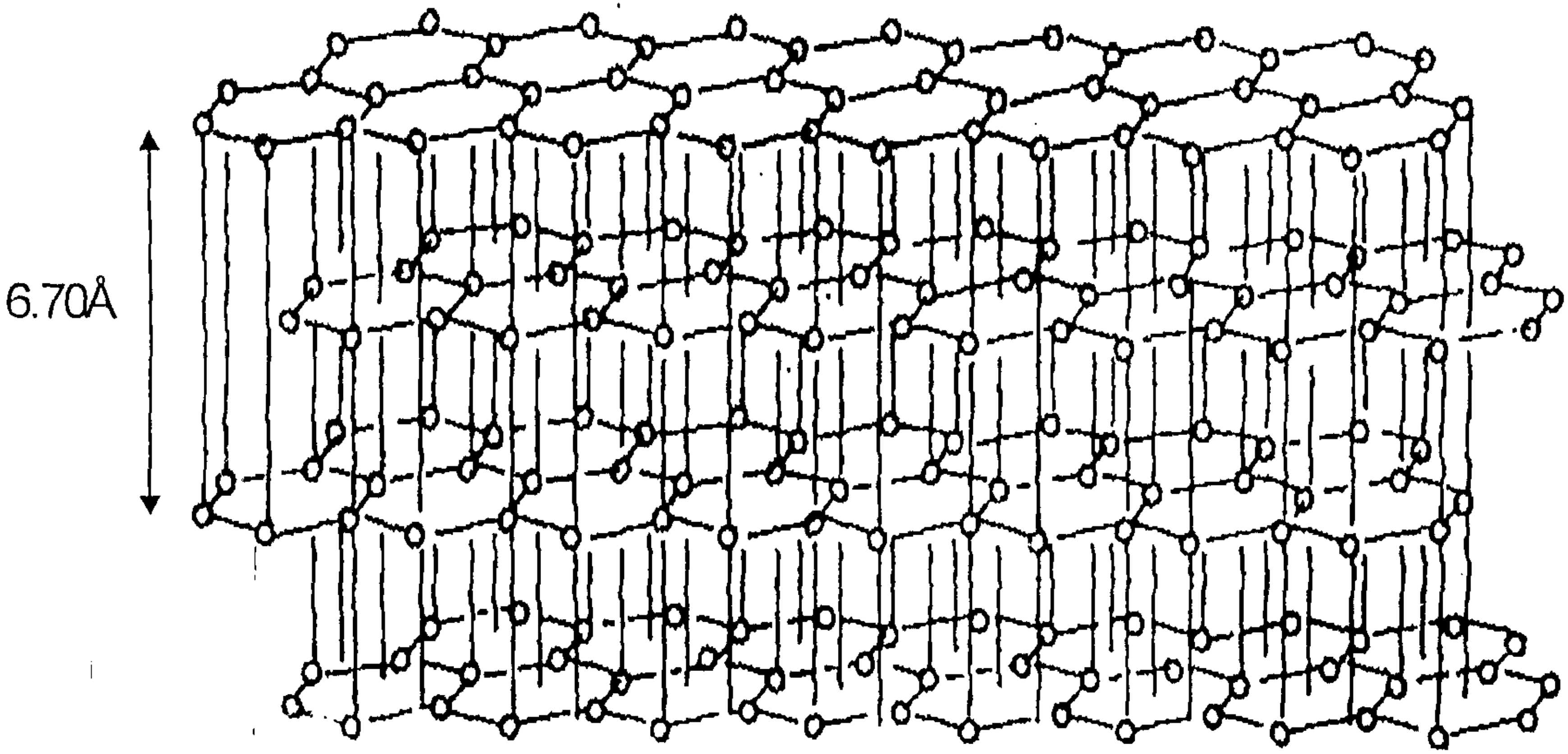


Figure 1.1 A schematic representation of the structure of graphite.

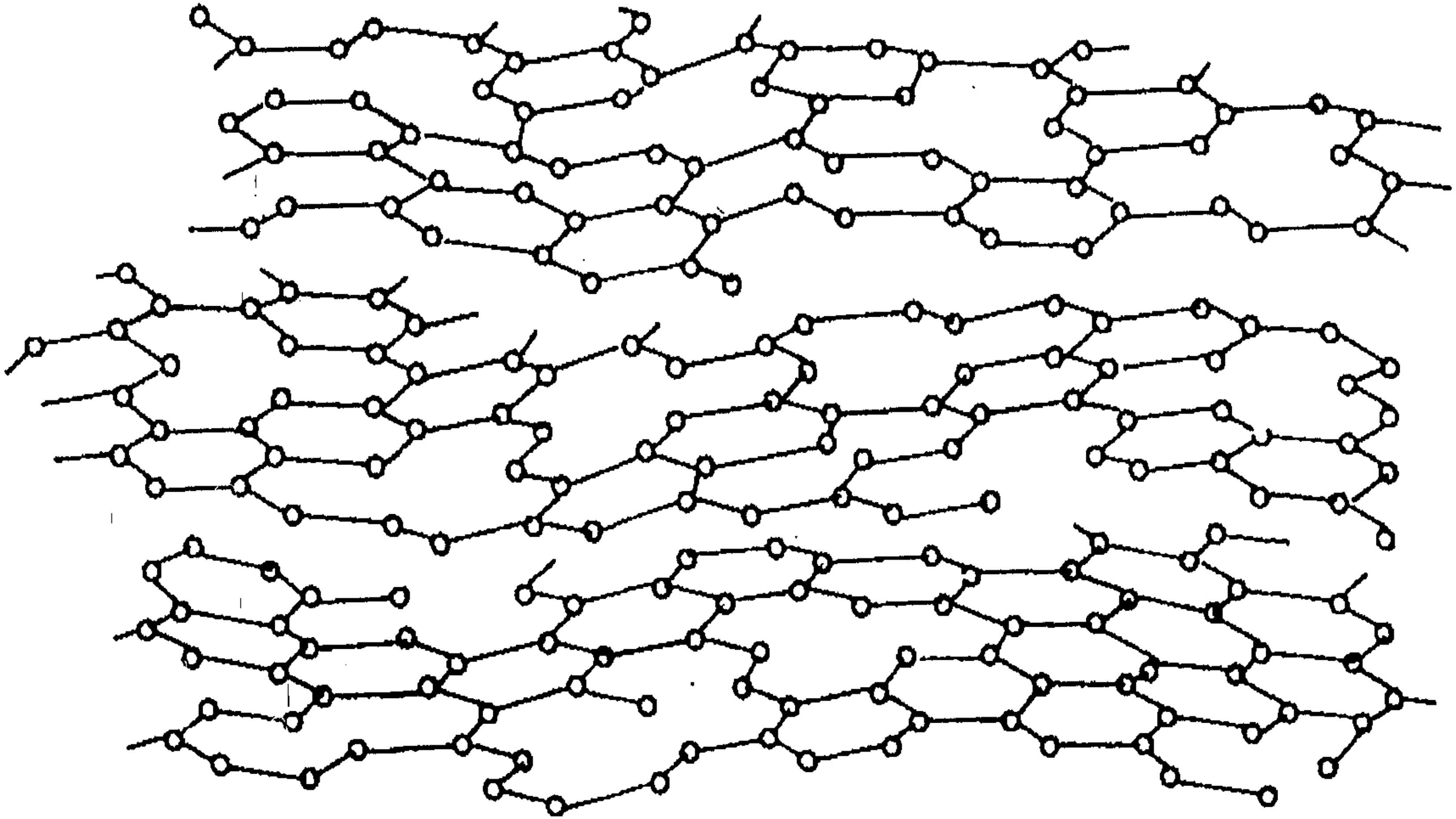


Figure 1.2 A schematic representation of the proposed structure of activated carbon.

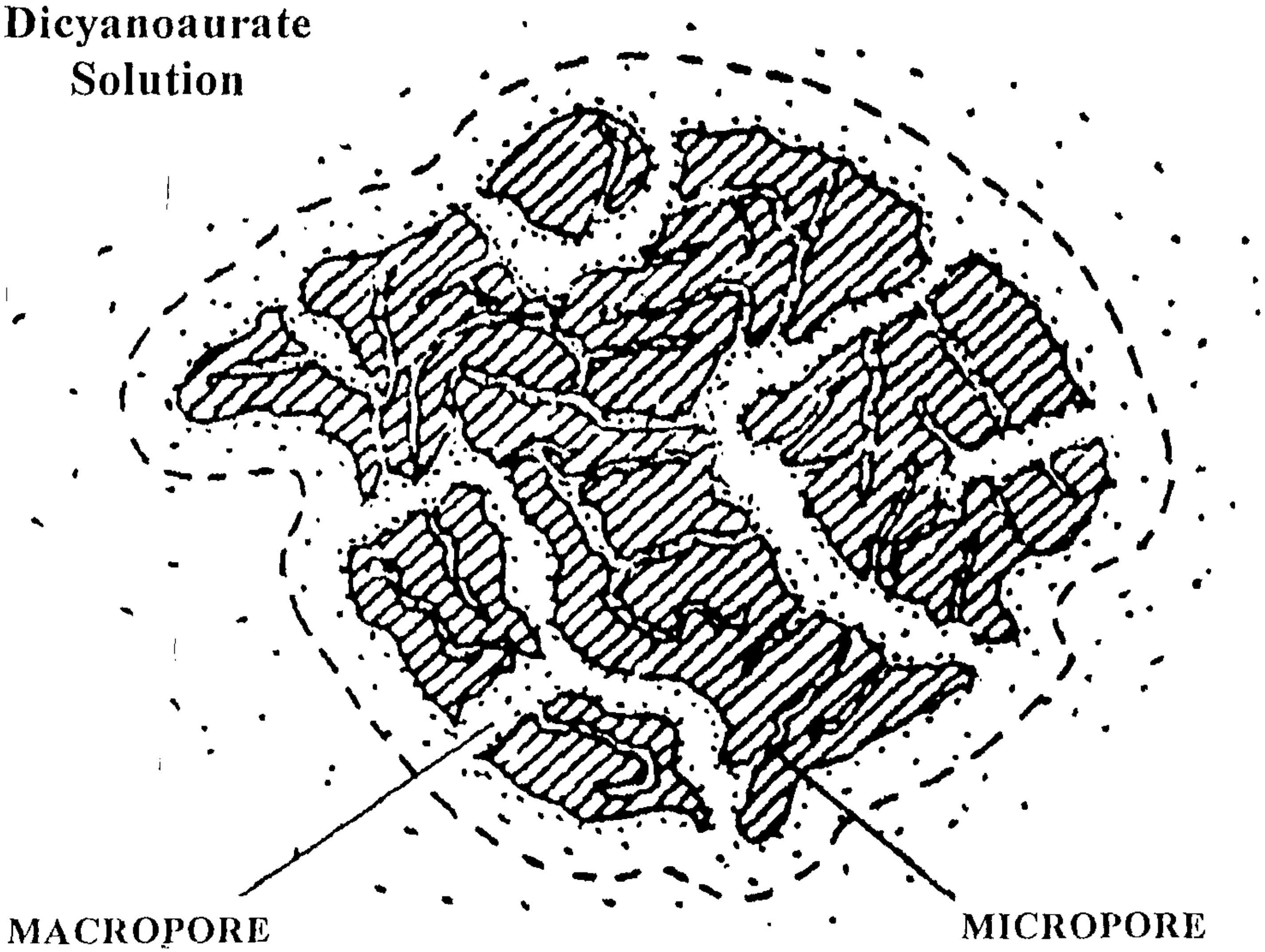


Figure 1.3 An illustration of the pore structure of activated carbon.

