

**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY,
KUMASI**

COLLEGE OF SCIENCE
KNUST
INSTITUTE OF DISTANCE LEARNING

**AN OPTIMAL CONTROL MODEL OF THE ADSORPTION PROCESS OF A
METALLURGICAL PLANT: A CASE STUDY OF GOLD**

**A DISSERTATION SUBMITTED TO THE DEPARTMENT OF
MATHEMATICS IN PARTIAL FULFILMENT OF REQUIREMENTS FOR
THE AWARD OF MASTER OF SCIENCE (MSc) DEGREE IN INDUSTRIAL
MATHEMATICS**

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DECLARATION

I Gorh Emmanuel, hereby declare that, this is the result of my own hand work and that no previous submission for a degree has been done here or elsewhere. Also the work of others which served as reference has been duly acknowledged.

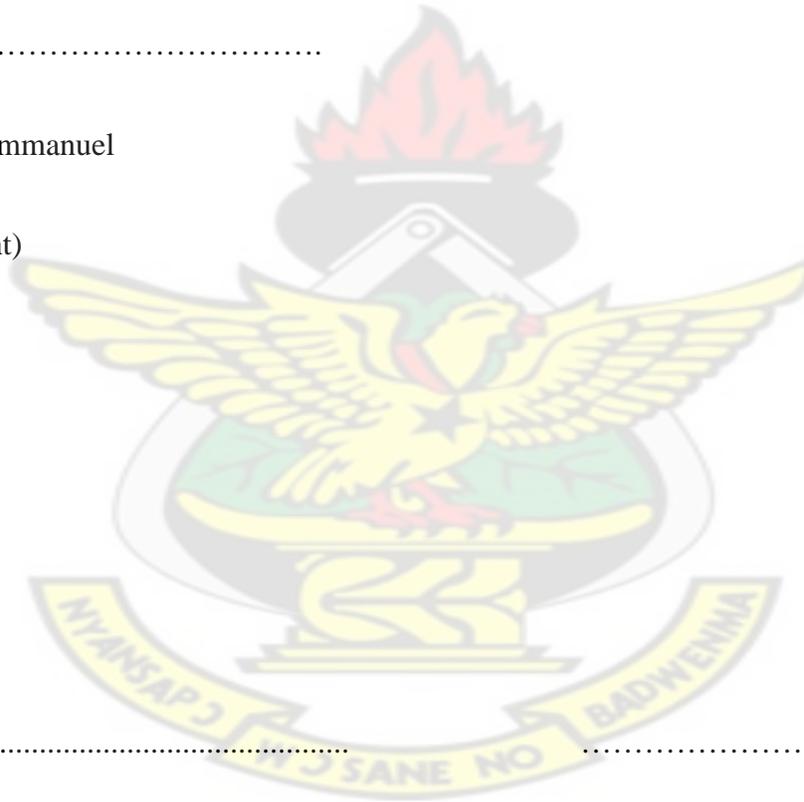
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DEDICATIONS

I dedicate this work to the Almighty God who has seen me through the duration of study. I also dedicate this work to my wife Vivian Gorh and my daughter Emerald Mwinomboh Gorh for their moral and spiritual supports.

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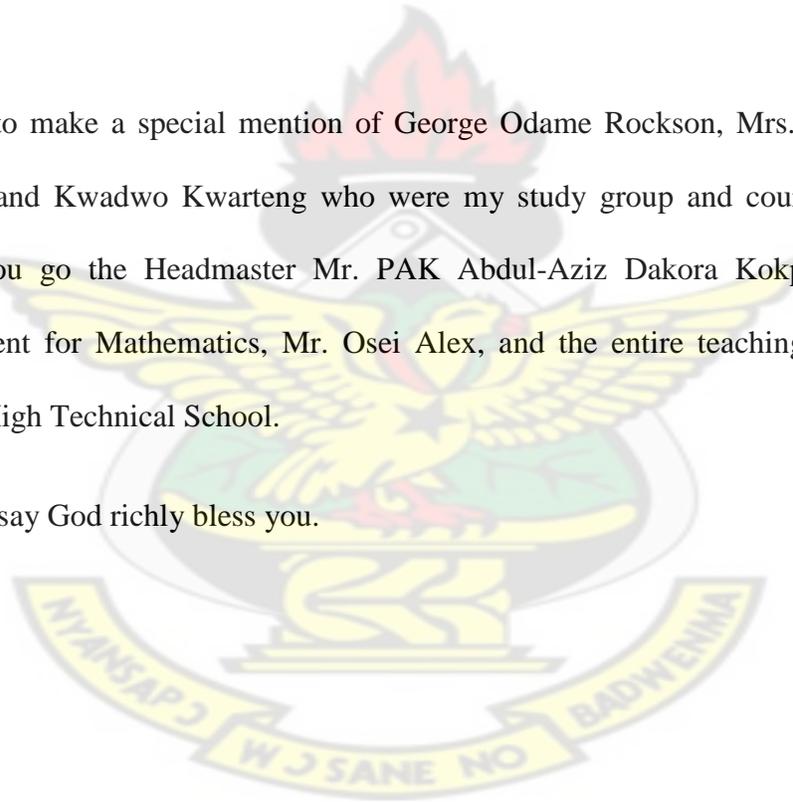
ACKNOWLEDGEMENT

The success story of this work cannot be told without mentioning the special part some people played. But first of all I want to show my endless gratitude to the Almighty God for His inspiration and guidance throughout the period of research.

I want to acknowledge to tremendous support of my academic supervisor, Dr F. T. Oduro for his guidance and correction which resulted in the success of this work.

I want to make a special mention of George Odame Rockson, Mrs. Beatrice Asante Appiah and Kwadwo Kwarteng who were my study group and course mates. A big thank you go the Headmaster Mr. PAK Abdul-Aziz Dakora Kokpi , the head of department for Mathematics, Mr. Osei Alex, and the entire teaching staff of Agona Senior High Technical School.

To all, I say God richly bless you.



LIST OF ABBREVIATIONS/ACRONYMS/SYMBOLS

Au	Gold
CCD	Counter Current Decantation
CIL	Carbon in leach
CIP	Carbon in pulp
CIC	Carbon in column
CN	Cyanide
CN ⁻	Cyanide ion
C_{Au}	Gold concentration in particles
C_{Au}^{∞}	Gold concentration in particles after infinite leaching
time	
C_{CN^-}	Cyanide concentration
C_{O_2}	Oxygen concentration
HCN	Hydrogen cyanide gas
Kg	Kilogramme
k	Overall rate constant
RIC	Resin-in-column

α	Reaction order for cyanide
β	Reaction order for oxygen
γ	Reaction order for gold
Φ	Endpoint cost
\mathcal{L}	Lagrangian



ABSTRACT

The model developed is an optimal control model of the adsorption process of a hydrometallurgical process called Carbon-In-Pulp. The model took into consideration the fact that the metallurgical process encounters several losses chief among them being gold solution losses. Several assumptions were made and among them was the assumption that the amount of gold in solution that goes to waste is equal to the amount of gold solution in the adsorption unit less the amount of gold adsorbed unto the activated carbon phase. With the rate of adsorption proportional to the capacity of activated carbon and the concentration of gold on the carbon phase, the model has a state variable $x(t)$ which is the concentration of gold in the solution phase at any given time and a control variable $u(t)$ which is the concentration of gold on the activated carbon phase at any given time. The optimal control model developed gives complete overview of the process of adsorption process of dissolved gold solution unto activated carbon. The model reveals that the process is fast and spontaneous initially and slows down with time until it reaches the carrying capacity of the activated carbon where the reverse process is observed. Activated carbons with high capacities (i.e. activated carbon that is believed to be fresh and therefore has not been fouled) have the ability to absorb gold faster. The model reveals that the rate at which gold is lost from the solution phase is the same but a reverse process to the rate at which it is adsorbed unto the activated carbon phase and this rate, as mentioned earlier, is dependent on the maximum capacity of the activated carbon. It has also been observed that the choice of concentration of activated carbon affects greatly the nature of adsorption. The rate at which gold is adsorbed unto activated carbon reduces with time but the process is

quicker and very spontaneous with increased amount of activated carbon in the adsorption circuit.

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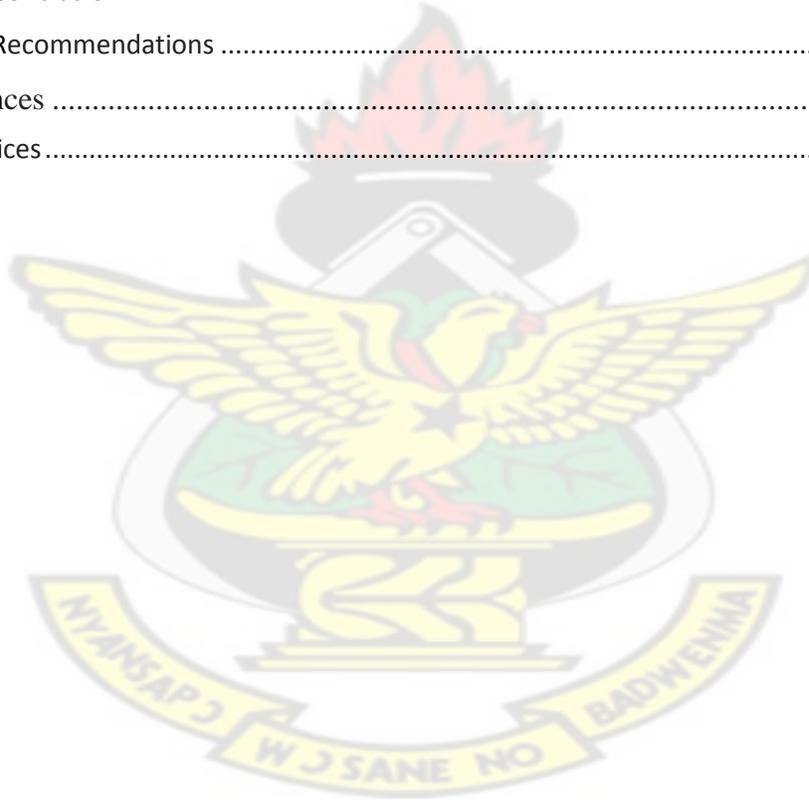


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CHAPTER 1

INTRODUCTION

1.0 Introduction

This chapter introduces some operational units of the metallurgical plant and highlights the fundamental problems encountered during such operations. It also entails the historical background and nature of gold. The chapter also looks at the set objectives, methods to be used and justification of the work.

1.1 Background of Study

The chemical element gold, symbol Au, is classified as a noble metal due to its inertness to chemical reactions in non-complex media. It does, however, react with numerous reagents. It belongs to the same group as copper and silver in the periodic table and it is commonly found to be associated with these elements in rocks. According to Marsden and House (1992), the average concentration of gold in earth's crust is 0.005 g/t, which is much lower than most other metals, for example, 0.07 g of silver/t and 50 g of copper/t. The gold content is dependent upon gold minerals as well as gold properties, for instance, electrum, specific gravity 16-19.3, is a mixture of silver and gold containing 45-75 % gold.

There are many possible methods to recover gold from ores such as leaching, gravity concentration and flotation. de Andrade Lima and Hodouin (2006), believe that leaching by cyanide solutions or gold cyanidation, however, has been the main metallurgical process for gold extraction for more than one century.

For several years mathematical models have been extensively studied in order to obtain predictions for the kinetics of leaching and adsorption reactions. A number of rate equations have been published based on different experimental conditions. Some of them are mechanistic rate equations and some are empirical ones. The first comprehensive study on the variation of the rate of gold dissolution with cyanide and oxygen concentration has been described since 1966. However, Roman et al (1974), explained that the limitation of the equation in the modelling of industrial gold cyanidation is due to the difficulty in measuring the exact surface area of gold in the ore and the Nernst boundary layer thickness. Additionally, according to Crundwell et al (1997) numerous researchers have claimed that two expressions can be derived from the electrochemical mechanism of gold leaching and the shrinking core model with surface passivation. Roman et al, (1974) agree that the gold leaching process often appears to be operated far from an optimum range. For example, excessive reagents (CN^- and O_2) consumption is expected and the behaviour of the process is very dependent on feed mineralogy.

Because of its noble nature, gold prefers to exist in its natural state as gold metal. Cyanide is one of the few chemicals that will react with gold. Gold must be 'concentrated up' using methods that rely on change of phase, thus from solid to solution in the process called leaching or dissolution. According to Bailey and Stanley (1987), it is much easier to 'concentrate up' gold from the solution phase than from the solid phase. They explained that activated carbon is an adsorbent that increases the concentration of gold in the solution phase.

The dissolution of gold from the ore results in gold in water as the gold cyanide ion is approximated as $\text{Au} + 2\text{CN}^- \rightarrow \text{Au}(\text{CN})_2^-$. The ion complex quickly reacts with another opposite charge ion especially calcium (Ca^{2+}), which is usually in abundant supply due to addition of CaCO_3 , to form a neutral specie. The structure of water does not accommodate disrupting species, hence forces the calcium gold cyanide complex out of its structure. As a result, the suspended neutrally charged activated carbon which has vast internal surface area becomes a readily available home for it. This is called adsorption.

1.2 Problem statement

The metallurgical process encounters losses which include cyanide and gold solution losses. Considering the current world market price of gold, the gold losses recorded by most mining companies have become very significant.

Metallurgists find it a difficult task in determining the aqueous gold or the amount of gold that has been absorbed by activated carbon. Sample solution is, from time to time, taken to metallurgical laboratories for testing. Sometimes in mines which don't have metallurgical laboratories on site take a long time to receive results since samples have to be taken outside the site and perhaps queue for testing. All these create inconveniences.