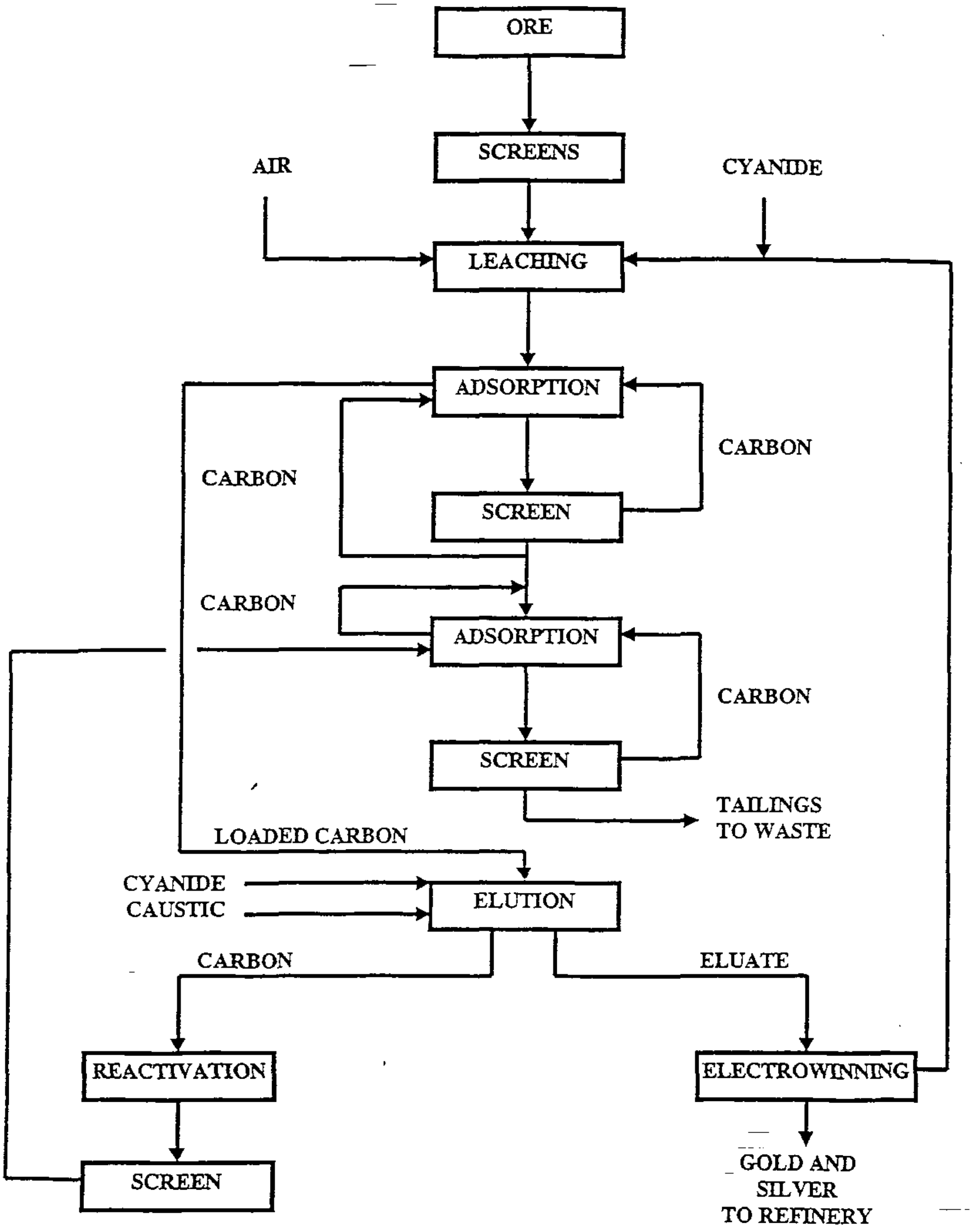


Figure 1.4 A flow diagram representing the Carbon-in-pulp circuit

CHAPTER 2

EXPERIMENTAL

This chapter describes the experimental procedures and analytical techniques utilised to conduct the work contained in this thesis.

2.1 Experimental Material

The ore made up synthetically consisted of silica sand purchased from Consol. The stock purchased was then screened to obtain the required particle size of less than 150 µm. The sand was washed with acetone for the removal of oil and soaked in water for the removal of acetone. After the slurry was made up from the ore, gold solution was added to produce the required concentration and density for the experimental work.

Norit and National Chemical Products Ltd. in South Africa supplied the coconut shell activated carbon, which was used in the study. The virgin carbon was washed with distilled water for the purpose of removing any fines and dried overnight in an oven at 50 °C. The carbon was then stored in a sealed container to avoid adsorption of moisture from the atmosphere.

The adsorbate used in the experiments was potassium dicyanoaurate, $KAu(CN)_2$, a crystalline salt of 98% purity. A mass of 1.493g of the $KAu(CN)_2$ was weighed off and made up in a 1L volumetric flask using distilled water, the product being a standard solution of 1000ppm Au in the form $Au(CN)^{-}_{2}$. A 100 ppm solution is then made up by adding 90 ml of water to 10 ml of the 1000 ppm solution. From this solution the concentration for the six tanks were made up. Concentrations for tanks one to six were 10.51, 7.39, 5.18, 3.12, 2.2 and 2.22 ppm respectively. The concentration of the slurry in the feed bin was 11.8ppm.

2.2 Experimental Set-up

The experiments described in sections 2.3 – 2.5 were performed in 5L perspex reactors. These reactors were made to a standard tank configuration, with an internal diameter of 192 mm and a height of 235 mm. Each tank was fitted with 4 evenly spaced baffles each with a width of 19 mm. A 3-blade impeller driven by a Heidolph electric motor provided the agitation. A sketch of the apparatus is shown in Figure 2.1. The entire apparatus consists of six tanks having a staggered layout to assist the flow of pulp. A pump was also required for the intermittent transfer of carbon.

2.3 Minimum Stirring Speed

Tests were performed to determine the minimum stirring speeds required for keeping slurries of various densities in suspension. A high initial stirring speed was used to ensure all solids were in suspension. The stirring speed was then reduced until settling was observed visually.

2.4 Adsorption rate

The adsorption rate and concentration profiles was determined by means of a atomic absorption spectrophotometer (AA).