The effluent of some metallurgical plants also usually contains gold in quantities that are economically unacceptable. The excess aqueous gold in the tailings is a financial loss to the metallurgical company.

Hence mining companies seek a mathematical model that ensures easy monitoring and prediction of aqueous gold concentration in the adsorption process at any stage.

1.3 Objectives

The objectives of this work include the following:

- To develop an optimal control mathematical model that depicts how aqueous gold solution leaves the solution phase into the activated carbon phase in a process called adsorption.
- To perform sensitivity analysis and simulations on the model developed.
- Using the model developed, to deduce the amount of gold present in the adsorption circuit at any given time and interpret the outcome.

1.4 Methodology

The following are the methods that will be employed in conducting this work:

- Optimal control modelling using Pontryagin's Minimum principle of solving constrained optimisation was employed.
- Standard engineering and chemical data were obtained from literature available at the KNUST main library, the internet and the metallurgical industry.
- Graphical outputs were obtained by the use of Microsoft office excel 2007.
- All computations were done manually.

1.5 Justification

The result of this work will help find and recommend better operational set points to enhancing the production of the company. In minimising the amount of gold in solution that goes to tails increases the recovery of the plant. The increase in recovery means increase in production and subsequent increase in profit margin. For a particular input, the output gold in solution could be predicted over a given time.

1.6 Limitation

This work was limited to the adsorption section of a metallurgical plant; a unit process which is called the carbon in pulp process.

1.7 Organization of thesis

Chapter 1 covers the background of two of the major unit operations in metallurgical process thus gold cyanidation and adsorption. It also looks at the problem statement for this work, the objectives, methods, justification and finally the limitations of the work.

Chapter 2 contains the review of work done by some people on gold cyanidation, adsorption and its kinetics. It also reviews mathematical models that were very helpful in conducting this work.

Chapter 3 covers the methodology, which looks at optimal control problem and optimal control solution.

Chapter 4 covers problem formulation results, analysis and discussion.

The last chapter covers conclusion and recommendations.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter reviews previous works done on mathematical modelling of metallurgical processes that are useful to this work. It also reviews chemical and kinetic rates of reactions for adsorption in metallurgical processes.

2.1 Heap leaching

Arbiter et al, (1990), believe that despite over 100 years of research and development with activated carbon, there is still not a complete understanding of the gold adsorption and desorption mechanism. Majority of the modelling work carried out for gold processing are empirical in nature. According to Leahy et al, (2005), limited studies on modelling of extraction and recovery processes have been carried out on other mineral ores.

The algorithm proposed here is based on the hypotheses that the heap may be conveniently represented by a simplified geometric shape, that the liquid flow throughout the heap bed is without axial dispersion (Plug flow), that the average residence time of the solution in the heap interior does not vary with time or with the vertical location, that the heap presents a homogeneous grade of leachable metals and size distribution, and, finally, that the ore/leaching agent reaction is controlled by

diffusion of the leaching solution through the large and "weakly porous" particles of the ore.

According to Wen, (1968), if a division of nl layers of equal thickness is set in a heap of rectangular shape, the pregnant solution and the leach solution that flow through the several layers of the heap are retained in each layer a time equal to $\Delta\tau = \tau/nl$.

Froment and Bischoff (1979), believe that if the ore is a spherical particle with little porosity composed of an inert and a reactant solid surrounded by a liquid reactant, a first-order kinetics of dissolution for each reactant ($r_A = \alpha r_B = \alpha k_S C_{AS} C_{B0}$), where α is the stoichiometric coefficient and k_S the kinetic constant, and assuming that the process of diffusion is slow compared with the reaction, it is possible to use a pseudo-steady state simplification, which, associated with the hypothesis of negligible density variation of the ore particle, gives:

Another mathematical model for heap leaching of gold ores by cyanidation was developed by Sanchez-Chacon and Lapidus (1997) which describes gold heap leaching as a function of the mass transport steps involved, employing a rigorous kinetic expression to describe gold cyanidation. The model incorporates the results of investigation on trickle bed reactors, which consider the wetting efficiency of the mineral particles in the bed as a function of the Reynolds number of the leaching solution as it flows through the bed. From this parameter an apparent effective diffusivity of the species in the partially wetted particles is calculated. The numerical solution of the model equations allows the description of the reactant and product concentration profiles in the heap. From these profiles, mass balances are performed

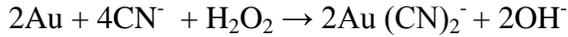
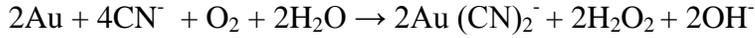
which show how the gold reacts and is transported until it finally leaves the heap. The effect of different process and mineral variables, such as the mineral porosity, particle radius, leaching solution flow rate, gold grain size, the concentration of reagents and the heap height, on the gold extraction rate were also evaluated. According to Wong and Arun, (2009), the results obtained show that the controlling phenomenon in the gold extraction rate is the diffusion of the gold cyanide complex out of the mineral particles. Parameters such as the particle radius and porosity and the solution flow rate are important in determining the extraction rate. The study of the gold distribution in each step of the process as a function of time, calculated from the mass balances, would allow the implementation of dynamic operating policies in aspects such as variable feed concentration of reagents to reduce heap rinsing before closure.

2.2 Phenomena in gold leaching

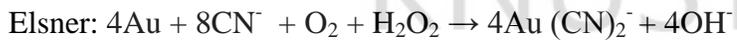
According to Marsden and House, (1992), the most important reactions in hydrometallurgical gold extraction processes are heterogeneous, involving the transfer of metals and minerals between solid and liquid phases. Heterogeneous reactions are controlled either by the inherent chemical reaction kinetics or by the rate of mass transfer of the individual reacting species across a phase boundary.

The oxidation of gold is a prerequisite for its dissolution in alkaline cyanide solution. Although gold is inert to oxidation, it is widely accepted that, in the presence of a suitable complex agent such as cyanide, gold is oxidized and dissolved to form the stable complex ion $[\text{Au}(\text{CN})_2^-]$. Oxygen is reduced and hydrogen peroxide is formed as an intermediate product in the first step and becomes the oxidizing agent in the second

step, leading to the following chemical reactions which proceed in parallel Marsden and House, (1992) and Senanayake, (2005):

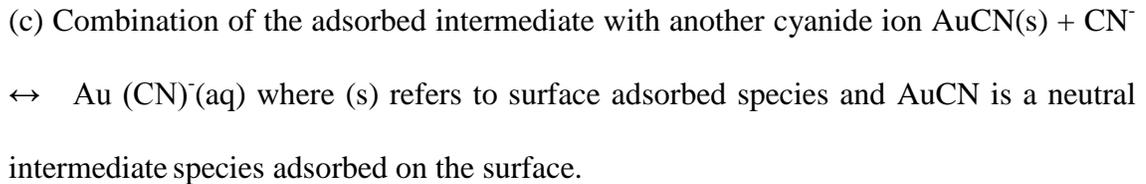
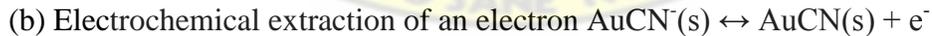


The summation of the two partial reactions is presented as proposed by

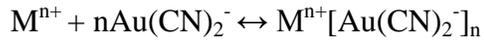


This equation, called Elsner's equation, is stoichiometrically correct. However, according to Marsden and House, (1992), it does not completely describe the cathodic reactions associated with the dissolution the dissolution mechanism has been debated under both acidic and alkaline conditions. Dissolution involves an electrochemical process in which the anodic reaction is gold oxidation while the cathodic reaction is oxygen reduction.

Wadsworth *et al*, (2000) explained that the important steps during the anodic reaction in the solution phase are presented below;



According to McDougall (1985), the mechanism of gold recovery from cyanide liquors is presented as below. The dissolved gold cyanide is adsorbed as the cation gold cyanide ion pair.



Where the ion pair, $M^{n+}[Au(CN)_2^-]_n$, is the adsorbed gold species. M can be H, Na, K and Ca. The rate steps are the mass transfer of gold cyanide and cations across the solution film surrounding the carbon particles to the outer surface of the carbon particles, transfer in the solution filling the pores, the adsorption reaction and possibly transfer of the adsorbed cation gold cyanide ion pair along the pore walls by surface diffusion Vegter, (1992). It has been claimed that film transfer controls the adsorption rate of aurocyanide onto the activated carbon in the initial stages of gold recovery Coetzee and Gray, (1999).

2.2.1 Reaction Kinetics

Liebengberg and Deventer (1997b), said many researchers have attempted to model the kinetics of gold dissolution. Roman et al, (1974), explained that the rotating gold discs have been used in fundamental studies to determine the rates at a constant surface area, assuming that the surface roughness does not change during the course of reaction. It was concluded that the rate of pure gold dissolution relies on the rate of film diffusion of cyanide ions or dissolved oxygen towards the gold surface.

From this analogy it can be seen easily that when $D_{CN^-}C_{CN^-} < 4D_{O_2}C_{O_2}$ or low cyanide concentration, gold dissolution rate depends primarily on that cyanide concentration.

Similarly, for high cyanide concentration, the gold dissolution rate becomes mainly dependent on the oxygen concentration.

According to Prosser and Box (1983), in practice a high level of cyanide has been maintained rather than a high dissolved oxygen level in the solution. Consequently the majority of the mills operate at cyanide levels such that gold dissolution is dependent on the dissolved oxygen level.

An expression of second order rate equation was proposed by Nicol *et al*, (1984). This equation, according to Crundwell and Gordon, (1997), the so called Mintek equation, was presented as an empirical equation based on the leaching behaviour of several South African gold ores and has the following form ($-\frac{dC_{Au}}{dt} = k(C_{Au} - C_{Au}^{\infty})^2 \text{ mgkg}^{-1}\text{s}^{-1}$)

where k is the overall rate constant, kg/mg s

C_{Au} is the gold concentration in particles, mg/kg

C_{Au}^{∞} is the gold concentration in particles after infinite leaching time, mg/kg. de Andrade Lima and Hodouin,(2005), explained that this equation neither accounts for the reagent concentration, C_{CN^-} and C_{O_2} nor for the particle size. Consequently, many researchers have further endeavored to present the kinetics involved a term of the reactants.

Roman *et al*, (1974), proposed a single rate equation on the assumption of pseudo-homogeneous ore behaviour. This rate equation can be expressed in terms of mass per mass of ore instead of mass per surface area of gold units, as follows:

$$-\frac{dC_{Au}}{dt} = k C_{CN}^{-\alpha} C_{O_2}^{\beta} (C_{Au} - C_{Au}^{\infty})^{\gamma} \text{ mgkg}^{-1}\text{h}^{-1}$$

Where C_{Au} is the gold concentration in particles, mg/kg

C_{Au}^{∞} is the gold concentration in particles after infinite leaching time, mg/kg

C_{CN} is the cyanide concentration, mg/dm³

C_{O_2} is the oxygen concentration, mg/dm³

k is the overall rate constant, unit depends on reaction orders reaction order for cyanide

α is the reaction order for cyanide

β is the reaction order for oxygen

γ is the reaction order for gold

Rees and van Deventer, (2001) believe that the kinetics of three-phase reactions can be very complex; however, in many ore leaching systems the pseudo-homogeneous approach has been sufficient to describe well the main features of the process. de Andrade Lima, (2007) added that for gold leaching, the kinetics may be empirically described as a second-order process with respect to the gold content of the ore and a first-order process with respect to the free cyanide concentration given as;

$$R_{AU} = k C_{cn} (C_s - C_{s\infty})^{\alpha}$$

Where k is the rate constant, C_{cn} is the concentration of cyanide in the liquid phase, C_s is the concentration of gold in the ore, α is the reaction order, and $C_{s\infty}$ is the residual gold content of the ore.

As explained by de Andrade Lima, (2007) The detailed mathematical description of the simultaneous gold leaching and adsorption on activated carbon that occurs in the carbon-in-leach process is somewhat intrinsically complex such as the heterogeneous nature of the system that includes ore, activated carbon, aqueous solution, and gas; also there are several physical and chemical phenomena that happen simultaneously.

Fang et al, (1998) explained that to describe a leaching process, the most important model equations are those which describe a developing period of the process at the beginning. The initial hypothesis of the proposed models for the leaching process is derived on the base of process kinetics and a resulting model is then modified according to the procedure of regression model building. A general phenomenological expression on the basis of a kinetic study and empirical model is $y = a + f(x_1, x_2)\exp(bx_3)$ where y stands for a dependent process variable, x_1 , x_2 and x_3 are three independent process variables which are, the partial pressure of oxygen, the initial concentration of sodium cyanide and the leaching time are considered to be the main controllable factors of process kinetics and may be taken as the independent variables, b the unknown parameters to be estimated, a , the constant and $f(x_1, x_2)$ the function of two process variables usually expressed as a product of polynomial of variables.

According to Fang and Muhammed, (2010), for the cyanidation process of the Au–Cu concentrate, the variables describing the process are the extracted fraction of gold and silver, the content of copper and iron dissolved in pregnant liquors, and the consumption of cyanide. According to Bethen, (1985), the results of the experimental kinetic study were used for deriving the initial hypothesis of proposed models concerning the leaching process with the following features and relations:

(a) The initial rate of gold dissolution is proportional to the initial concentration of cyanide and the partial pressure of oxygen for low values, but turns out to be independent at higher values.

(b) Dissolution of silver consists of two reactions. The rate of first one is rather sensitive to the partial pressure of oxygen, and little linked to the concentration of cyanide while the rate of the second reaction is very slow and almost independent of the leaching time.

(c) The kinetics of dissolution of copper is similar to that of gold. The rate is a linear function of the initial concentration of cyanide on the leaching time.

(d) For the dissolution of iron, strong aeration accelerates the precipitation reaction of the hydroxide and causes the decrease of the concentration of ferrous ions. The reaction rate is proportional to the initial concentration of cyanide and seems to be independent on the partial pressure of oxygen after leaching for 2 hour as has been proved by Sharaf et al, (1986).

(e) The consumption of cyanide is correlated with the partial pressure of oxygen and also with the concentration of cyanide.

(f) The leaching is done under conditions where no influence of stirring speed, particle size of the concentrate on the yield is observed and therefore their influence was omitted here.

2.3 Free Cyanide Consumption

According to Adams, (1990), the kinetics of cyanide consumption can be empirically described by taking into account two superimposed effects. The first one explains the constant rate of cyanide consumption by copper and iron minerals and the second explains the effect of cyanide consumption proportional to the free cyanide content, such as the losses by hydrolysis to hydrogen cyanide and ammonia and the oxidation to cyanate or cyanogen; the rate of consumption is thus $R_{CN} = e + f C_{cn}$ where C_{cn} is the cyanide concentration in the liquid phase, e is the zero-order rate constant, and f is the first-order rate constant.

2.4 The adsorption of gold onto activated carbon

Fleming and Nicol, (1984), show how kinetic models are used to model and optimize CIP absorption with respect to parameters such as the carbon concentration in each stage and the number of stages required to produce a certain value in the barren solution.

These models are of great value in the optimization of the performance on any particular CIP plant. However, if differences in the rate of extraction from one CIP plant to another are to be rationalized, the various parameters that influence the rate of extraction must be examined in detail and their relative importance in the rate expression assessed. This aspect is considered in this paper, as is the effect on the rate of extraction of variables such as the concentrations of gold, free cyanide, and organic solvents in solution; the pH value, ionic strength, and temperature of the solution; the

particle size of the carbon; and the mixing efficiency. In addition, the effect of these variables on the equilibrium loading of gold cyanide on carbon is examined.

According to Fleming and Nicol, (1984), the results of an experiment carried out in a 500 ml glass cell filled with clarified gold cyanide solution were treated with a rate equation in which it is assumed that the rate is proportional to the concentration of gold in solution but independent of the concentration of gold on the carbon, as found for the initial stages of loading when the reaction is far from equilibrium.

In the experimental procedure used here, the rate is given by:

$$\frac{d[Au]_c}{dt} = \frac{VC}{McT}$$

Where V is the volume (litres) of concentrated gold solution added from the external source in time T(h), C is the concentration of gold in the external source ($\text{mg} \cdot \text{l}^{-1}$), and Mc is the mass of carbon (kg) in the reactor cell. The values of k obtained by this procedure were determined from the loading results over the first 30 minutes of extraction. During that period, the rate as defined in the model was always approximately constant. For the batch-extraction tests, the rate results were analyzed by use of the integrated form combined with a mass balance of gold in the reaction, i.e.

$$\ln \frac{[Au]_{s0}}{[Au]_s} = \frac{kMcT}{Ms}$$

Where $[Au]_{s0}$ and $[Au]_s$ are the concentrations of gold in solution at time zero and 't' respectively, Mc is the mass of carbon, and Ms the mass (or volume) of solution.

Dixon et al., (1978) explained that the detailed kinetic models for gold adsorption that include diffusion in the activated carbon particles or in the external film require the use of several parameters whose estimation using laboratory and plant experiments can be laborious. In this study, the simple linear adsorption-desorption rate equation is used.

Deventer, (1986) believes that in aqueous solutions, the adsorption of single chemical specie on a substrate in a closed reactor and at constant temperature can be described by equilibrium isotherms, which are empirical equations that relate the concentration of the chemical species in the liquid phase (C_l) to their concentration on the surface of the substrate (C_c). The following classical adsorption isotherms have been used to describe gold adsorption on activated carbon: the linear ($C_c = A C_l$), the Freundlich ($C_c = A C_l^n$), and the Langmuir ($C_c = A C_l / (B + C_l)$). In the case of multiple component adsorption, these equations have been modified to account for competition between the solutes.

The adsorption kinetic used by Carrier et al., (1987) in their study is described by the lumped equation given by the linear adsorption-desorption equation, which assumes that adsorption is a reversible process:

$$R_{CB} = k_c C_l (C_c^* - C_c) - k_d C_c$$

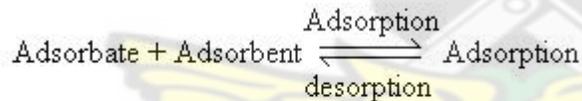
Where C_l is the gold concentration in the liquid phase, C_c is gold content in the activated carbon, C_c^* is the maximum gold content of the activated carbon, and k_c and k_d are empirical kinetic constants of adsorption and desorption for gold. Note that under equilibrium conditions ($R_{CB} = 0$) this model becomes the classical Langmuir equation, where $A = C_c^*$ and $B = k_d/k_c$

2.5 Adsorption Isotherms

The process of Adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature. Different adsorption isotherms have been Freundlich, Langmuir and BET theory.

2.5.1 Basic Adsorption Isotherm

In the process of adsorption, adsorbate gets adsorbed on adsorbent.



Seabela (2008) explained that according to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favored.

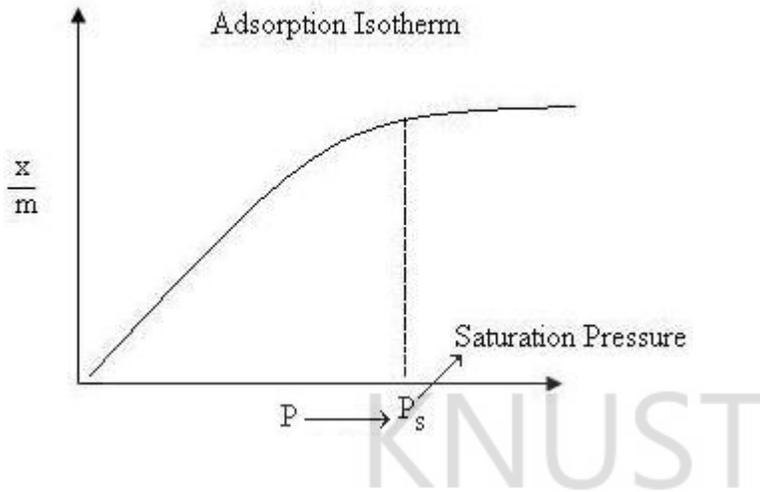


Fig. 2.1: Basic Adsorption Isotherm

From the graph, we can predict that after saturation pressure P_s , adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of vacancies on the surface of the adsorbent. Effirim-Williams (2006) believes that at high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, Adsorption is independent of pressure.

2.5.2 Freundlich Adsorption Isotherm

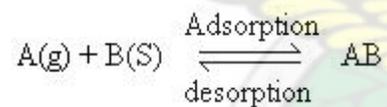
In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm.

$$\frac{x}{m} = k_c P^{\frac{1}{n}}$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k , n are constants whose values depend upon adsorbent and gas at particular temperature. Simons (2006) explained that though the Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure.

2.5.3 Langmuir Adsorption Isotherm

In 1916 Langmuir proposed another Adsorption Isotherm known as Langmuir Adsorption isotherm. Simons (2006) agrees that this isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.



Where $A(g)$ is unadsorbed gaseous molecule, $B(s)$ is unoccupied metal surface and AB is Adsorbed gaseous molecule.

Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

$$\theta = \frac{KP}{1 + KP}$$

Where θ the number of sites of the surface which are covered with gaseous molecule, P represents pressure and K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase. According to Asiam (2007) the basic limitation of Langmuir adsorption equation is that it is valid at low pressure only.

At lower pressure, KP is so small, that factor $(1+KP)$ in denominator can almost be ignored. So Langmuir equation reduces to

$$\theta = KP$$

At high pressure KP is so large, that factor $(1+KP)$ in denominator is nearly equal to KP . So Langmuir equation reduces to

$$\theta = \frac{KP}{KP} = 1$$

2.5.4 BET adsorption Isotherm

BET Theory put forward by Brunauer, Emmett and Teller explained that multilayer formation is the true picture of physical Adsorption.

One of the basic assumptions of Langmuir Adsorption Isotherm was that adsorption is monolayer in nature. According to Amankwah and Yen (2005), Langmuir adsorption equation is applicable under the conditions of low pressure. Under these conditions, gaseous molecules would possess high thermal energy and high escape velocity. As a

result of this less number of gaseous molecules would be available near the surface of adsorbent.

Under the condition of high pressure and low temperature, thermal energy of gaseous molecules decreases and more and more gaseous molecules would be available per unit surface area. Due to this multilayer adsorption would occur. The multilayer formation was explained by BET Theory.

2.6 Reactor model

Carrier et al, (1987) noted that a dynamic model for a Carbon In Leach (CIL) process, assuming monosize particles, consists of conservation of the masses of the ore, liquid phase, carbon, gold in the ore, gold in the liquid phase, gold in the carbon, and cyanide in the liquid phase. In such a case the variables that can be used to describe the process, include the flow rates, the concentrations, the holdups, the kinetic rates, the volume, and pump capacity.

2.7 Merrill-Crowe process

Chi et al, (1997), believe that the Merrill-Crowe Process is a separation technique for removing gold from a cyanide solution. The solution is separated from the ore by methods such as filtration and Counter Current Decantation (CCD) and is then clarified in special filters, usually coated with diatomaceous earth to produce a clarified solution. Oxygen is then removed by passing through a vacuum deaeration column. Zinc dust is

then added to the clarified, deaerated solution which precipitates the gold because zinc has a higher affinity for the cyanide ion than gold.

The gold precipitate is then filtered out of the solution, mixed with fluxes and smelted to form crude and impure bars which are sent to a refinery to remove the copper and silver, the process used depending on the impurities in the gold.

The major advantage of carbon-in-pulp recovery over Merrill Crowe recovery is the elimination of the leached ore solids and liquid separation unit operation. The separation step typically involves a series of expensive gravity separation thickeners or continuous filters arranged for counter-current washing or filtration of the solids. For ores exhibiting slow settling or filtration rates, such as ores with high clay content, the counter-current decantation (CCD) step can become cost prohibitive. Ores with high silver content will generally suggest that Merrill-Crowe recovery be used. This is because of the very large carbon stripping and electrowinning systems required for processing large quantities of silver. The typical rule of thumb states that economic silver to gold ratios of greater than 4 to 1, will favour installation of a Merrill-Crowe system, but this decision can be altered if the ore exhibits very slow settling rates.

2.8 Electrowinning

According to Dankwah (2006), electrowinning, also called electroextraction, is the electrodeposition of metals from their ores that have been put in solution or liquefied. Electrorefining uses a similar process to remove impurities from a metal. Both processes use electroplating on a large scale and are important techniques for the

economical and straightforward purification of non-ferrous metals. The resulting metals are said to be *electrowon*.

In electrowinning, a current is passed from an inert anode through a liquid *leach* solution containing the metal so that the metal is extracted as it is deposited in an electroplating process onto the cathode. In electro-refining, the anodes consist of unrefined impure metal, and as the current passes through the acidic electrolyte the anodes are corroded into the solution so that the electroplating process deposits refined pure metal onto the cathodes.

2.9 Ion-Exchange/Solvent-Extraction

This is one of the emerging technologies which involve the recovery of precious metals from pregnant solutions by ion-exchange resins using the resin-in-column (RIC) technique. Arbiter et al, (1990), believe that the process is similar to Carbon In Column (CIC). One major exception involves the operation of the elution (stripping) stage which does not require elevated temperatures and pressures for removal of precious metals from loaded resins. Either strong or weak base resins may be used. Stripping of the loaded gold values from the resin has proven to be difficult and requires further research.

CHAPTER 3

METHODOLOGY

3.0 Introduction

This chapter covers optimal control problems and some of the methods that could be used to find solutions to optimal control problems.

3.1 Optimal control Problem

Optimal control deals with the problem of finding a control law for a given system such that a certain optimality criterion is achieved. A control problem includes a cost functional that is a function of state and control variables. An optimal control is a set of differential equations describing the paths of the control variables that minimize the cost functional. The optimal control can be derived using Pontryagin's Principle (Ross, 2009), or by solving the Hamilton-Jacobi-Bellman equation.

We begin with a simple example. Consider a car traveling on a straight line through a hilly road. The question is, how should the driver press the accelerator pedal in order to minimize the total traveling time? The "system" consists of both the car and the road, and the optimality criterion is the minimization of the total traveling time. Control problems usually include ancillary constraints. For example the amount of available fuel might be limited; the accelerator pedal cannot be pushed through the floor of the car, speed limits, etc.

A proper cost functional is a mathematical expression giving the traveling time as a function of the speed, geometrical considerations, and initial conditions of the system. It is often the case that the constraints are interchangeable with the cost functional.

Another optimal control problem is to find the way to drive the car so as to minimize its fuel consumption, given that it must complete a given course in a time not exceeding some amount. Yet another control problem is to minimize the total monetary cost of completing the trip, given assumed monetary prices for time and fuel.

A more abstract framework goes as follows. Minimize the continuous-time cost functional

$$J = \Phi [\mathbf{x}(t_0), t_0, \mathbf{x}(t_f), t_f] + \int_{t_0}^{t_f} \mathcal{L} [\mathbf{x}(t), \mathbf{u}(t), t] dt$$

Subject to the first-order dynamic constraints

$$\dot{\mathbf{x}}(t) = \mathbf{a} [\mathbf{x}(t), \mathbf{u}(t), t],$$

The algebraic path constraints

$$\mathbf{b} [\mathbf{x}(t), \mathbf{u}(t), t] \leq \mathbf{0},$$

And the boundary conditions

$$\phi [\mathbf{x}(t_0), t_0, \mathbf{x}(t_f), t_f] = 0$$

Where $\mathbf{x}(t)$ is the state, $\mathbf{u}(t)$ is the control, t is the independent variable (generally speaking, time), t_0 is the initial time, and t_f is the terminal time. The terms Φ and \mathcal{L} are called the endpoint cost and Lagrangian, respectively. Furthermore, it is noted that the path constraints are in general inequality constraints and thus may not be equal to zero at the optimal solution. It is also noted that the optimal control problem as stated above may have multiple solutions (i.e., the solution may not be unique). Thus, it is most often the case that any solution $[\mathbf{x}^*(t^*), \mathbf{u}^*(t^*), t^*]$ to the optimal control problem is locally minimizing.