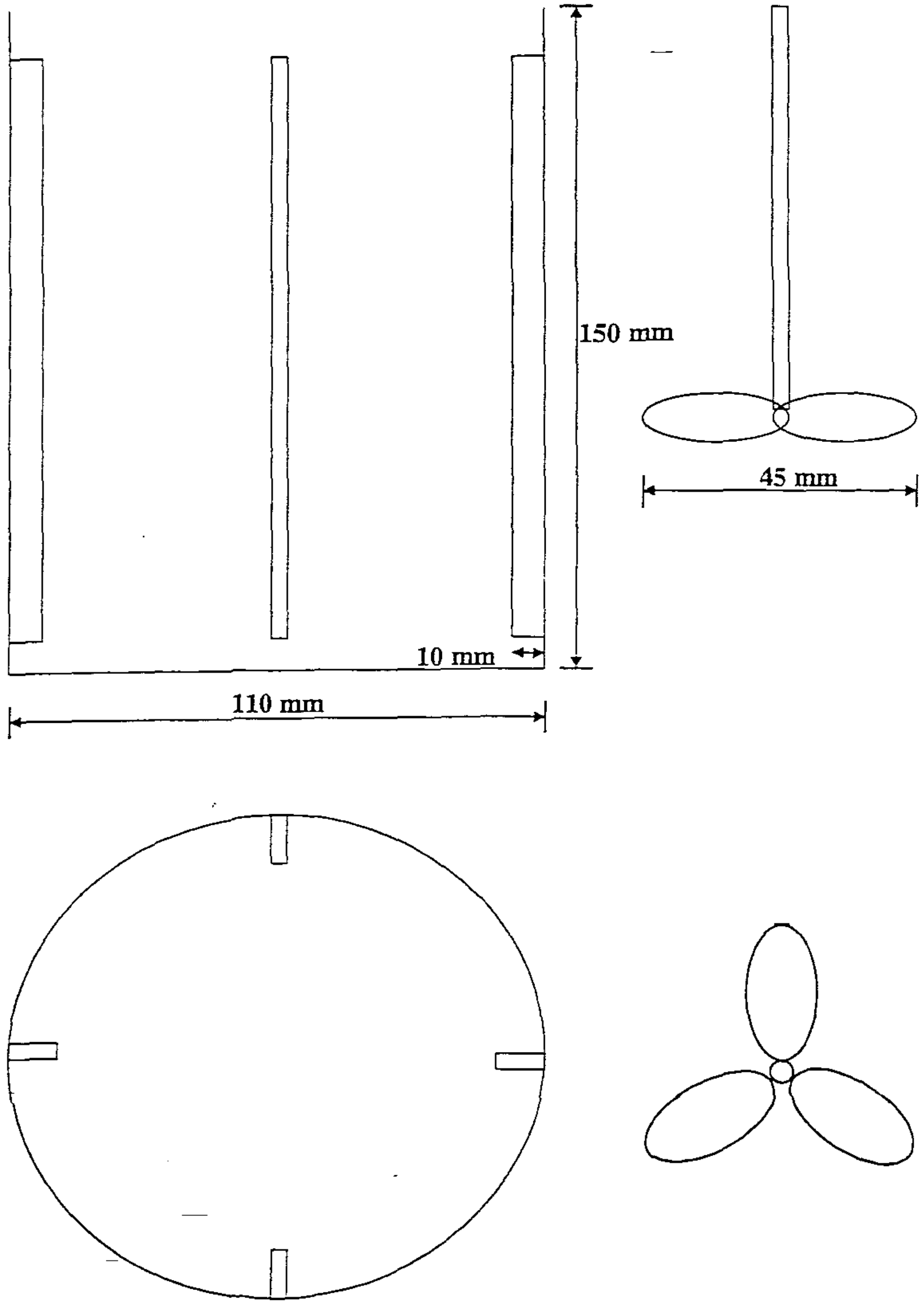


Figure 1.5 The apparatus for experiments performed in 1 L reactors

CHAPTER 3

PLANT LAYOUT AND COMMISIONING

3.1 Design of Cascade System

3.1.1 Tanks in cascade

The tank configuration of the six tanks in the cascade was intended to be as close as practically possible to a standard tank configuration.

Each of the six tanks are joined to those on either side by a channel of 150 mm in length at a slope of 1:3 to ensure a high linear velocity of the slurry to avoid slurry settling in the channels. The shape (semi-circular or v-shaped) and diameter (expected to be in the range 10-20 mm) of the channels that facilitates the smooth flow of slurry was determined experimentally during the construction phase of the plant. Each channel was fitted with a 1.0 –1.3 mm screen to prevent loss of carbon down the system.

Each tank has an agitator (10 mm shaft) associated with it including a marine impeller (rather than the 6-blade impeller of a standard tank configuration). This is considered more suitable given the slurry environment. Each of the stirrers is driven by the same motor, which has a controller to control the agitation speed to within a few rpm.

Each tank rests on a stainless steel tray to trap the solution in the event of leakage from the tanks.

3.1.2 Feed and waste tank

These tanks are specified as 210 litre polypropylene drums. A marine impeller fitted to a ¾ horsepower motor is specified for the feed tank to ensure that the slurry is a homogeneous suspension.

3.1.3 Pumps

PUMP	TYPE	REASON FOR CHOICE
Feed pump	Peristaltic pump	Self-priming Suitable for slurry environment Very stable flow rate achievable

Table 3.1 Pumps utilized in pilot plant

It was decided that the carbon will be transported manually in the initial investigation to minimize carbon breakage.

3.1.4 Motors

MOTOR	TYPE	REASON FOR CHOICE
Agitation of cascade tanks	2.2 kW squirrel cage high precision controller	Safe Very precise agitation rate can be achieved
Feed agitation	250 W motor	Expected to be adequate for agitation task, already available in the department

Table 3.2 Motors utilized in pilot plant

3.1.5 Materials of construction

COMPONENT	MATERIAL	REASONS FOR CHOICE
Impellers and shafts	Stainless steel	Resistance to corrosion and wear by cyanide slurry
Feed and waste tanks	Polypropylene	Resistant to wear by cyanide slurry Light weight Readily avaiable
Cascade tanks	PVC	Resistant to wear by cyanide slurry Light weight Easily constructed from PVC tubing and sheets
Channels and tubing	PVC or silicon tubing	Resistant to wear by cyanide slurry Strong enough for suction side of pumps
Framework	Cast iron coated with corrosion resistant paint	Strong Paint to protect from corrosion caused by spills ans splashing
Drip trays	Stainless steel	Resistant to corrosion and wear by cyanide slurry

Table 3.3 Materials of construction

3.2 Preparation of feed slurry

The slurry to be used in the cascade is required to be oil free with all particles ≤ 150 μm. 700 kg No. 2 Silica Sand was purchased from Consol. Consol could not guarentee that the sand was oil free. Since only 45 % of the No. 2 sand were smaller than 150 μm it was necessary to sieve the sand.

The sand was sieved through a 150 µm screen using a Rollogram sieve. Approximately 260 kg of sand passing through this screen was collected.

3.2.1 Washing of Sand

In order to wash the oil from the sand, the fine material was washed in 20 kg loads as follows:

20 Kg of sand was added to a 25 litre bucket. 10 Litres of acetone was added and the slurry was stirred for 30 minutes to ensure all oil in the sand had dissolved. The stirrer was switched off and the sand allowed to settle. Acetone was pumped off using a paristaltic pump until the sand was as dry as possible. 15 Litres of water was then added and the slurry agitated for 20 minutes to allow residual acetone to mix with the water. The agitation was stopped and the sand allowed to settle. Any oil slick visible on the top of the water was removed and the water was drained off using a centrifugal pump. The washed sand was placed in the feed drum.

1 Litre of the acetone used to dissolve the oil was filtered through filter paper and the paper left to dry. No oily mark was visible indicating that the level of oil contamination was very low. For this reason only one acetone wash was done per load. The quantity of oil still remaining was very low (it only formed a partial slick on the water surface) and hence pumping it off was sufficient for complete removal.

The combined washed sand was repeatedly washed with water to ensure that all acetone was removed.

3.2.2 Make up of slurry

The density of the sand particles was determined by placing a known mass of sand into a known volume of water and measuring the volume increase. This was repeated in triplicate and the relative density of the sand was found to be 2.6.

Calculations to obtain slurry with RD 1.5:

For 1 litre of slurry let mass sand required be	x kg
Mass water required	(1.5 – x) kg
Volume of water	(1.5 – x) litres
Volume of sand	x/2.6 litres
Total volume	$1.5 - x + x/2.6 = 1$
Thus	x= 0.8125 kg
i.e For every litre of slurry required. mass of sand is	0.8125 kg
and mass of water is	0.6875 kg

The volumes are assumed additive. which is a valid assumption since the sand is completely insoluble in water.

To make up 210 litres of slurry 171 kg of sand and 144 kg of water was required.

In practice the slurry was made up by placing a 10 litre bucket of accurately known mass and volume on a balance and adding water and sand until the final mass and the calibrated mass corresponds to a relative density of 1.5.

3.3 Construction of cascade system

3.3.1 Tanks

The tanks were cut from PVC tubing (od 200 mm, thickness 4 mm) to a height of 235 mm. Circles for the bases were cut from 4 mm PVC sheeting and secured with UPVC weld. These were left for 24 hours after which they were filled with water and left for 48 hours to check for leaks. Leaking tanks were dried and additional UPVC weld was added. This was repeated until all tanks passed the leak test.

19 mm wide baffles were cut from 4 mm PVC and attached using UPVC weld. The baffles were placed about 10 mm from the bottom of the tanks to prevent sand settling at the bottom of the baffles.

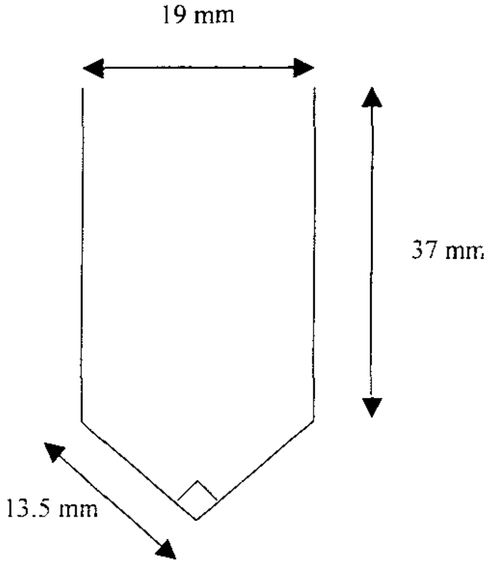
A hole was drilled into one of the tanks near the top and a piece of glass tubing attached for an inlet to which the tubing from the feed pump was attached.

Covers were made for each tank to contain splashes. This was done by cutting 300 mm diameter circles from 4 mm PVC and cutting a rectangular slot of 20 mm by 200 mm along the diameter to allow space for the turning shaft and to fit firmly against the channels.

3.3.2 Channels

3.3.2.1 Testing for suitability of channels and feed pump

Once the tanks were constructed two of these were set up in a temporary arrangement with slurry in both and the peristaltic pump intended for use in the CIP plant was used to circulate slurry continuously through the two tanks which had a test channel installed. This set-up was used to test the suitability of the pump selected and whether the channels being tested were satisfactory. A triangular channel was used and was satisfactory. It was decided to give the channels straight shoulders to increase their strength and allow for a substantial increase in flow of slurry for any future projects using the CIP cascade plant. The channel shape was as follows (inside measurements given).



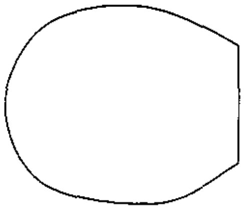
A solid model of the channel was made by cutting wood to the appropriate shape. This was then used as a mould to vacuum mould each of the channels from 1.2 mm PVC. The slots in the tanks were filed to the correct angle and the channels inserted and welded in place. An additional piece of pipe (of the same size as he tanks) was cut into rectangles and the same slot was cut. These pieces were then welded onto the tanks to add extra strength to the channels and reduce the chance of leaks developing where the channels were joined to the tanks.

The screens were made using 1.3 mm plastic coated fiberglass mosquito mesh. A piece of pipe cut into rectangles from which a slot shaped as above was cut. A piece of mesh was stretched and welded over the opening using UPVC weld. These screens were then welded to the inside of each tank in such a way that the slots lined up.

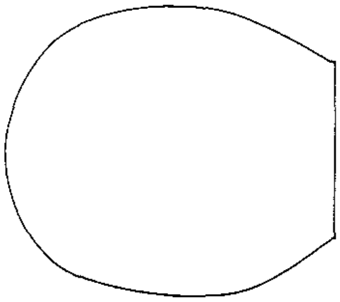
3.3.3 Framework, Agitator, Motor and Associated Construction

The impeller blade design is shown below (actual size). The blades are attached to a collar at an angle of 45°. The blade shown for the feed tank is the final blade used after the tank size was changed (see commissioning below).

CASCADE TANK IMPELLER



FEED TANK IMPELLER



The framework was constructed in such a way so that the impeller shafts are at a fixed height. The height of the blades from base of each tank were set so that they ranged from 35 mm to 53 mm. Calculations predict the ideal height to be in the region of 64 mm

3.4 Commissioning of CIP plant

3.4.1 Feed tank agitation

The first problem encountered when attempting to run the system was that of maintaining the feed as a homogeneous slurry. The motor for the feed agitator was not powerful enough to get the slurry into suspension, thus it was decided to make up the feed in 50 litre drums and top it up every 5 hours.

The motor was able to maintain the slurry in suspension at 1400 rpm, but overheated after an hour of continuous use. It was only possible to fill 2 tanks in this time. It will be necessary to use a larger motor to run the plant for longer runs. The homogeneity of the slurry was tested by taking repeated 100 ml samples from the feed tank during agitation and determining the masses obtained. The sample was returned to the feed tank before the next sample was taken.

The results are tabulated below:

SAMPLE NO.	SLURRY MASS	RELATIVE DENSITY
1	170.8	1.455
2	180.7	1.539
3	170.9	1.456
4	173.2	1.475
5	175.8	1.497
MEAN RELATIVE DENSITY		1.484
STANDARD DEVIATION		0.035

Table 3.4 Results of the homogeneity test

Since the standard deviation is only 2.4 % of the mean value it was concluded that the slurry is being homogeneously mixed.

3.4.2 Feed pump

During the initial tests gear stripping of the peristaltic pump occurred due to incorrect tubing used. These were replaced for future runs. Prior to this the slurry was pumped satisfactorily at 167 ml/min (the design specified flow rate). The slurry can be pumped up to 560 ml/min with the current pump but settles out when speeds of less than 120 ml/min are attempted. The extreme values were determined using the temporary test set up described under the channel construction section

3.4.3 Cascade belts and pulleys

The correct belts did not arrive in time to commission the plant hence, temporary pulleys were constructed from PVC tubing. These slipped as they became heated during operation and one broke so that the minimum stirring speed to keep the slurry in suspension could not be determined and only the first 4 tanks in the cascade could be stirred.

Only 8 of the pulleys used were of the correct size.

3.4.4 Fixed cascade tank impellers

The impellers of the tanks were set at a fixed height along the framework. This was done to overcome certain construction problems. This set up is not ideal since the trays must be removed and tanks lifted while the stirrers are in operation in order to suspend settled material. This operation requires 2 people and is not ideal since spilling of material occurs and it is in general a safety hazard.

The impeller shafts were not set at the design height of 64 mm from the base of the tanks. The first tank in the cascade had the impeller blade at 35 mm and the second one at 53 mm (the last 4 impellers were set at heights between these extremes). After running the cascade system for 1 hour the contents of the first two tanks were allowed to settle out and it was noted that the second tank contained less solids than the first one. This had to be rectified.

3.4.5 Calibration of speed controller revolution counter

The revolution counter on the speed controller associated with the motor turning the cascade tank impellers was calibrated using a tachometer. It was found to over read by 7 rpm over the full range of operation.

3.4.6 Performance of screens

The screens on the channels did not block when the system was run with slurry for one hour. However. it was still to be tested during longer periods and with carbon in the system.

3.5 Final note

All proposed modifications and adjustments were made prior .o a continuous run that lasted for five hours.

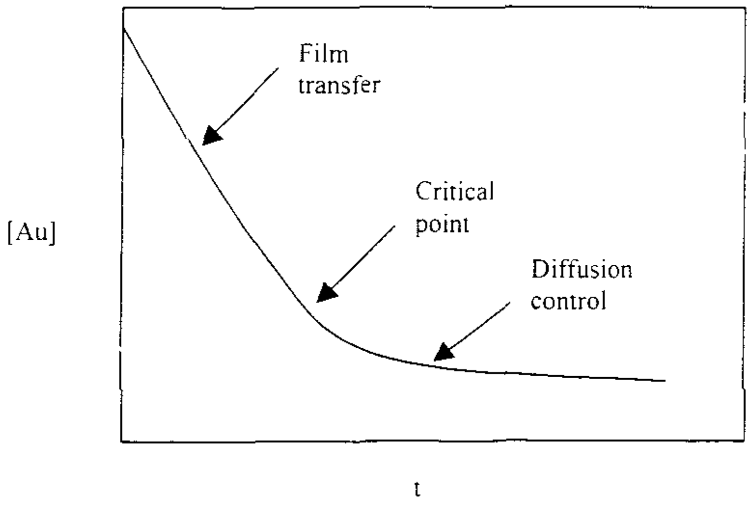
CHAPTER 4

MODEL DEVELOPMENT

This chapter describes the development of a solution concentration model for CIP simulation.

4.1 Batch adsorption

The following is a typical adsorption profile of gold onto activated carbon in a batch reactor.

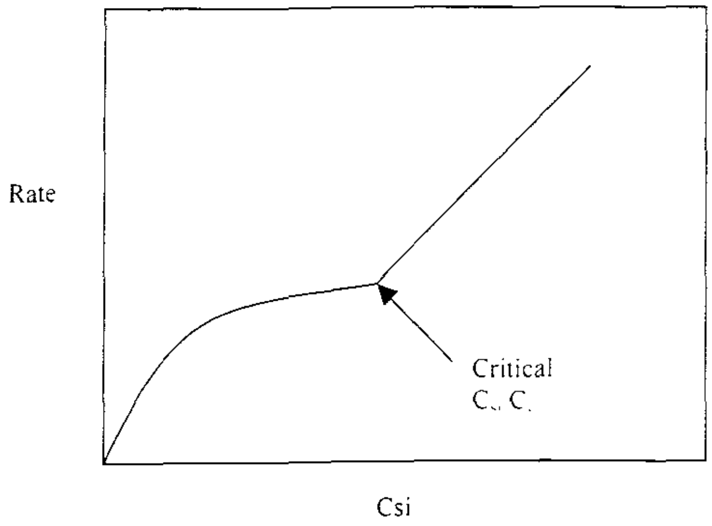


During the so-called film transfer phase, carbon loading increases and solution concentration decreases but the adsorption rate remains constant. This generated the idea that a rate equation based on the difference between solution concentration and carbon loading could result in significant errors. Hence, it was decided to develop a model for CIP operations based on solution concentration only, with carbon loading having an indirect effect.

4.2 Hypothesis

- Solution concentration is the main mass transfer driving force given normal CIP operating variables.
- Adsorption kinetics is a linear function of solution concentration if the ratio, C_{si}/C_c is larger than a certain critical value.
- Adsorption kinetics is a logarithmic function of solution concentration once the critical ratio has been reached, i.e. diminishes at a diminishing rate as C_{si}/C_c decreases.

This is graphically illustrated below:



$$\text{Thus : rate} = k_c C_{si} \quad if \quad \frac{C_{si}}{C_c} \rangle \; critical$$

$$\text{rate} = k_d \ln(C_{si}) + K \quad if \quad \frac{C_{si}}{C_c} \langle \; critical$$

Where :

k_c = unitless constant rate constant

k_d = unitless diminishing rate constant

K = constant (g/t)

A mass balance over reactor i yields the following expressions

$F_s(C_{sI} - C_{si}) = F_c(C_{ci} - C_{i+1}) =$ rate of gold recovery in tank i

Therefore.

$$F_c(C_{ci} - C_{ci+1}) = M_c.k_c.C_{si} \quad if \ \frac{C_{si}}{C_c} \ \rangle \ critical$$

And

$$F_c(C_{ci} - C_{ci+1}) = M_c(k_d.\ln(C_{si}) + K) \quad if \ \frac{C_{si}}{C_c} \ \langle \ critical$$

Hence :

$$C_{si} = \frac{F_c(C_{ci} - C_{ci+1})}{M_c.k_c}$$

OR

$$C_{si} = \exp\left[\frac{\left[\frac{F_c(C_{ci} - C_{ci+1})}{M_c} - K\right]}{k_d}\right]$$

CHAPTER 5

COMPUTER PROGRAM OVERVIEW

This chapter describes the program used to compare the solution concentration model to the other simplified models (i.e. kn and updated kn models) and also to test the accuracy of the new model.

5.1 General

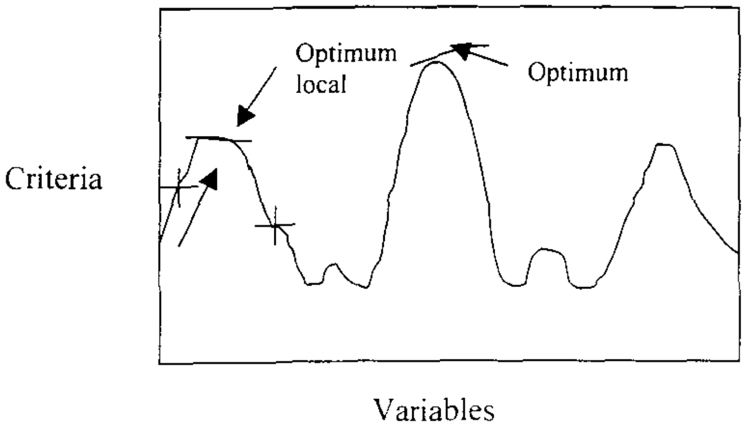
An object orientated C++ program was developed. OOP was selected in order for the program to be re-used by other programs if required as well as the simplification of using variables in various functions. The program is shown as Appendix A. The class and source code has been separated for the purpose of readability.

The H file declares a class named CIP with the cpp file containing the source code. Public and private data and functions are declared and implemented in the cpp file.