3.1.1 Linear quadratic control

A special case of the general nonlinear optimal control problem given above is the linear quadratic (LQ) optimal control problem. The LQ problem is stated as follows. Minimize the quadratic continuous-time cost functional.

$$J = \frac{1}{2} \mathbf{x}^T(t_f) \mathbf{S}_f \mathbf{x}(t_f) + \frac{1}{2} \int_{t_0}^{t_f} [\mathbf{x}^T(t) \mathbf{Q}(t) \mathbf{x}(t) + \mathbf{u}^T(t) \mathbf{R}(t) \mathbf{u}(t)] dt$$

Subject to the linear first-order dynamic constraints

$$\dot{\mathbf{x}}(t) = \mathbf{A}(t) \mathbf{x}(t) + \mathbf{B}(t) \mathbf{u}(t),$$

And the initial condition

$$\mathbf{x}(t_0) = \mathbf{x}_0$$

A particular form of the LQ problem that arises in many control system problems is that of the linear quadratic regulator (LQR) where all of the matrices (i.e., \mathbf{A} , \mathbf{B} , \mathbf{Q} , and \mathbf{R}) are constant, the initial time is arbitrarily set to zero, and the terminal time is taken in the limit $t_f \rightarrow \infty$ (this last assumption is what is known as infinite horizon). The LQR problem is stated as follows. Minimize the infinite horizon quadratic continuous-time cost functional

$$J = \frac{1}{2} \int_0^{\infty} [\mathbf{x}^T(t)\mathbf{Q}\mathbf{x}(t) + \mathbf{u}^T(t)\mathbf{R}\mathbf{u}(t)] dt$$

Subject to the linear time-invariant first-order dynamic constraints

$$\dot{\mathbf{x}}(t) = \mathbf{A}\mathbf{x}(t) + \mathbf{B}\mathbf{u}(t),$$

And the initial condition

$$\mathbf{x}(t_0) = \mathbf{x}_0$$

In the finite-horizon case the matrices are restricted in that \mathbf{Q} and \mathbf{R} are positive semi-definite and positive definite, respectively. In the infinite-horizon case, however, the matrices \mathbf{Q} and \mathbf{R} are not only positive semi-definite and positive-definite, respectively, but are also constant. These additional restrictions on \mathbf{Q} and \mathbf{R} in the infinite-horizon case are enforced to ensure that the cost functional remains positive. Furthermore, in order to ensure that the cost function is bounded, the additional restriction is imposed that the pair (\mathbf{A}, \mathbf{B}) is controllable. Note that the LQ or LQR cost functional can be thought of physically as attempting to minimize the control energy.

The infinite horizon problem (i.e., LQR) may seem overly restrictive and essentially useless because it assumes that the operator is driving the system to zero-state and hence driving the output of the system to zero. This is indeed correct. However the problem of driving the output to a desired nonzero level can be solved *after* the zero output one is. In fact, it can be proved that this secondary LQR problem can be solved in a very straightforward manner.

3.2 Optimal Control Problem Solutions

3.2.1 Numerical methods for optimal control

There are several approaches that can solve optimal control problems. According to Bryson and Ho (1969), these can be divided into analytical methods that have been used originally and numerical methods preferred nowadays. Optimal control problems are generally nonlinear and therefore, generally do not have analytic solutions (e.g., like the linear-quadratic optimal control problem). As a result, it is necessary to employ numerical methods to solve optimal control problems. In the early years of optimal control the favoured approach for solving optimal control problems was that of indirect methods. In an indirect method, the calculus of variations is employed to obtain the first-order optimality conditions. These conditions result in a two-point (or, in the case of a complex problem, a multi-point) boundary-value problem. This boundary-value problem actually has a special structure because it arises from taking the derivative of a Hamiltonian. Thus, the resulting dynamical system is a Hamiltonian system.

In the numerical method, we shall however concentrate on the Pontryagin's Maximum or Minimum Principle of solving optimal control problems. Consider the following equations;

$$I_{xi(u(t))} = G((x(t_f), t_f) + \int_{t_0}^{t_f} F(x(t), u(t), t) dt \quad (1)$$

$$\dot{x}(t) = f(x(t), u(t), t), x(t_0) = x_0 \quad (2)$$

It is supposed, that this optimal control problem (2) has a solution. Consider the following function, also called Bellman's function, defined as:

$$V(x(t), t) = \min_{u(t)} [G(x(t_f), t_f) + \int_{t_0}^{t_f} F(x(t), u(t), t) dt] \quad (3)$$

Differentiating (3) leads to Bellman's partial differential equation (4)

$$-\frac{\partial V}{\partial t} = \min_{u(t)} [F(x, u, t) + \left(\frac{\partial V}{\partial x}\right)^T f(x, u, t)] \quad (4)$$

This must satisfy boundary condition;

$$V(x_f, t_f) = G(x_f, t_f) \quad (5)$$

By treating optimal control problems it is convenient to define Hamiltonian function as follows:

$$H(x, u, \frac{\partial V}{\partial x}, t) = F(x, u, t) + \left(\frac{\partial V}{\partial x}\right)^T f(x, u, t) \quad (6)$$

and mark $\frac{\partial V}{\partial x}$ in (6) as adjoint variable $p(t)$. The appropriate Hamiltonian function takes the following form:

$$H(x, u, p, t) = F(x, u, t) + p^T [f(x, u, t)] \quad (8)$$

Bellman's partial differential equation takes after the following form:

$$-\frac{\partial V}{\partial t} = \min_{u(t)} H(x, u, p, t) \quad (9)$$

Differentiating left and right side of $\frac{\partial V}{\partial x} = p(t)$ with respect to x separately gives

$$-\frac{\partial^2 V}{\partial x \partial t} = \frac{\partial H}{\partial x} + \frac{\partial^2 V \partial H}{\partial x^2 \partial p} \quad (10)$$

$$\dot{p} = \frac{\partial^2 V}{\partial x^2} \dot{x} + \frac{\partial^2 V}{\partial x \partial t} \quad (11)$$

From this follow canonical differential equations of the principle of minimum (12)

$$\dot{x} = \frac{\partial H}{\partial p} \quad (12a)$$

$$\dot{p} = -\frac{\partial H}{\partial x} \quad (12b)$$

Necessary conditions for the optimization problem (12) using Pontryagin's minimum principle can be formulated as follows:

- Optimality condition for the control variable:

$$\frac{\partial H}{\partial u} \Big|_T = 0 \quad (13a)$$

- Definition of adjoint variables:

$$\dot{p}^T = - \frac{\partial H}{\partial x} \Big|_T \quad (13b)$$

- Terminal conditions for adjoint variables:

$$p^T \Big|_{(tf)} = \frac{\partial G}{\partial x} \Big|_{(tf)} \quad (13c)$$

That is the augmented Hamiltonian and in an indirect method, the boundary-value problem is solved (using the appropriate boundary or transversality conditions). The beauty of using an indirect method is that the state and adjoint (i.e., λ) are solved for and the resulting solution is readily verified to be an extremal trajectory. The disadvantage of indirect methods is that the boundary-value problem is often extremely difficult to solve (particularly for problems that span large time intervals or problems with interior point constraints).

3.2.2 The direct method

The approach that has risen to prominence in numerical optimal control over the past two decades (i.e., from the 1980s to the present) is that of so called direct methods. In a direct method, the state and/or control are approximated using an appropriate function approximation (e.g., polynomial approximation or piecewise constant parameterization). Simultaneously, the cost functional is approximated as a cost

function. Then, the coefficients of the function approximations are treated as optimization variables and the problem is "transcribed" to a nonlinear optimization problem of the form:

Minimize

$$F(\mathbf{z})$$

Subject to the algebraic constraints

$$\begin{aligned} \mathbf{g}(\mathbf{z}) &= \mathbf{0} \\ \mathbf{h}(\mathbf{z}) &\leq \mathbf{0} \end{aligned}$$

Depending upon the type of direct method employed, the size of the nonlinear optimization problem can be quite small or may be quite large. In the latter case, the nonlinear optimization problem may be literally thousands to tens of thousands of variables and constraints. Given the size of many NLPs arising from a direct method, it may appear somewhat counter-intuitive that solving the nonlinear optimization problem is easier than solving the boundary-value problem. It is, however, the fact that the NLP is easier to solve than the boundary-value problem.

3.3 Example of optimal control problem

Consider the problem of a mine owner who must decide at what rate to extract ore from his mine. He owns rights to the ore from date 0 to date t . At 0 date there is x_0 ore in the ground, and the instantaneous stock of ore $x(t)$ declines at the rate the mine owner extracts it $u(t)$. The mine owner extracts ore at cost $u(t)^2/x(t)$ and sells ore at a

constant price P . He does not value the ore remaining in the ground at time T (there is no "scrap value"). He chooses the rate of extraction in time $u(t)$ to maximize profits over the period of ownership with no time discounting.

3.3.1 Discrete-time version

The manager maximizes profit Π :

$$\Pi = \sum_{t=0}^{T-1} \left[pu_t - \frac{u_t^2}{x_t} \right]$$

Subject to the law of evolution for the state variable x_t

$$x_{t+1} - x_t = -u_t$$

Form the Hamiltonian and differentiate:

$$H = pu_t - \frac{u_t^2}{x_t} - \lambda_{t+1}u_t$$

$$\frac{\partial H}{\partial u_t} = p - \lambda_{t+1} - 2\frac{u_t}{x_t} = 0$$

$$\lambda_{t+1} - \lambda_t = -\frac{\partial H}{\partial x_t} = -\left(\frac{u_t}{x_t}\right)^2$$

As the mine owner does not value the ore remaining at time T ,

$$\lambda_T = 0$$

Using the above equations, it is easy to solve for the x_t and λ_t series

$$\lambda_t = \lambda_{t+1} + \frac{(p - \lambda_{t+1})^2}{4}$$

$$x_{t+1} = x_t \frac{2 - p + \lambda_{t+1}}{2}$$

and using the initial and turn-T conditions, the x_t series can be solved explicitly, giving u_t .

3.3.2 Continuous-time version

The manager maximizes profit Π :

$$\Pi = \int_0^T \left[pu(t) - \frac{u(t)^2}{x(t)} \right] dt$$

subject to the law of evolution for the state variable $x(t)$

$$\dot{x}(t) = -u(t)$$

Form the Hamiltonian and differentiate:

$$H = pu(t) - \frac{u(t)^2}{x(t)} - \lambda(t)u(t)$$

$$\frac{\partial H}{\partial u} = p - \lambda(t) - 2\frac{u(t)}{x(t)} = 0$$

$$\dot{\lambda}(t) = -\frac{\partial H}{\partial x} = -\left(\frac{u(t)}{x(t)}\right)^2$$

As the mine owner does not value the ore remaining at time T ,

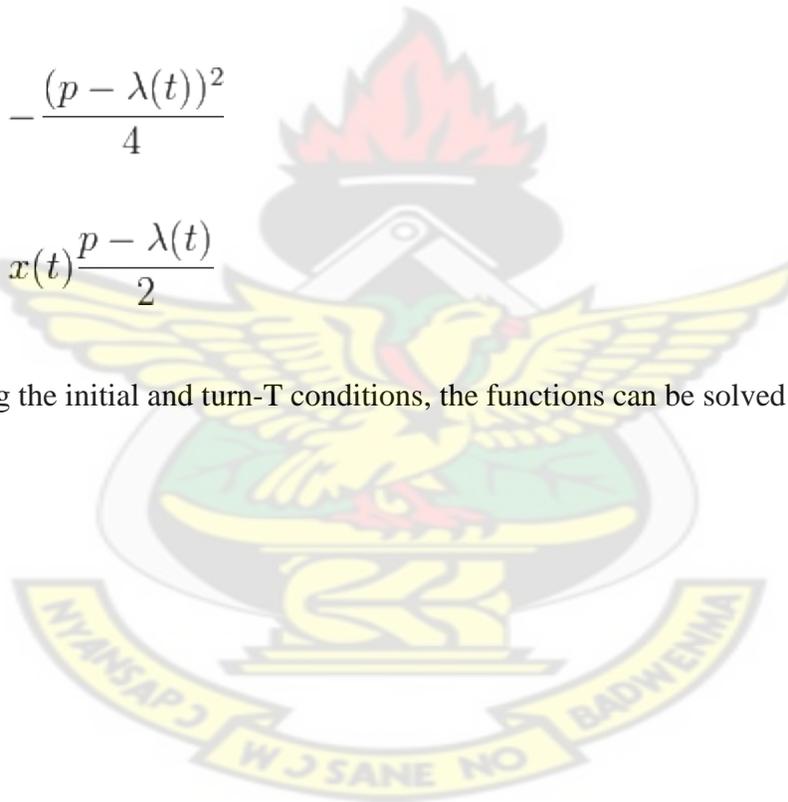
$$\lambda(T) = 0$$

Using the above equations, it is easy to solve for the differential equations governing $u(t)$ and $\lambda(t)$

$$\dot{\lambda}(t) = -\frac{(p - \lambda(t))^2}{4}$$

$$u(t) = x(t)\frac{p - \lambda(t)}{2}$$

and using the initial and turn-T conditions, the functions can be solved numerically.