A tank structure is used that contains the necessary data for variable determination. A vector of pointers is used to access, change and use members of the structure. The new member is used to create tanks to overcome the difficulty of not necessarily having prior knowledge of the number of CIP reactors in the train. These are destructed separately in the destructer once the program goes out of scope. Data is read and written from and to text files to eliminate the need for re-entering data needed for variable determination.

5.2 Optimum Determination

Numerical techniques are often unstable in the optimum region or produce local maxima if the correct numerical technique is not selected. In other words the calculations cease once an optimum local is reached. This is graphically illustrated below.



With this in mind the program created ignores these local optima and continues with the calculations in the range set. This is considered the "nuclear bomb" approach and guarantees the optimum result from the calculations executed. Although not as time efficient as most numerical techniques an optimum is a stable point with time not considered a serious problem keeping in mind the process speed of new computers.

The functions utilized in the program all have an outer loop so as to investigate the optimum for each reactor. The inner loops determine the optimum variable values using an error criterion.

A percentage error criterion was used in order to compare errors incurred when making solution concentration predictions. This was done in order to compare errors directly, as the magnitude of actual solution concentration can be deceptive. This may best be explained by example.

Tank no.	**Actual C_{si}**	**Predicted C_{si}**	**Error**	**% error**
x	1.5	1.3	0.2	13.3
y	0.1	0.01	0.09	90

In the above example tank x results in a much larger error than tank y although the % error is quite the opposite.

CHAPTER 6

RESULTS AND DISCUSSION

Plant conditions for experimental and simulation were as follows:

Volume of tank : 5l

Initial concentration : 11.8mg/l

Tip speed : 0.9421/t

Relative density : 1.1mg/l

Carbon concentration : 2g/l

Mass of carbon per transfer : 0.4g/l

Loading on fresh carbon : 0mg/g

Starting concentrations for laboratory scale pilot plant experiment

- Feed to tank 1(Feed bin) : 11.8mg/l
- Feed to tank 2(Tank 1) : 10.51mg/l

- Feed to tank 3(Tank 2) : 7.39mg/l
- Feed to tank 4(Tank 3) : 5.18mg/l
- Feed to tank 5(Tank 4) : 3.12mg/l
- Feed to tank 6(Tank 5) : 2.2mg/l
- Residue (Tank 6) : 2.22mg/l

The results obtained are listed below:

Experimental Run

Time	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5	Tank 6
60min	9.67	7.78	5.31	4.73	3.39	3.23
120min	9.34	8.01	6.63	5.46	4.73	5.11
180min	9.1	7.69	6.4	5.49	4.83	4.45
240min	9.51	7.48	6.83	5.64	4.19	5.41
300min	9.24	9.05	7.69	6.46	5.39	4.59

Table 6.1 Results of the experimental run performed on the CIP pilot plant

Gray found the critical value (as explained in chapter 4) to be approximately 0.003. However, this value is dependent on process variables such as agitation rate. Hence, a specific critical value had to be determined. Also, due to the erratic behavior of the pilot plant, actual plant data was obtained to test the simulation developed.

Pilot Plant

As mentioned before, the laboratory scale pilot plant did not yield meaningful results. Thus, the developed model could not be evaluated with confidence on this data. It was concluded that a larger plant should be constructed to simulate actual plant conditions effectively. The data obtained was erratic in nature and meaningful conclusions could not be drawn.

Plant Data

In an attempt to test the model developed actual plant data was obtained from Anglogold.

- Critical **C_{si}/C_c**

The critical value was determined from the average monthly values received. These averages were calculated by the computer program. The values are shown below:

Tank no.	**Actual C_{si}(ppm)**	**C_c(g/t)**	**M_c(tons)**
1	1.35	2719	4.6
2	0.86	1360	3.92
3	0.21	624	3.4
4	0.12	366	4.2
5	0.04	275	3.7
6	0.02	211	4.2
7	0.01	155	3.97
8	0.01	119	3.7

Table 6.2 Results received from the Anglogold CIP plant

The carbon flow rate (F_c) is 0.5 t/h and the incoming carbon concentration (Cc) 90 g/t.

The critical value approach was tested with the plant data received. A plot of rate ($F_c(C_{ci}-C_{i-1})/M_c$) vs C_{si} is shown below and clearly indicates that rate increases as solution concentration increases although carbon loading is also increasing with C_{si} in the system.

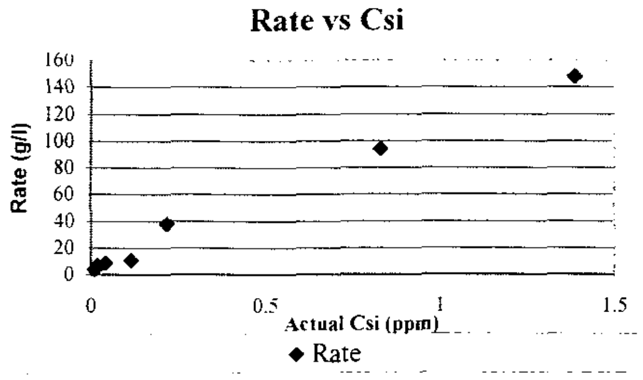


Figure 6.1 Graphical representation of rate vs C_{si}

The above suggests a linear relationship between rate and solution concentration. However, if the data is divided into two sections it becomes clear that only a section of Figure 6.1 is effectively linear. This is shown below in Figures 6.2 and 6.3 by selecting a critical value of 0.0003.

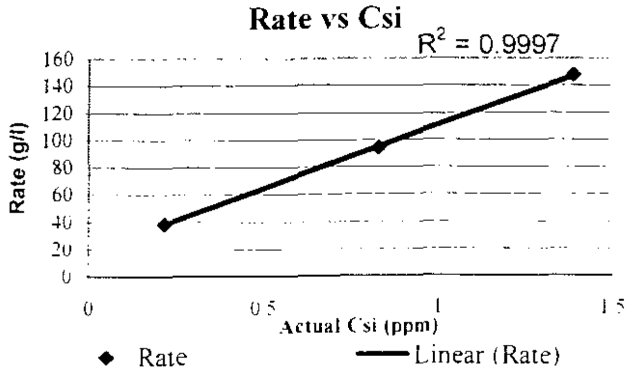


Figure 6.2 Sectional graphical representation of C_{si} vs rate

Figure 6.2 is a plot of the first three reactors in the CIP train. The plot reveals that a change in rate is almost 100% explained by a change in solution concentration ($R^2 = 0.9997$). In all three cases $C_{si}/C_c < 0.0003$. The result manifests the hypothesis that rate can be explained by a linear solution concentration relationship if the critical value is larger than some predetermined value. A plot of the last 5 reactors is shown below.

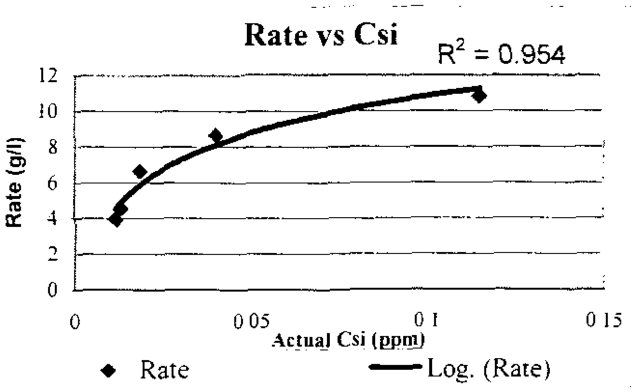


Figure 6.3 Sectional graphical representation of C_{si} vs rate

Figure 6.3 reveals the logarithmic relationship between rate and C_{si}. In all the reactors under consideration $C_{si}/C_c < 0.0003$. Also, the percentage variation in rate is 95% explained by changes in solution concentration as 0.954 is obtained for R^2.

A comparison is drawn between the Solution Concentration model (SCModel) and the kn models. These two models were selected on the basis of industrial acceptance and their simplicity.

The kn model

Tank	Actual C_{si}(ppm)	Predicted C_{si}(ppm)	k values	n values
1	1.35	2.82	160	0.95
2	0.86	0.88	60	0.6
3	0.21	0.46	150	0.6
4	0.12	0.09	95	0.15
5	0.04	0.04	120	0.2
6	0.02	0.01	70	0.1
7	0.01	0.01	70	0.05
8	0.01	0.00	50	0.05

Table 6.3 k and n values calculated from the kn model of the data received from the Anglogold CIP plant.

These values are calculated by a program created using the kn model's mathematical expressions.

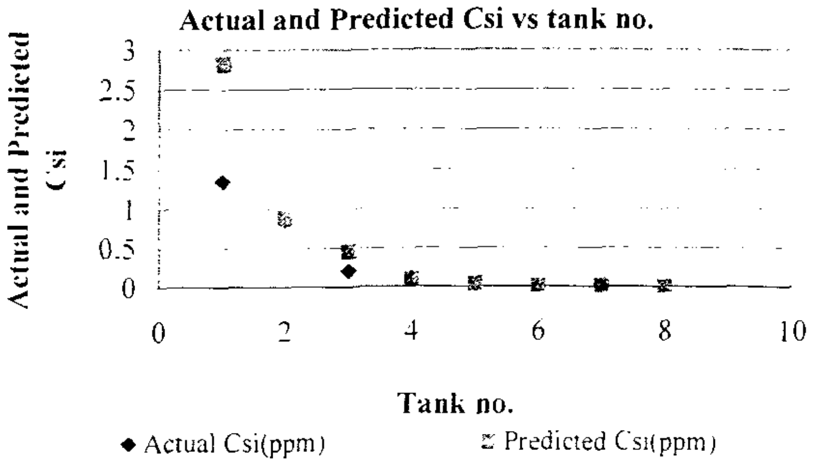


Figure 6.4 Graphical representation of the actual and the predicted C_{si} results

From the above it is clear that this model over-predicts at higher C_{si} values.