CHAPTER 4

RESULTS AND DISCUSSIONS

4.0 Introduction

This chapter looks at the hydrometallurgical process into details and also presents some assumptions on which basis the model was obtained. It also covers the problem formulation, results and discussions.

4.1 Process description

Hydrometallurgical processes consist of several unit operations of which, to me, adsorption is the most decisive importance for the economy of the integrated process. This is especially true for the recovery of precious metals by cyanide leaching. The dissolution of metals is brought about by contacting the ore minerals with solutions with a given composition under suitable conditions and sufficient period of time. The recovery and the impact of the effluent environment are always of much concern.

For several years mathematical models have been extensively studied in order to obtain predictions for the kinetics of leaching and adsorption reactions. A number of rate equations have been published based on different experimental conditions. The first comprehensive study on the variation of the rate of gold dissolution with cyanide and oxygen concentration has been described since 1966. However, the limitation of the equation in the modelling of industrial gold cyanidation is due to the difficulty in measuring the exact surface area of gold in the ore and the Nernst boundary layer thickness Roman *et al*, (1974). Most of these mathematical models are differential equations.

The metallurgical process encounters losses which include cyanide and gold solution losses. Considering the current world market price of gold, the gold losses recorded by most mining companies have become very significant.

Metallurgists find it a difficult task in determining the aqueous gold or the amount of gold that has been dissolved in the system. Sample solution is, from time to time, taken to metallurgical laboratories for testing. The loss of gold in the form of solution is in the range of 0.20 – 0.005 ppm (mg/l).

This work is concentrating on developing an optimal control mathematical model that depicts how aqueous gold solution leaves the solution phase unto the activated carbon phase in a process called adsorption.

4.1.1 Assumptions

It is assumed that the mixture in the tanks is instantly and uniformly mixed at all time. This is achieved by the turbulence resulting from the flow as well as the agitators installed on each of the leaching and adsorption tanks in the carbon in leach circuit.

The pH of the medium is assumed to be maintained basic to prevent the loss of cyanide in the form of hydrogen cyanide gas (HCN). It has been tested and found that in a pH below 9.5 cyanide ions form hydrogen cyanide gas (a very harmful gas) which quickly leaves the system causing a loss of cyanide in the system.

It is also assumed that there are no substances that consume cyanide from the system. These substances are called cyanicides. The common cyanicides usually found in the mining environment are the sulphides. Their removal from the CIL process is achieved

by the addition of lead nitrate which forms an insoluble PbS and hence nullifying sulphide's ability to consume cyanide.

Solution gold loss as a result of spillage is assumed to be negligible. There are occasional spillages on the CIL plant. This is however curbed by the provision of an extension of the tanks a little above the outlet and the inlet gates unless there are differences in pulp densities in the tanks or sometimes inter-tank screen blinding.

It is assumed that there no other substances that consume dissolved gold other than the activated carbon.

The volumetric flow rate of the pulp is assumed to be constant at any time.

The volumes of the leaching and adsorption tanks are kept equal.

Lastly, all the conditions that affect dissolution of the precious metal (for instance dissolved oxygen, pH, cyanide concentration, etc) are available and in their right quantities in all the tanks.

4.2 Problem Formulation

(The amount of dissolved gold in solution at a given time) – (The amount of dissolved gold adsorbed unto the activated carbon at a given time) = (The amount of dissolved gold that leaves the system to the waste dam at a given time). These amounts are obtained by finding the product of the concentrations and their respective volumetric flow rates.

Hence, $\text{Min } I_{x_i}(u) = \int_{t_i}^{t_f} (qx(t) - ru(t))^2 dt$

Subject to:

$$\dot{x} = k\alpha x - kux$$

Where;

$X(t)$ = the concentration of gold in solution at any given time (t).

$U(t)$ = the concentration of gold on activated carbon at any given time (t).

T = Time measured in hours

Q = the volumetric flow rate of the solution containing the dissolved gold

R = the activated carbon flow rate

k = the empirical kinetic constants of adsorption for gold

α = the maximum gold content of the activated carbon

4.3 Solving with Pontryagin's Minimum Principle

$$H = (qx - ru)^2 + pk\alpha x - pkux$$

$$H = F + pf$$

$$\frac{\partial H}{\partial x} = 2q(qx - ru) + pk\alpha - pku = -\dot{p} \quad (1)$$

$$\frac{\partial H}{\partial u} = -2r(qx - ru) - pkx = 0 \quad (2)$$

$$\frac{\partial H}{\partial p} = k\alpha x - kux = \dot{x} \quad (3)$$

From (2) $(qx - ru) = -\frac{pkx}{2r}$

Put into equation (1)

$$-\dot{p} = \frac{pqkx}{r} + pk\alpha - pku \quad (4)$$

But from equation (2),

$$u(t) = \frac{pkx}{2r^2} + \frac{qx}{r} \quad (5)$$

Put u into equations (3) and (4)

$$\dot{x} = k\alpha x - k\left(\frac{pkx}{2r^2} + \frac{qx}{r}\right)x$$

This is simplified to obtain the equation below;

$$\dot{x} = k\alpha x - \frac{qkx^2}{r} - \frac{pk^2x^2}{2r^2}$$

$$\dot{p} = \frac{pqkx}{r} + pk\alpha - pk\left(\frac{pkx}{2r^2} + \frac{qx}{r}\right)$$

This is also simplified to obtain the equation below;

$$\dot{p} = \frac{2pqkx}{r} + \frac{p^2k^2x}{2r^2} - pk\alpha$$

Now we have two non-linear differential equations

$$\dot{x} = k\alpha x - \frac{qkx^2}{r} - \frac{pk^2x^2}{2r^2} \quad \dot{x} = k\alpha x - \frac{qkx^2}{r} - \frac{pk^2x^2}{2r^2}$$

$$\dot{p} = \frac{2pqkx}{r} + \frac{p^2k^2x}{2r^2} - pk\alpha$$

4.3.1 Equilibrium points

But at equilibrium, $\dot{x}=0$ and $\dot{p}=0$

Hence;

$$k\alpha x - \frac{qkx^2}{r} - \frac{pk^2x^2}{2r^2} = 0 \quad (a)$$

$$k\alpha x - \frac{qkx^2}{r} - \frac{pk^2x^2}{2r^2} = 0 \quad (a)$$

$$\frac{2pqkx}{r} + \frac{p^2k^2x}{2r^2} - pk\alpha = 0 \quad (b)$$

Now solving the two simultaneously and from equation (a);

$$p = \frac{2\alpha r^2}{kx} - \frac{2qr}{k} \quad (c)$$

Putting p into equation (b) and simplifying we obtain;

$$8qr\alpha - 6q^2x - \frac{4\alpha^2r^2}{x} = 0$$

$$6q^2x^2 - 8qr\alpha x + 4\alpha^2r^2 = 0$$

$$x = \frac{2\alpha r}{3q} \pm \sqrt{\frac{-2r^2\alpha^2}{9q^2}}$$

For the sake of simplicity, I will drop the imaginary part of x and proceed with the real part.

Now substituting $x = \frac{2\alpha r}{3q}$ into equation (c) and simplifying we obtain;

$$p = \frac{qr}{k}$$

The equilibrium points are therefore given as;

$$(0,0), \text{ and } \left(\frac{2\alpha r}{3q}, \frac{qr}{k}\right)$$

4.3.2 Linearization using the Jacobian Matrix Method

$$J(x, p) = \begin{bmatrix} \frac{\partial a}{\partial x} & \frac{\partial a}{\partial p} \\ \frac{\partial b}{\partial x} & \frac{\partial b}{\partial p} \end{bmatrix}$$

But;

$$\frac{\partial a}{\partial x} = k\alpha - \frac{2kqx}{r} - \frac{pk^2x}{r^2}$$

$$\frac{\partial a}{\partial p} = -\frac{k^2x^2}{2r^2}$$

$$\frac{\partial b}{\partial x} = \frac{p^2k^2}{2r^2} + \frac{2pkq}{r}$$

$$\frac{\partial b}{\partial p} = \frac{pk^2x}{r^2} + \frac{2pkq}{r} - k\alpha$$

At equilibrium point (0, 0);

$$J(0,0) = \begin{bmatrix} k\alpha & 0 \\ 0 & -k\alpha \end{bmatrix}$$

4.3.3 Finding the eigenvalues at equilibrium point (0, 0)

$$|A - \lambda I| = 0$$

$$\left| \begin{bmatrix} k\alpha & 0 \\ 0 & -k\alpha \end{bmatrix} - \begin{bmatrix} \lambda & 0 \\ 0 & \lambda \end{bmatrix} \right| = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\left| \begin{bmatrix} k\alpha - \lambda & 0 \\ 0 & -k\alpha - \lambda \end{bmatrix} \right| = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$(k\alpha - \lambda)(-k\alpha - \lambda) = 0$$

$$\lambda = -k\alpha \text{ or } k\alpha$$

At equilibrium point $\left(\frac{2\alpha r}{3q}, \frac{qr}{k}\right)$

$$J\left(\frac{2\alpha r}{3q}, \frac{qr}{k}\right) = \begin{bmatrix} -k\alpha & \frac{-k^2\alpha^2}{9q^2} \\ \frac{5q^2}{2} & 2k\alpha \end{bmatrix}$$

4.3.4 Finding the eigenvalues at equilibrium point $\left(\frac{2\alpha r}{3q}, \frac{qr}{k}\right)$

At equilibrium point $\left(\frac{2\alpha r}{3q}, \frac{qr}{k}\right)$,

$$|A - \lambda I| = 0$$

$$\left| \begin{bmatrix} -k\alpha & \frac{-k^2\alpha^2}{9q^2} \\ \frac{5q^2}{2} & 2k\alpha \end{bmatrix} - \begin{bmatrix} \lambda & 0 \\ 0 & \lambda \end{bmatrix} \right| = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\begin{bmatrix} -k\alpha - \lambda & \frac{-k^2\alpha^2}{9q^2} \\ \frac{5q^2}{2} & 2k\alpha - \lambda \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$(-k\alpha - \lambda)(2k\alpha - \lambda) - \left(\frac{5q^2}{2}\right)\left(\frac{-k^2\alpha^2}{9q^2}\right) = 0$$

$$\lambda^2 - k\alpha\lambda - 1.722k^2\alpha^2 = 0$$

Solving this equation using the quadratic formula we obtain;

$$\lambda = 1.905k\alpha \text{ or } -0.905k\alpha$$

4.3.5 Finding the eigenvectors for eigenvalues $\lambda = -k\alpha \text{ or } k\alpha$

When $\lambda = \lambda_1 = k\alpha$

$$\left\| \begin{bmatrix} k\alpha - k\alpha & 0 \\ 0 & -k\alpha - k\alpha \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} \right\| = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\left\| \begin{bmatrix} 0 & 0 \\ 0 & -2k\alpha \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} \right\| = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$0v_1 - 2k\alpha v_2 = 0$$

When $v_1 = 1, v_2 = 0$

$$v^{(1)} = \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

When $\lambda = \lambda_2 = -k\alpha$

$$\left[\begin{array}{cc} k\alpha + k\alpha & 0 \\ 0 & -k\alpha + k\alpha \end{array} \right] \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\left[\begin{array}{cc} 2k\alpha & 0 \\ 0 & 0 \end{array} \right] \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$2k\alpha v_1 + 0v_2 = 0$$

When $v_2 = 1, v_1 = 0$

$$v^{(2)} = \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

4.3.6 Finding the eigenvectors for eigenvalues

$(\lambda = 1.905k\alpha \text{ or } -0.905k\alpha)$

When $\lambda = \lambda_1 = -0.905k\alpha$

$$\left[\begin{array}{cc} -k\alpha + 0.905k\alpha & \frac{-k^2\alpha^2}{9q^2} \\ \frac{5q^2}{2} & 2k\alpha + 0.905k\alpha \end{array} \right] \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\left[\begin{array}{cc} -0.095k\alpha & \frac{-k^2\alpha^2}{9q^2} \\ 2.5q^2 & 2.905k\alpha \end{array} \right] \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$-0.095k\alpha v_1 - \frac{-k^2\alpha^2}{9q^2} v_2 = 0 \quad (i)$$

$$2.5q^2 v_1 + 2.905k\alpha v_2 = 0 \quad (ii)$$

When $v_1 = 1$, $v_2 = -0.885 \frac{q^2}{k\alpha}$

$$v^{(1)} = \begin{bmatrix} 1 \\ -0.885 * \frac{q^2}{k\alpha} \end{bmatrix}$$

When $\lambda = \lambda_2 = 1.905k\alpha$

$$\begin{bmatrix} -k\alpha - 1.905k\alpha & \frac{-k^2\alpha^2}{9q^2} \\ \frac{5q^2}{2} & 2k\alpha - 1.905k\alpha \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\begin{bmatrix} -2.905k\alpha & \frac{-k^2\alpha^2}{9q^2} \\ 2.5q^2 & 0.095k\alpha \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$-2.905k\alpha - \frac{k^2\alpha^2}{9q^2} v_2 = 0 \quad (iii)$$

$$2.5q^2 v_1 + 0.095k\alpha = 0 \quad (iv)$$

When $v_1 = 1$, $v_2 = -26.145 * \frac{q^2}{k\alpha}$

$$v^{(2)} = \begin{bmatrix} 1 \\ -26.145 * \frac{q^2}{k\alpha} \end{bmatrix}$$

But for the purpose of this work and its objective, I will continue with the eigenvalues and eigenvectors at the equilibrium point $(0, 0)$. This is from the fact that the rate of adsorption of gold unto the activated carbon phase is equal (but opposite in sign) to the rate at which gold is lost from the solution phase.