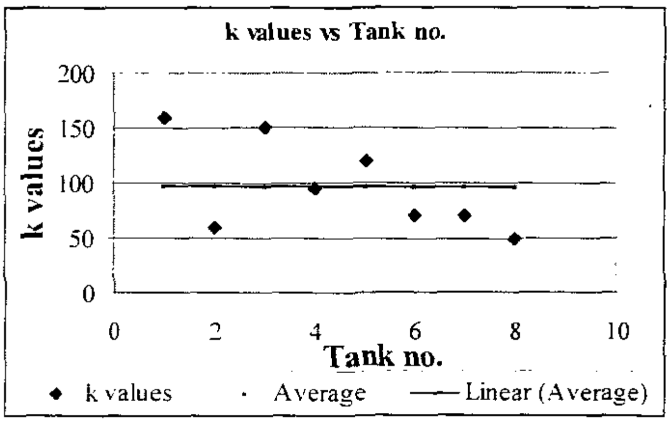


Figure 6.5 **Graphical representation of the k values calculated from the kn model for each tank in the system**

The standard deviation was calculated for k and equals 41.998. The average value for k was found to be 96.88. Thus, a relatively large standard deviation results.

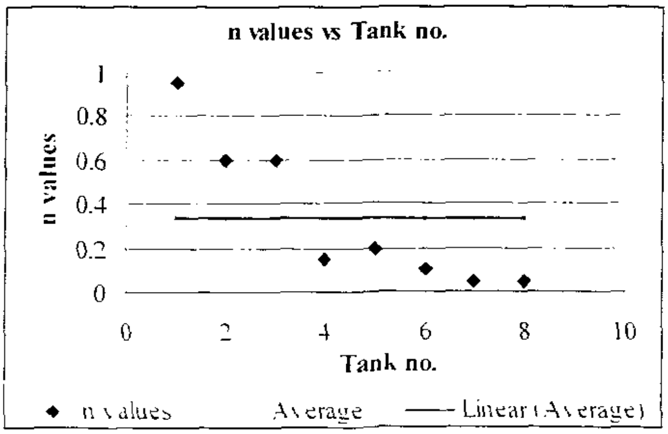


Figure 6.6 **Graphical representation of the n values calculated from the kn model for each tank in the system**

The standard deviation was calculated for n and equals 0.3357. The average value for n was found to be 0.3375. Again a large standard deviation results. The sum of the percentage error for the kn model is 438.1and the average percentage error per tank therefore equals 54.76. In other words, on average the predicted C_{si} and actual C_{si} differ by almost 55%.

- The updated kn model

Tank	Actual C_{si} (ppm)	Predicted C_{si} (ppm)	k values	K values
1	1.35	0.41	1.25	2100
2	0.86	0.21	1	1700
3	0.21	0.10	1	3100
4	0.12	0.05	1.3	3200
5	0.04	0.04	1.15	6600
6	0.02	0.03	0.25	10300
7	0.01	0.02	0.45	13500
8	0.01	0.02	1.65	14900

Table 6.4 k and K values calculated from the updated kn model of the data received from the Anglogold CIP plant.

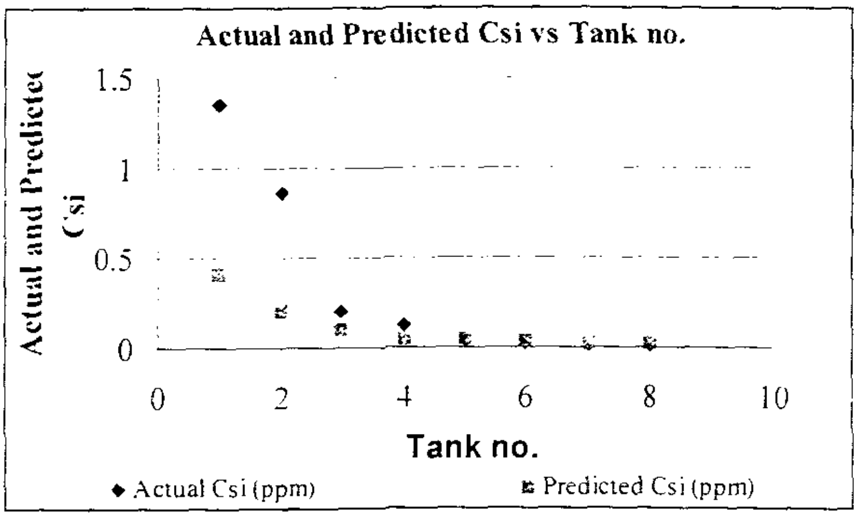


Figure 6.7 Graphical representation of the Actual and Predicted C_{si} results

The updated kn model under-predicts at high C_{si} values and over-predicts at low C_{si} values.

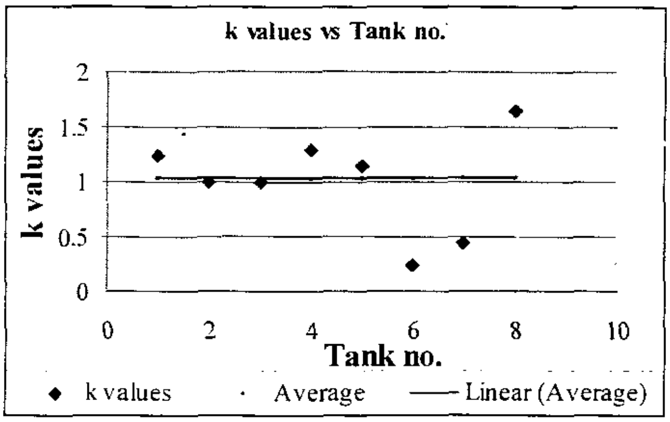


Figure 6.8 Graphical representation of the k values calculated from the updated kn model for each tank in the system

The standard deviation was calculated for k and equals 0.457. The average value for k was found to be 1.006.

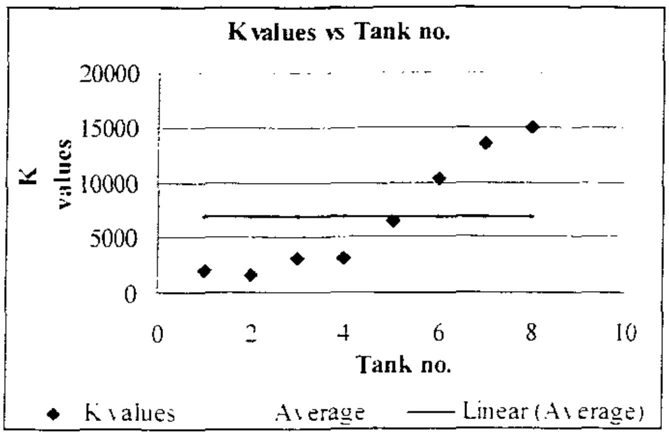


Figure 6.9 Graphical representation of the K values calculated from the updated kn model for each tank in the system

The standard deviation was calculated for K and equals 5310.569. The average value for K was found to be 6925. As with the kn model the updated kn model produces large standard deviation results. The variables estimated are therefore erratic and vary greatly with tank number. The sum of the percentage errors for the updated kn model is 501.2 and the average error per tank therefore equals 62.65. Hence, a difference of almost 63% between actual and calculated C_{si} is experienced per tank.

- The solution concentration model

Tank	Actual C_{si}(ppm)	Predicted C_{si}(ppm)	k_c values	k_d values	K values
1	1.35	1.12	109.5	0	0
2	0.86	0.71	109.5	0	0
3	0.21	0.29	177.5	0	0
4	0.12	0.08	0	2.2	15.6
5	0.04	0.04	0	4	21.4
6	0.02	0.02	0	1	10.5
7	0.01	0.01	0	3.8	21.2
8	0.01	0.01	0	4	23.2

Table 6.5 k_c, k_d and K values calculated from the solution concentration model of the data received from the Anglogold CIP plant.

A plot of the predicted and actual solution concentrations is shown below

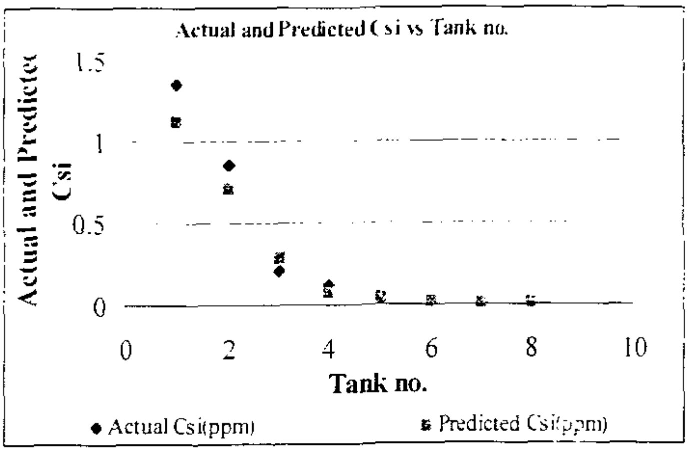


Figure 6.10 Graphical representation of actual and predicted C_{si}

The SCModel provides a very accurate prediction at lower C_{sl} values and underpredicts at higher solution concentrations. However, the errors experienced at higher solution concentrations are small.

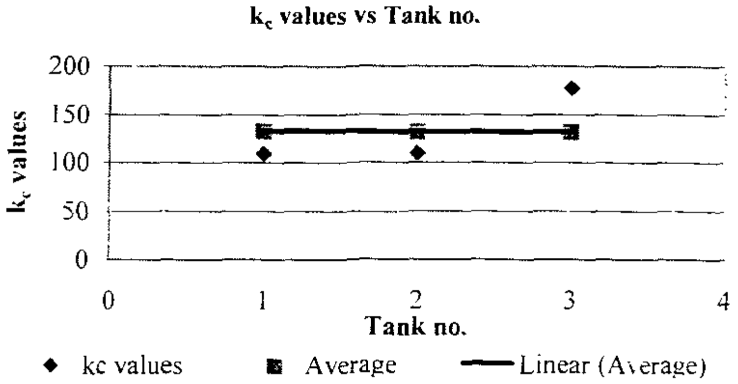


Figure 6.11 Graphical representation of the k_c values calculated from the solution concentration model for each tank having a critical value > 0.0003

The standard deviation was calculated for k_c and equals 39.26. The average value for k_c was found to be 132.2.

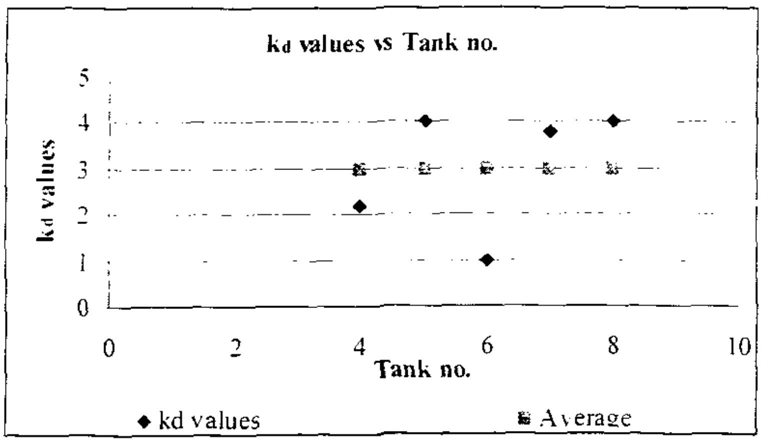


Figure 6.12 Graphical representation of the k_d values calculated from the solution concentration model for each tank in the system with critical value <0.0003

The standard deviation was calculated for k_d and equals 1.35. The average value for k_d was found to be 3.

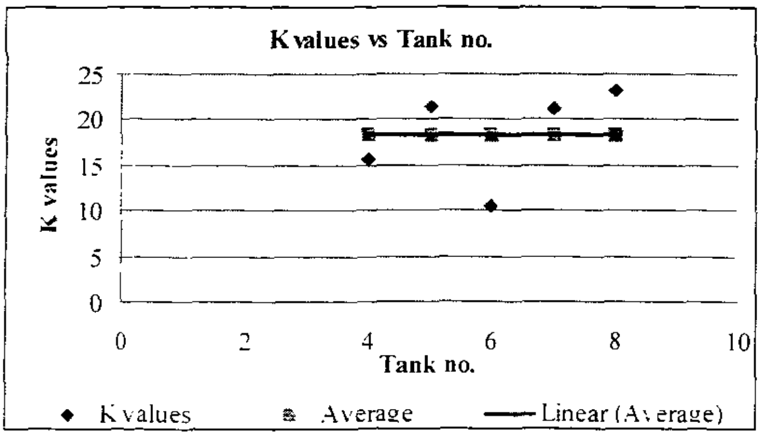


Figure 6.13 Graphical representation of the K values calculated from the solution concentration model for each tank in the system with critical value < 0.0003

The standard deviation was calculated for K and equals 5.25. The average value for K was found to be 18.38. The sum of the percentage errors for the solution concentration model is 135.2 and the average error per tank therefore equals 16.9%.

From the above it is clear that the solution concentration model provides more accurate predictions than the other two used for comparative purposes. Thus, it seems that a rate based on solution concentration and a critical value could be used for CIP modeling.

In summary

Criterion	**kn model**	**Updated kn model**	**Solution concentration model**
∑ % error	438.1	501.2	135.2
Average % error per tank	55	63	17
Average (standard deviation /actual value of parameter	0.72	0.61	0.34

CHAPTER 7

CONCLUSIONS AND RECOMENDATIONS

The objective of this study was to determine whether a simplified semi empirical model could be used to simulate carbon-in-pulp performance and whether the results obtained justifies further studies related to this topic.

The following is concluded:

- A model based on solution concentration provided more accurate results than other simplified models such as the kn and updated kn models

- The solution concentration model should be tested on higher grade plant data to ensure reproducibility.

- The laboratory scale pilot plant should be modified and capacity increased to yield accurate results that could be compared to actual plant data

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APPENDIX A

C++PROGRAM FOR SIMULATION OF GOLD ADSORPTION ONTO ACTIVATED CARBON

MAIN

```
#include "cip.h"

int main()
{
cip z:
return 0:
}
```

INTERFACE

```
#ifndef _CIP_H_
#define _CIP_H_

//interface for CIP class

#include <iostream>
#include <fstream>
#include <vector>
#include <string>
#include "Math.h"

class cip
{
public:
        cip ();
        ~cip();

private:
        void read();
        void control():
        void get_Averages():
        void model_kn():
        void model_knO ():
        void  model_updateO():
        void model_update():
```

```
        void model_new();
        double k1, k2, n1, K1, kc, kd, SD, Fc,V;
        int t, step, tn;
        ifstream fin;
        ofstream fout;
        vector<double> a;
        const string A, B, c, D, E, F, G;
        struct Tank {
                int No;
                double Csl, Csi, Mc, Fs, Cc
                double estimate, error, pererror;
                double k, n, K;
        };
        vector<Tank *> vP;
};

#include "c.cpp"
#endif
```