Hence;

$$\begin{pmatrix} p(t) \\ x(t) \end{pmatrix} = c_1 e^{\lambda_1 t} [v^{(1)}] + c_2 e^{\lambda_2 t} [v^{(2)}]$$

$$\begin{pmatrix} p(t) \\ x(t) \end{pmatrix} = c_1 e^{\lambda_1 t} \begin{bmatrix} 1 \\ 0 \end{bmatrix} + c_2 e^{\lambda_2 t} \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

This implies that;

$$p(t) = c_1 e^{\lambda_1 t}$$

$$x(t) = c_2 e^{\lambda_2 t}$$

Now putting $p(t)$ and $x(t)$ into equation (5) we obtain;

$$u(t) = \frac{k}{2r^2} (c_1 e^{\lambda_1 t})(c_2 e^{\lambda_2 t}) + \frac{q}{r} (c_2 e^{\lambda_2 t})$$

$$u(t) = c_1 * c_2 * \frac{k}{2r^2} * e^{(\lambda_1 + \lambda_2)t} + c_2 * \frac{q}{r} * e^{\lambda_2 t}$$

But at $t = 0$ $x(0) = x_0$ and $U(0) = U_0$

$$c_2 = x_0$$

$$c_1 * c_2 * \frac{k}{2r^2} + c_2 = U_0 \tag{v}$$

Putting $c_2 = x_0$ into equation (v) we obtain;

$$c_1 = (U_0 - x_0) \frac{2r^2}{x_0 k}$$

4.4 Results

The result of the model for gold concentration in solution, $x(t)$ and gold concentration on the activated carbon $u(t)$ at any given time now becomes:

$$x(t) = x_0 e^{\lambda_2 t}$$

$$u(t) = \left(\frac{U_0 - x_0}{x_0} \right) e^{(\lambda_1 + \lambda_2)t} + \frac{qx_0}{r} e^{\lambda_2 t}$$

However, the values of the estimated parameters for the kinetic equation of adsorption agree with the values found in literature according to Schubert et al., (1993), where the

maximum activated carbon loading (α) is generally between 3600 and 14200 mg/kg and the rate constant (k) is between 0.012 and 0.12 kg/mg h. Considering an old metallurgical plant that has recycled its activated carbon for some time now, the carbon become fouled with calcium and other compounds which are usually present in the system. Hence I will assume an activated carbon of average capacity of about $\alpha = 7000\text{mg/kg}$ and an average kinetic rate of adsorption of about $k = 0.07\text{kg/mgh}$ and if $q = 40000\text{l/h}$ and $r = 60\text{l/h}$ then we obtain;

$$x(t) = 0.80e^{-490t}$$

$$u(t) = -e^{(490-490)t} + 533.33 e^{-490t}$$

It is worth noting that the volumetric flow rate of the activated carbon 'r' took into consideration the percentage of the pump discharge which is actually activated carbon.

4.5 Analysis

Considering the initial gold concentration of a metallurgical plant $x_0 = 0.80\text{mg/l}$, and $u_0 = 0$ with $\alpha = 7000\text{mg/kg}$, $k = 0.07\text{kg/mgh}$ then; $\lambda_1 = 490$, $\lambda_2 = -490$

$$x(t) = 0.80e^{-490t}$$

$$u(t) = -1 + 533.33 e^{-490t}$$

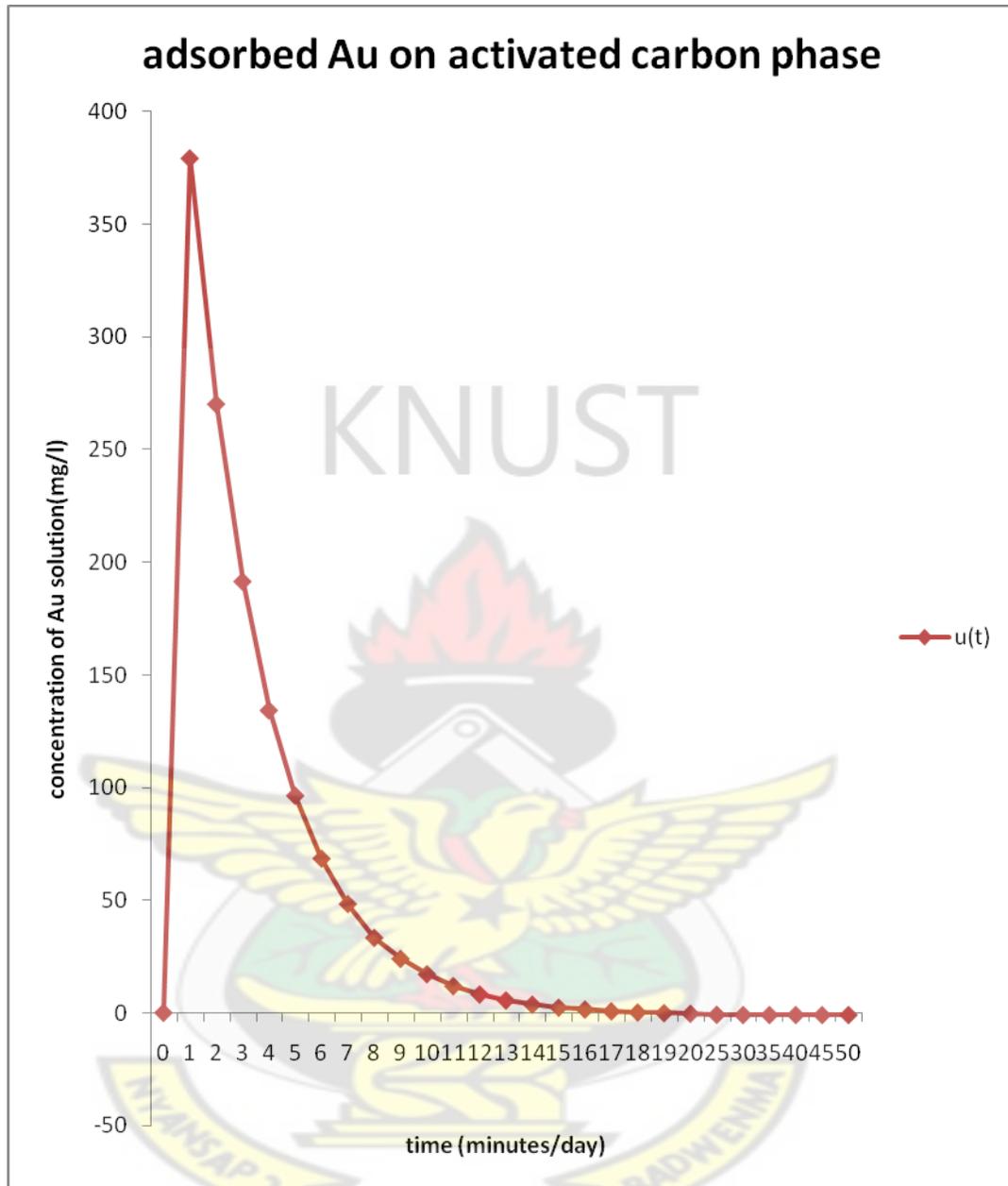


Fig 4.1(a): the plot of gold (Au) adsorbed unto activated carbon against time

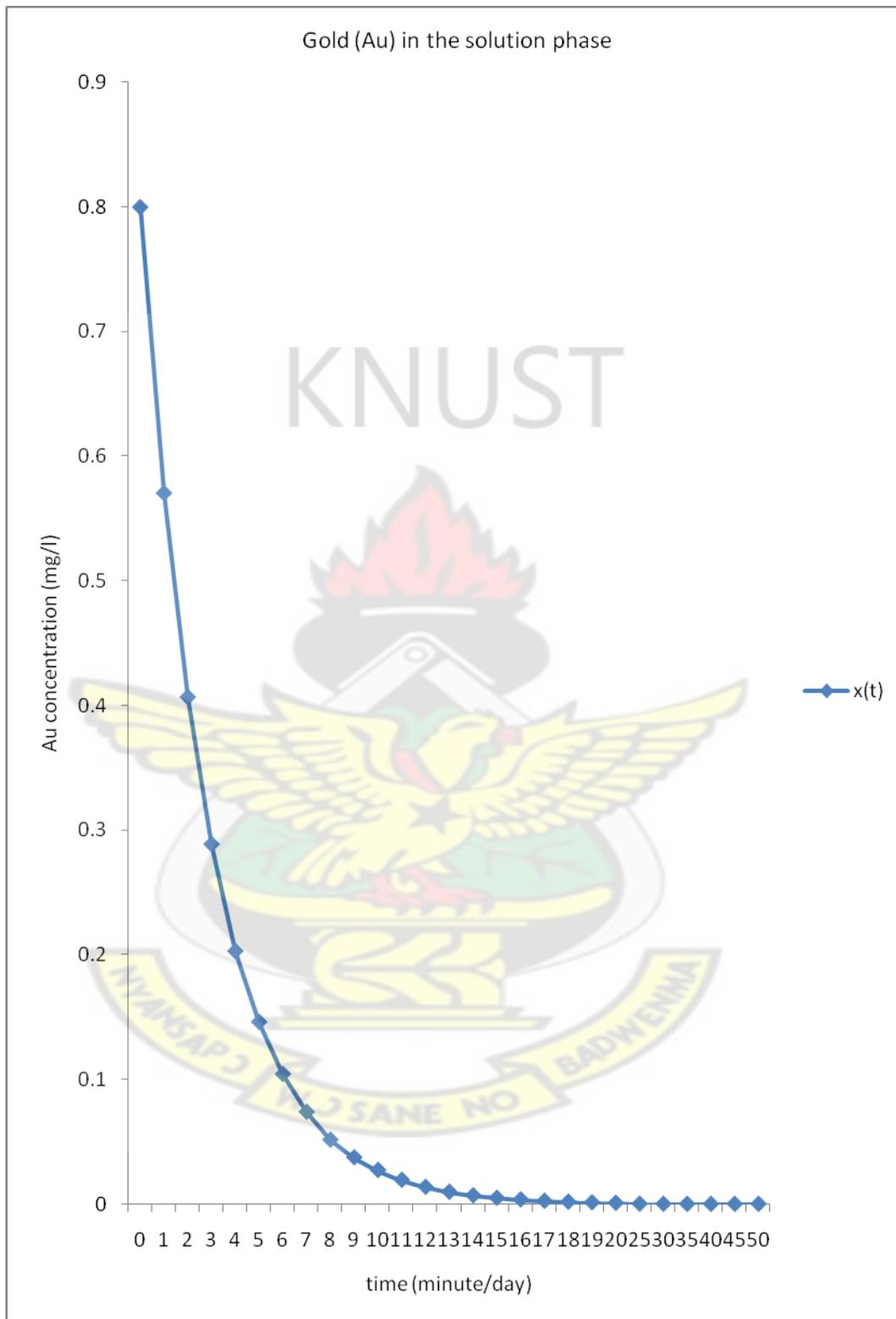


Fig 4.1(b): the plot of gold (Au) concentration in the solution phase against time

4.6 Discussions

The initial gold concentration in the adsorption circuit reduces exponentially with time during the contact period with the activated carbon. Meanwhile, the activity on the activated carbon is the direct opposite of that which goes on in the solution. While the gold solution is lost from the solution phase, the gold content on the activated carbon is increased with the same amount.

Because the model is a logistic model, the loading on the activated carbon is positive until after the 18th minute when it changes to negative. Here it is assumed to have reached its carrying or maximum capacity. Meanwhile, just at the point when the activated carbon has reached its carrying capacity, the gold in solution is minimal and practically the reverse of adsorption, which is termed desorption, sets in.

Now considering the accumulation (using the expression, $\sum_{t_i}^{t_n} (r \cdot u(t))$) where t_i is the zeroth minute or the initial time and t_n is the nth minute of gold on the activated carbon from initial to the final time, we obtain this graph;

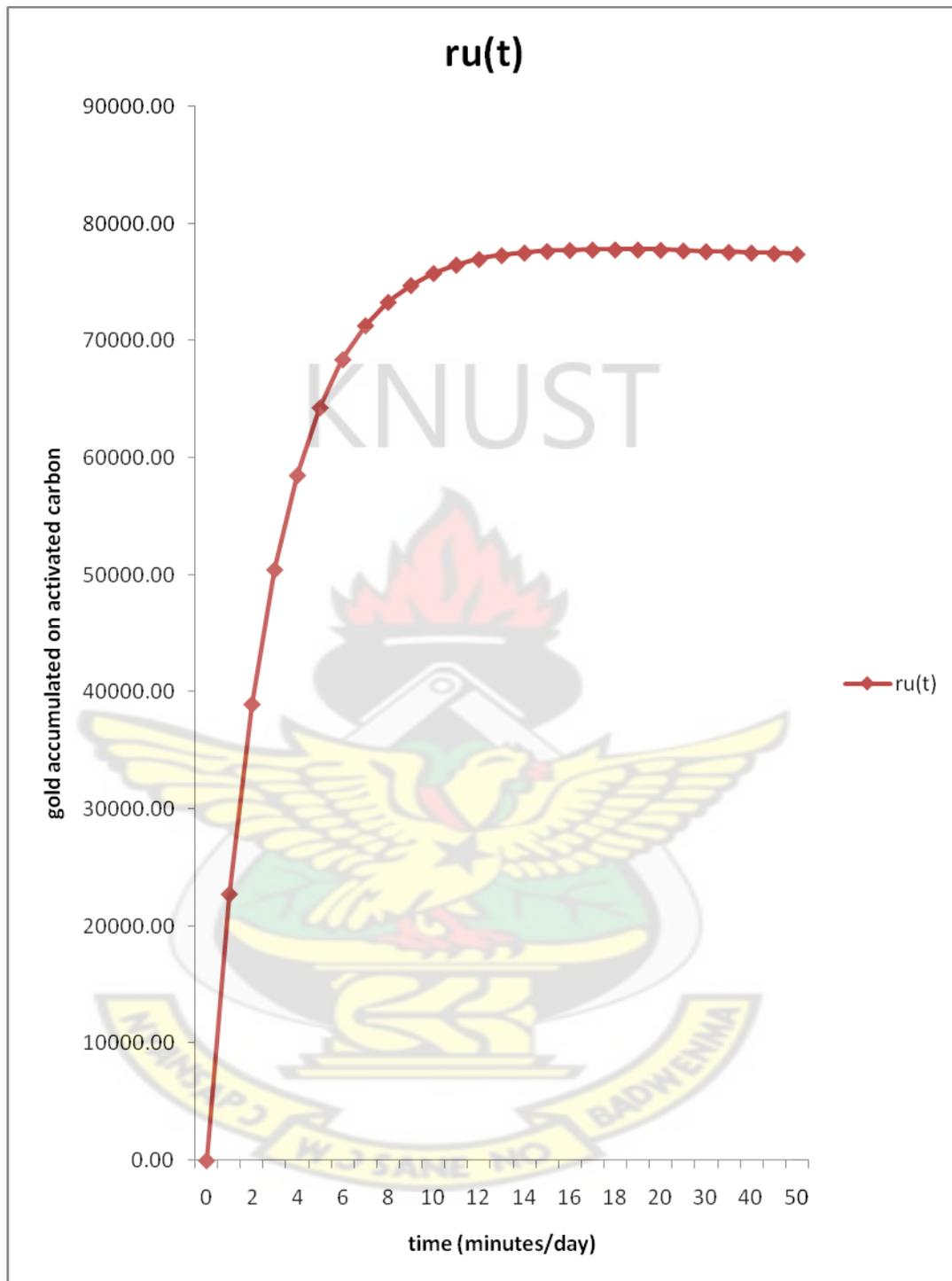


Fig 4.2: graph of accumulated gold on the activated carbon against time

It shows clearly from this graph that the activated carbon accumulates gold until at a certain capacity it is unable to take any more. At this capacity the reverse of the process is observed. The reverse process called desorption begin when we begin to observe negative adsorption values as observed in the previous graph.

Considering the initial gold concentration of a metallurgical plant $x_0 = 0.80\text{mg}/\ell$, and $u_0 = 0$, on an assumption that the activated carbon is fresh from the factory and hence has a very high adsorption potential and high capacity, with $\alpha = 14000\text{mg}/\text{kg}$, $k = 0.10\text{kg}/\text{mgh}$ then; $\lambda_1 = 1400$, $\lambda_2 = -1400$.

It could be seen here that even though the carrying capacity is increased, the process takes few minutes to reach that maximum value. The process is faster with increased maximum activated carbon capacity and increased kinetic rate of adsorption. The process however is less influenced by the initial conditions of the process most especially the initial concentration of gold in solution.

Manipulating the flow rates of the process, I noticed that this does not affect the concentration of gold in solution in any way but rather the gold on the activated carbon phase. Hence it does not affect the amount of gold remaining in the solution phase at a given time but rather the amount of gold adsorbed unto the activated carbon.

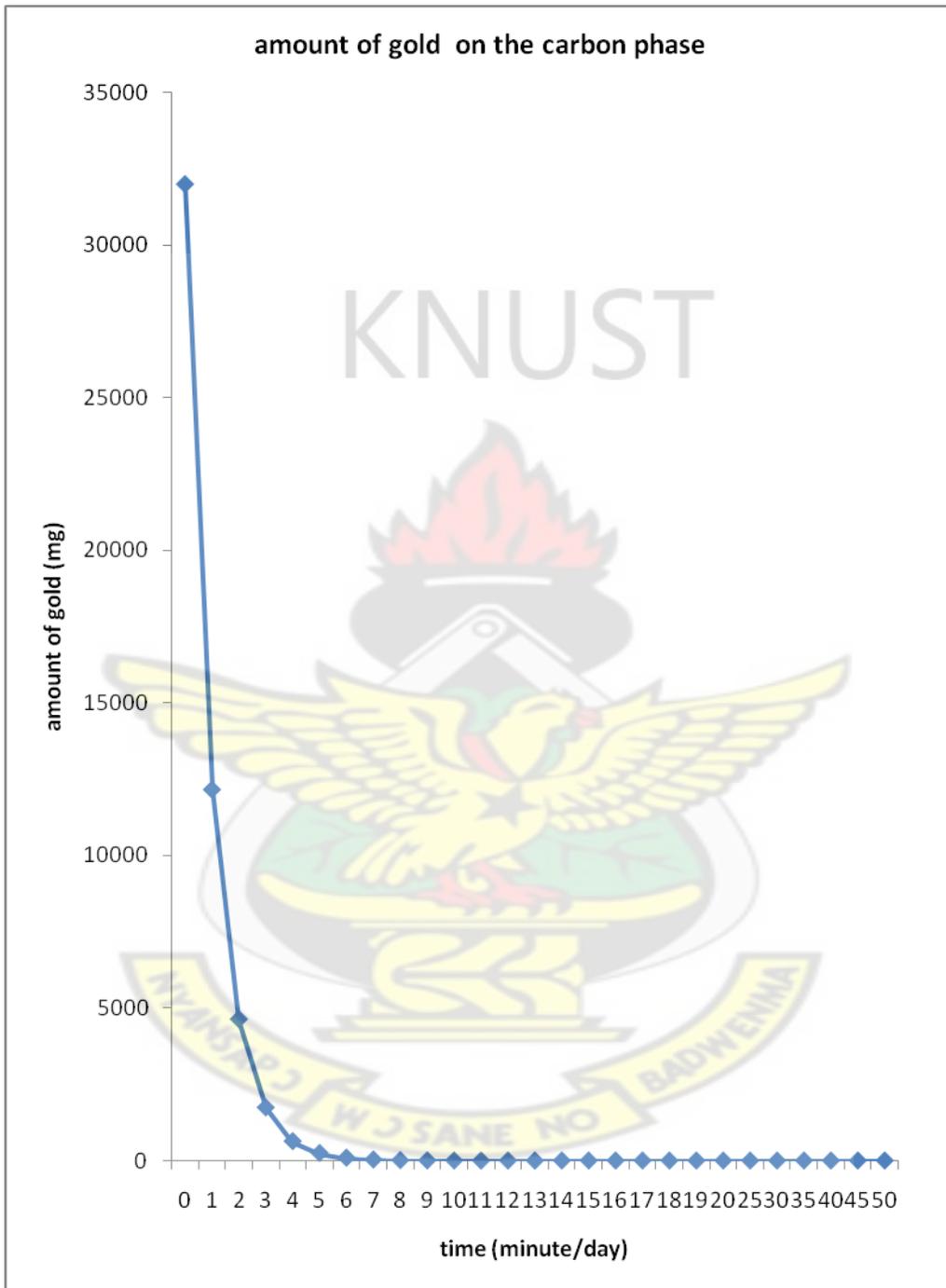


Fig 4.3(a): the plot of amount of gold (Au) on the solution phase against time

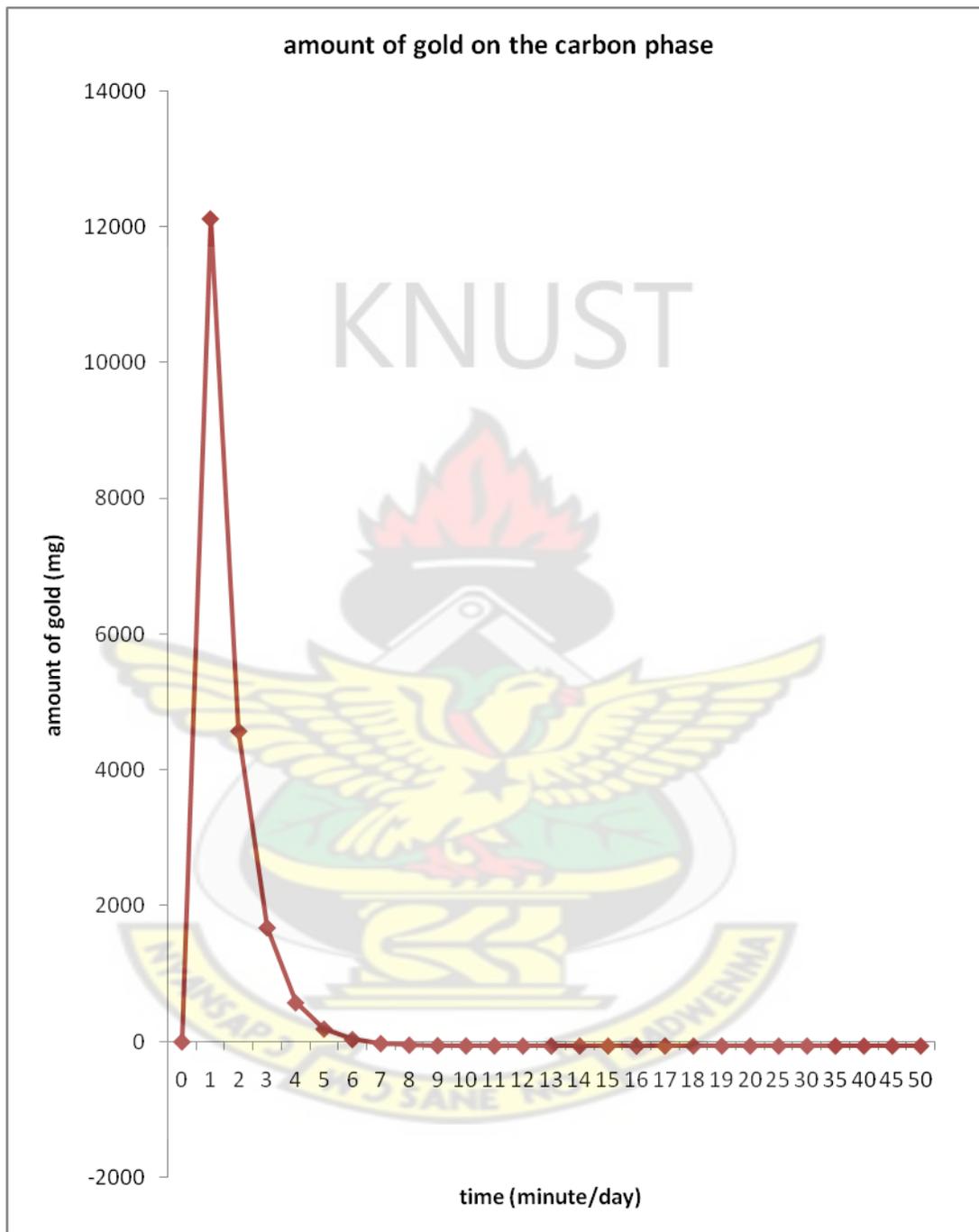


Fig 4.3(b): the plot of amount of gold (Au) in the carbon phase against time

Now let's look at the changes observed as the activated carbon input is controlled over time. It is clear from the graph below that for 15 or less minutes of adsorption, the process was very spontaneous as the amount of carbon added increased from 10mg/l to 100mg/l. The adsorption for 25 or more minutes of adsorption process was gradual for the same amounts of activated carbon. This implies that the rate at which gold is adsorbed unto activated carbon reduces with time and this process is quicker and very spontaneous with increased amount of activated carbon in the adsorption circuit.

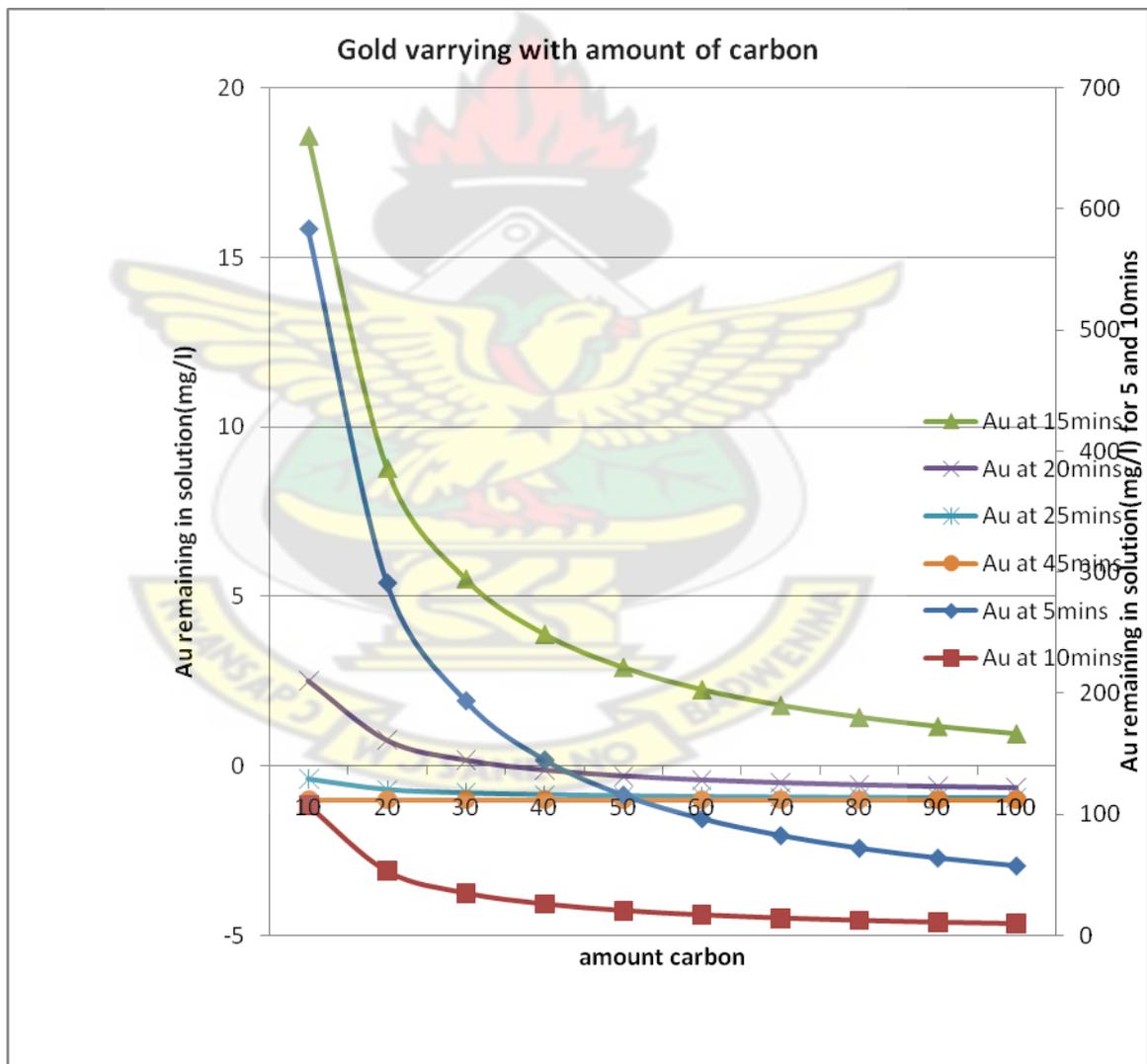


Fig 4.4: the amount of gold varying with activated carbon added

4.7 Simulation

Now varying the activated carbon flow rate of the system, and maintaining the other parameters; average capacity of activated carbon of about $\alpha = 7000\text{mg/kg}$ and an average kinetic rate of adsorption of about $k = 0.07\text{kg/mgh}$ and volumetric flow rate of the solution containing the gold $q = 40000\ell/h$ then we obtain;