SOURCE CODE

```
//Source code
#include <iomanip>

cip::cip() : A("Result for kn model"), B("Tank  "), c ("  Actual Csi  "),
D("  Calculated Csi  "), E("  Error"), F("Results for updated kn model"),
G("----------------------------------------------------------------------")
{
//Initialise
k1 = 0;
k2 = 0;
n1 = 0;
K1 = 0;
cout<<"Welcome to the Dependancy simulation for CIP operations"<<endl;
cout<<"You are required to enter at least two constants and a data sheet"<<endl;
cout<<"Four other constants are optional"<<endl;
cout<<"----------------------------------------------------------------------"<<endl;
cout<<"IMPORTANT : "<<endl;
cout<<"The data must be stored in a txt file of name data in the current directory"<<endl;
```

```
cout<<"as follows : CsI, Csi, Mc, Fs and Cc for each tank"<<endl;
cout<<"The results may be found in results.txt in the current directory"<<endl;
cout<<"------------------------------------------------------------------"<<endl;
fin.open("data.txt");
fout.open("results.txt");
read();
}

cip :: ~cip()
{
//delete tank structures created by new
for (int i = 0; i < t; i++)
delete vP[i];
fin.close();
fout.close();
}

void cip::read()
{
double value;
char answer1, answer2;
cout<<"===================================="<<endl;
cout<<"Please enter the number of tanks in the CIP train  "<<endl;
cin>>t;
cout<<"Enter the carbon flow rate in t/hr  ";
cin>>Fc;
cout<<"Would you like to enter k and n for the kn  model [y or n]  ";
cin>>answer1;
if ((answer1 == 'y') || (answer1 == 'Y'))
{
cout<<"k  ";
cin>>k1;
cout<<"n  ";
cin>>n1;
}
cout<<" "<<endl;
cout<<"Would you like to enter k and K for the updated kn model [y or n]  ";
cin>>answer2;
if ((answer2 == 'y') || (answer2 == 'Y'))
{
cout<<"k  ";
```

```
cin>>k2;
cout<<"K  ";
cin>>K1;
}
cout<<" "<<endl;
//read all values from the data file into vector a
while (fin>>value)
        a.push_back(value);
control();
}

void cip::control() //A function to control the simulation
{
char decision;
get_Averages ();
if (k1 != 0)
        model_knO();
else model_knO ();
cout<<"Would you like to continue with the updated model?  [Y or N]  ";
cin>>decision;
if (((decision == 'Y') || (decision == 'y')) && (k2 == 0))
        model_updateO();
else model_update();
cout<<"Would yo like to continue with the SCModel model ? [Y or N]   ";
cin >> decision;
if ((decision == 'y') || (decision == 'Y'))
        model_new();
}

void cip :: model_kn () //function to determine accuracy of kn model with k and n
provided
{
fout<<A<<endl;
fout<<G<<endl;
fout<<B<<c<<D<<E<<endl;
for (int j = 0; j < t; j++)
{
        fout<<j + 1<<"    ";
        fout<<setprecision(4)<<vP[j] -> Csi;
        vP[j] -> estimate = vP[j] -> CsI/pow((1 + k1 * pow((vP[j] -> Mc/Fc), n1) *
        (Fc/vP[j] -> Fs)), (j+1));
```

```
        fout<<setprecision(4)<<vP[j] -> estimate<<"   ";
        vP[j] -> error = fabs(vP[j] -> estimate - vP[j] -> Csi);
        fout<<setprecision(4)<<vP[j] -> error<<endl;
        vP[j] -> pererror = fabs((vP[j] -> Csi - vP[j] -> estimate)/vP[j] -> Csi) * 100;
}
double total(0);
for (int j = 0; j < t; j++)
        total += vP[j] -> pererror;
fout<<"The total percentage error is   "<<setprecision(4)<<total<<endl;
fout<<"================================="<<endl;
}

void cip :: get_Averages() //function to determine average input values
{
int step(0);
double V1, V2, V3, V4, V5;
int j(0);
while (j < t)
{
        V1 = 0;
        V2 = 0;
        V3 = 0;
        V4 = 0;
        V5 = 0;
        for (int z = 0 + step; z < a.size(); z += (t*5))
        {
                V1 += a[z];
                V2 += a[z+1];
                V3 += a[z+2];
                V4 += a[z+3];
                V5 += a[z+4];
        }
        V1 /= (a.size()/(t*5));
        V2 /= (a.size()/(t*5));
        V3  /= (a.size()/(t*5));
        V4 /= (a.size()/(t*5));
        V5 /= (a.size()/(t*5));
        //create a tank
        vP.push_back(new Tank);
        vP[j] -> No = j;
        vP[j] -> CsI = V1;
```

```
        vP[j] -> Csi = V2;
        vP[j] -> Mc = V3;
        vP[j] -> Fs = V4;
        vP[j] -> Cc = V5;
        step += 5;
        ++j;
        }
}

void cip:: model_knO () //function to obtain k and n values if not supplied
{
double EST, ERROR, CERROR, C;
int i(0);
//Outer loop, t tanks
while (i < t)
{
        k1 = 50;
        n1 = 0.05;
        vP[i] -> error = 1000000;
        //Middle loop for k determination
        while (k1 < 200)
        {
                n1 = 0.05;
                //Inner loop for n determination
                while (n1 < 1)
                {
                        if (i < (t-1)) C = vP[i+1] -> Cc;
                        else C = 90;
                        EST = vP[i] -> CsI/pow((1 + k1 * pow((vP[i] -> Mc/Fc), n1) *
                        (Fc/vP[i] -> Fs)), (i+1));
                        //Acceptance criteria
                        if ((vP[i] -> error  > fabs (vP[i] -> Csi - EST)) && (EST > 0))
                        {
                                vP[i] -> error = fabs(vP[i] -> Csi - EST);
                                vP[i] -> k = k1;
                                vP[i] -> n = n1;
                        }
                        n1 += 0.05;
                }
                k1 += 5;
        }
```

```
        ++i;
}
// Calculate average k and n
ERROR = 0;
k1 = 0;
n1 = 0;
for (int i = 0; i < t; i++)
{
        k1 += vP[i] -> k;
        n1 += vP[i] -> n;
}
k1  /= t;
n1 /= t;
fout<<F<<endl;
fout<<G<<endl;
fout<<B<<c<<D<<E<<endl;
for (int j = 0; j < t; j++)
{
        if (j < (t-1)) C = vP[j+1] -> Cc;
        else C = 90;
        vP[j] -> estimate = vP[j] ->  CsI/pow((1 + k1 * pow((vP[j] -> Mc/Fc), n1) *
        (Fc/vP[j] -> Fs)), (j+1));
        vP[j] -> error = fabs(vP[j] -> Csi - vP[j] -> estimate);
        vP[j] -> pererror = vP[j] -> error * 100/ vP[j] -> Csi;
        ERROR += vP[j] -> pererror;
        fout<<j+1<<"      ";
        fout<<setprecision(4)<<vP[j] -> Csi<<"       "<<setprecision(4)<<vP[j] ->
        estimate <<"     "<<setprecision(4)<<vP[j] -> error<<endl;
}
fout<<"k  =  "<<setprecision(4)<<k1<<endl;
fout<<"n  =  "<<setprecision(4)<<n1 <<endl;
fout<<"With sum of percentage errors  =  "<<setprecision(4)<<ERROR<<endl;
fout<<"======================================"<<endl;
fout<<"The individual constants calculated are as follows :"<<endl;
fout<<"tank    "<<"k   "<<"n   "<<endl;
for (int i = 0; i < t; i++)
        fout<<i+1<<"   "<<setprecision(4)<<vP[i] -> k<<"   "<<setprecision(4)<<vP[i] ->
        n<<endl;
fout<<"======================================"<<endl;
}
```

```
void cip :: model_update () //function to determine accuracy of updated kn model with k
and K supplied
{
double C, total(0);
fout<<"====================================="<<endl;
fout<<F<<endl;
fout<<G<<endl;
fout<<B<<c<<D<<E<<endl;
for (int i = 0; i < t; i++)
{
        fout<<i + 1<<"      "<<endl;
        fout<<setprecision(4)<<vP[i] -> Csi;
        if (i < t-1) C = vP[i+1] -> Cc;
        else C = 90;
        vP[i] -> estimate = (vP[i] -> Cc * (1+k2*(vP[i] -> Mc/Fc)) - C)/(K1 *k2*vP[i] ->
        Mc/Fc);
        fout<<setprecision(4)<<vP[i] -> estimate<<"      ";
        vP[i] -> error = fabs(vP[i] -> estimate - vP[i] -> Csi);
        fout<<setprecision(4)<<vP[i] -> error<<endl;
        vP[i] -> pererror = fabs((vP[i] -> Csi/vP[i] -> estimate)/vP[i] -> Csi)*100;
}
for (int j = 0; j < t; j++)
        total += vP[j] -> pererror;
fout<<"The total percentage error is   "<<setprecision(4)<<total<<endl;
fout<<"==================================="<<endl;
}

void cip :: model_updateO () //function to determine k and K for updated kn model
{
double EST, ERROR, CERROR, C;
int i(0);
//Outer loop , t tanks
while (i < t)
{
        K1 = 500;
        k2 = 0.05;
        vP[i] -> error = 1000000;
        //Middle loop for K determination
        while (K1 < 15000)
        {
```

```
            k2 = 0.05;
            //Inner loop for k determination
            while (k2 < 2)
            {
                if (i < (t-1)) C = vP[i+1] -> Cc;
                else C = 90;
                EST = (vP[i] -> Cc * (1 + k2 * (vP[i] -> Mc/Fc)) - C)/(K1 * k2 *
                (vP[i] -> Mc/Fc));
                //Acceptance criteria
                if ((vP[i] -> error > fabs(vP[i] -> Csi - EST)) && (EST > 0))
                {
                    vP[i] -> error = fabs(vP[i] -> Csi - EST);
                    vP[i] -> k= k2;
                    vP[i] -> K = K1;
                }
                k2 += 0.05;
            }
            K1 += 100;
        }
        ++i;
}
// Calculate average k and K
ERROR = 0;
K1 = 0;
k2 = 0;
for (int i = 0; i < t; i++)
{
        K1 += vP[i] -> K;
        k2 += vP[i] -> k;
}
K1  /= t;
k2 /= t;
fout<<F<<endl;
fout<<G<<endl;
fout<<B<<c<<D<<E<<endl;
for (int j = 0; j < t; j++)
{
        if (j < (t-1)) C = vP[j+1] -> Cc;
        else C = 90;
        vP[j] -> estimate = (vP[j] -> Cc * (1 + k2 * (vP[j] -> Mc/Fc)) - C)/(K1 * k2 *
        (vP[j] -> Mc/Fc));
```

```
        vP[j] -> error = fabs(vP[j] -> Csi - vP[j] -> estimate);
        vP[j] -> pererror = vP[j] -> error * 100/ vP[j] -> Csi;
        ERROR += vP[j] -> pererror;
        fout<<j+1<<"     ";
        fout<<setprecision(4)<<vP[j] -> Csi<<"       "<<setw(4)<<vP[j] -> estimate <<"
        "<<setw(4)<<vP[j] -> error<<endl;
}
fout<<"k  =  "<<setprecision(4)<<k2<<endl;
fout<<"K  =  "<<setprecision(4)<<K1 <<endl;
fout<<"With sum of percentage errors  =  "<<setprecision(4)<<ERROR<<endl;
fout<<"========================================"<<endl;
fout<<"The individual results are as follows :"<<endl;
fout<<"tank   "<<"k   "<<"K"<<endl;
for (int i = 0; i < t; i++)
        fout<<i + 1<<"    "<<setprecision(4)<<vP[i] -> k<<"    "<<setprecision(4)<<vP[i]
        -> K<<endl;
fout<<"==========================================="<<endl;
}

void cip :: model_new () //function to determine parameters of the SCModel model
{
double EST, ERROR, C;
int i(0);
//Outer loop for number of tanks
while (i < t)
{
        vP[i] -> error = 1000000;
        k1 = 1;
        k2 = 1;
        K1 = 1;
        //Loop for k1 determination
  //Criteria
        if ((vP[i] -> Csi/vP[i] -> Cc) > 0.00033)
        {
                //Set irrelevant parameters to zero
                vP[i] -> n = 0;
                vP[i] -> K = 0;
                while (k1 < 200)
                {
                        if (i < (t-1)) C = vP[i+1] -> Cc;
                        else C = 90;
```

```
            EST = (Fc * (vP[i] -> Cc - C))/(vP[i] -> Mc  * k1);
            //Criteria
            if ((vP[i] -> error > fabs(vP[i] -> Csi - EST)) && (EST > 0))
            {
                vP[i] -> k = k1;
                vP[i] -> error = fabs(vP[i] -> Csi -EST);
            }
            k1 += 0.5;
        }
    }
    else
    {
        //Set irrelevant parameter to zero
        vP[i] -> k = 0;
        //Loop for k2 determination
        while (k2 < 4)
        {
            K1 = 1;
            if (i < (t-1)) C = vP[i+1] -> Cc;
            else C = 90;
            //Inner loop for K1 determination
            while (K1 < 30)
            {
                EST = exp(((Fc * (vP[i] -> Cc - C)/vP[i] -> Mc) - K1)/k2);
                /Criteria
                if ((EST > 0) && (vP[i] -> error > fabs(vP[i] -> Csi -
                EST)))
                {
                    vP[i] -> K = K1;
                    vP[i] -> n = k2;
                    vP[i] -> error = fabs(vP[i] -> Csi - EST);
                }
                K1 += 0.1;
            }
            k2 += 0.05;
        }
    }
    ++ i;
}
ERROR = 0;
k1 = 0;
```

```
k2 = 0;
K1 = 0;
int count(0);
for (int j = 0; j < t; j++)
{
        k1 += vP[j] -> k;
        k2 += vP[j] -> n;
        K1 += vP[j] -> K;
        if (vP[j] -> n == 0) count++;
}
k1 /= count;
k2 /= (t - count);
K1 /= (t - count);
for (int j = 0; j < t; j++)
{
        if (j < (t-1)) C = vP[j+1] -> Cc;
        else C = 90;
        if (vP[j] -> n == 0)
        vP[j] -> estimate = (Fc * (vP[j] -> Cc - C))/(vP[j] -> Mc * k1);
        else vP[j] -> estimate = exp(((Fc * (vP[j] -> Cc - C)/vP[j] -> Mc) - K1)/k2);
        vP[j] -> error = fabs(vP[j] -> Csi - vP[j] -> estimate);
        vP[j] -> pererror = vP[j] -> error * 100/ vP[j] -> Csi;
        ERROR += vP[j] -> pererror;
}
fout<<"Result of SCModel"<<endl;
fout<<G<<endl;
fout<<B<<c<<D<<E<<endl;
for (int j = 0; j < t; j++)
        fout<<j + 1<<"   "<<setprecision(4)<<vP[j] -> Csi<<"
        "<<setprecision(4)<<vP[j] -> estimate<<"    "<<setprecision(4)<<vP[j] ->
        error<<endl;
fout <<"k1  =   "<<k1<<endl;
fout<<"k2 =  "<<k2<<endl;
fout<<"K =  "<<K1<<endl;
fout<<"With sum of percentage errors  =  "<<setprecision(4)<<ERROR<<endl;
fout<<"========================================"<<endl;
fout<<"The individual results are as follows :"<<endl;
fout<<"tank    "<<"k   "<<"k2   "<<"K    "<<endl;
for (int i = 0; i < t; i++)
        fout<<i + 1<<"   "<<setprecision(4)<<vP[i] -> k<<"  "<<setprecision(4)<<vP[i] -
        > n<<"    "<<setprecision(4)<<vP[i] -> K<<endl;
```

```
fout<<"========================================================="<<endl;
}
```