$$u(t) = -1 + \frac{32000}{r_t} e^{-kt}$$

The choice of the flow of activated carbon into an adsorption system is dependent on the system design specifications. Thus the residence time of the system is a determining factor. This is evident in the graph below which depicts the effect of gold solution adsorbed unto the activated carbon at any given time when the activated carbon flow rate is varied. For instance for a system which has a residence time of 25minutes would require not less than $40\text{m}^3/\text{hr}$ flow of activated carbon into the system to ensure efficient performance of the system. Likewise another system with a residence time of 15 minutes would require not less than $100\text{m}^3/\text{hr}$ of activated carbon flow into the adsorption system.

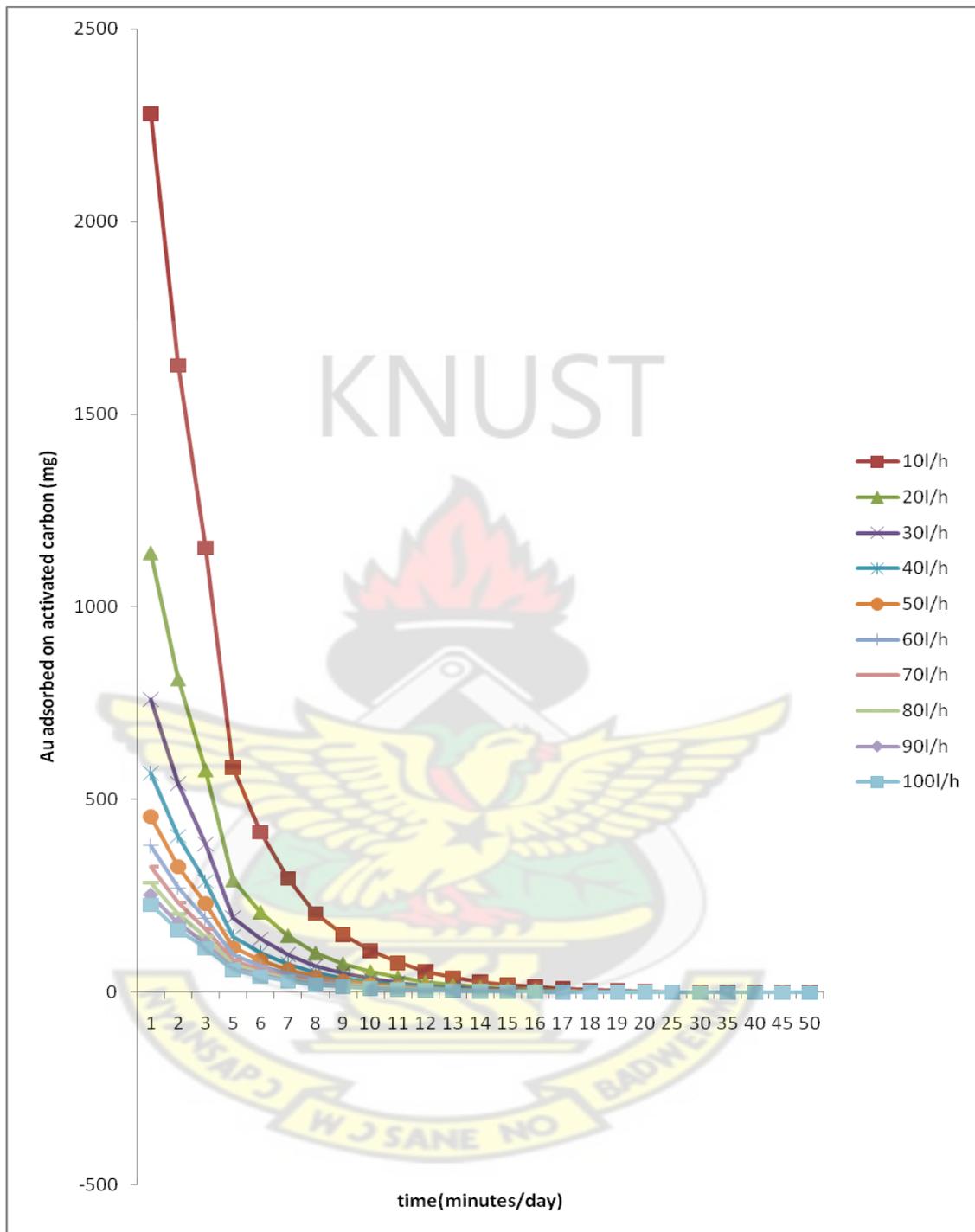


Fig 4.5: the plot of amount of gold (Au) in the carbon phase against time for variable carbon inputs

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.0 Introduction

This chapter gives vivid information on the findings of this work with respect to the set objectives. It also includes recommendations that should be taken note of by stakeholders and all readers.

5.1 Conclusion

The model developed is an optimal control model of the adsorption process of a hydrometallurgical process called Carbon-In-Pulp. The model took into consideration the fact that the metallurgical process encounters several losses chief among them being gold solution losses. Several assumptions were made and among them was the assumption that the amount of gold in solution that goes to waste is equal to the amount of gold solution in the adsorption unit less the amount of gold adsorbed onto the activated carbon phase. With the rate of adsorption proportional to the capacity of activated carbon and the concentration of gold on the carbon phase, the model has a state variable $x(t)$ which is the concentration of gold in the solution phase at any given time and a control variable $u(t)$ which is the concentration of gold on the activated carbon phase at any given time.

The optimal control model developed gives complete overview of the process of adsorption process of dissolved gold solution onto activated carbon. The model reveals that the process is fast and spontaneous initially and slows down with time until it

reaches the carrying capacity of the activated carbon where the reverse process is observed. Activated carbons with high capacities (i.e. activated carbon that is believed to be fresh and therefore has not been fouled) have the ability to absorb gold faster.

The model reveals that the rate at which gold is lost from the solution phase is the same but a reverse process to the rate at which it is adsorbed onto the activated carbon phase and this rate, as mentioned earlier, is dependent on the maximum capacity of the activated carbon.

It has also been observed that the choice of concentration of activated carbon affects greatly the nature of adsorption. The rate at which gold is adsorbed onto activated carbon reduces with time but the process is quicker and very spontaneous with increased amount of activated carbon in the adsorption circuit.

5.2 Recommendations

From the results obtained above and the analyses made, the following are recommended:

- This optimal control model should be adopted by the metallurgical industry especially those companies practicing the Carbon-In-Pulp process.
- Prospective thesis candidates should look at weakening the assumptions and parameters of the model a bit to observe the effect.
- A non-linear objective function of the optimal control model of gold adsorption process should be looked at in future by interested candidates.

- Lastly, this model was developed for a typical Carbon-In-Pulp (CIP) process. Further studies should be done on the other processes especially the carbon in leach (CIL) process.

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Appendices

time(minutes)	min/day	x(t)	u(t)
0	0	0.8	0
1	0.00069	0.5705	379.33
2	0.00138	0.4068	270.22
3	0.00208	0.2887	191.47
4	0.0028	0.2029	134.25
5	0.00347	0.1461	96.4
6	0.00416	0.1042	68.46
7	0.00486	0.0739	48.29
8	0.0056	0.0515	33.3
9	0.00625	0.0374	23.94
10	0.0069	0.0272	17.14
11	0.0076	0.0193	11.87
12	0.0083	0.0137	8.135
13	0.009	0.0097	5.483
14	0.0097	0.0069	3.6
15	0.0104	0.0049	2.265
16	0.011	0.0036	1.433
17	0.0118	0.0025	0.644
18	0.0125	0.00175	0.1667
19	0.0132	0.00124	-0.172
20	0.0139	0.0009	-0.41
25	0.0174	0.00016	-0.89
30	0.021	0.00003	-0.982
35	0.0243	5.40E-06	-0.996
40	0.028	8.80E-07	-0.999
45	0.031	2.00E-07	-0.9998
50	0.035	2.90E-08	-1.000

Table 1: the concentration of gold in solution(x(t)) and that being adsorbed unto activated carbon phase (u(t))

time(minutes)	min/day	qx(t)	ru(t)
0	0	32000	0
1	0.00069	22820	22759.8
2	0.00138	16272	16213.2
3	0.00208	11548	11488.2
4	0.0028	8116	8055
5	0.00347	5844	5784
6	0.00416	4168	4107.6
7	0.00486	2956	2897.4
8	0.0056	2060	1998
9	0.00625	1496	1436.4
10	0.0069	1088	1028.4
11	0.0076	772	712.2
12	0.0083	548	488.1
13	0.0090	388	328.98
14	0.0097	276	216
15	0.0104	196	135.9
16	0.0110	144	85.98
17	0.0118	100	38.64
18	0.0125	70	10.002
19	0.0132	49.6	-10.32
20	0.0139	36	-24.6
25	0.0174	6.4	-53.4
30	0.021	1.2	-58.92
35	0.0243	0.216	-59.76
40	0.0280	0.0352	-59.94
45	0.0310	0.008	-59.988
50	0.0350	0.00116	-59.994

Table 2: the amount of gold in solution(x(t)) and that being adsorbed unto activated carbon phase (u(t))

time(minutes)	$\sum_{t_i}^{t_n} (r \cdot u(t))$
0	0.00
1	22759.80
2	38973.00
3	50461.20
4	58516.20
5	64300.20
6	68407.80
7	71305.20
8	73303.20
9	74739.60
10	75768.00
11	76480.20
12	76968.30
13	77297.28
14	77513.28
15	77649.18
16	77735.16
17	77773.80
18	77783.80
19	77773.48
20	77748.88
25	77695.48
30	77636.56
35	77576.80
40	77516.86
45	77456.87
50	77396.88

Table 3: accumulated gold on activated carbon

time(minutes)	min/day	x(t)	u(t)
0	0	0.80000	0
1	0.00069	0.30400	201.980
2	0.00138	0.11590	76.2570
3	0.00208	0.04350	27.9950
4	0.0028	0.01590	9.5800
5	0.00347	0.00621	3.1420
6	0.00416	0.00236	0.5760
7	0.00486	0.00089	-0.4080
8	0.0056	0.000315	-0.7900
9	0.00625	0.000128	-0.9150
10	0.0069	5.1E-05	-0.9660
11	0.0076	1.915E-05	-0.9870
12	0.0083	7.188E-06	-0.9950
13	0.009	2.698E-06	-0.9980
14	0.0097	1.01E-06	-0.9990
15	0.0104	3.80E-07	-0.99970
16	0.011	1.64E-07	-0.99980
17	0.0118	5.35E-08	-0.99990
18	0.0125	2.01E-08	-0.99998
19	0.0132	7.54E-09	-0.99999
20	0.0139	2.83E-09	-0.999998
25	0.0174	2.107E-11	$\cong -1$
30	0.021	1.364E-13	$\cong -1$
35	0.0243	1.344E-15	-1.0000
40	0.028	7.564E-18	-1.0000
45	0.031	1.134E-19	-1.0000
50	0.035	4.194E-22	-1.0000

Table 4: the concentration of gold in solution(x(t)) and that being adsorbed unto activated carbon phase (u(t)) after the kinetic rate of adsorption and the maximum capacity of carbon have been increased.

time(minutes)	min/day	qx(t)	ru(t)
0	0	32000	0
1	0.00069	12160	12118.8
2	0.00138	4636	4575.42
3	0.00208	1740	1679.7
4	0.0028	636	574.8
5	0.00347	248.4	188.52
6	0.00416	94.4	34.56
7	0.00486	35.6	-24.48
8	0.0056	12.6	-47.4
9	0.00625	5.12	-54.9
10	0.0069	2.04	-57.96
11	0.0076	0.766	-59.22
12	0.0083	0.28752	-59.7
13	0.0090	0.10792	-59.88
14	0.0097	0.0404	-59.94
15	0.0104	0.0152	-59.982
16	0.0110	0.00656	-59.988
17	0.0118	0.00214	-59.994
18	0.0125	0.000804	-59.9988
19	0.0132	0.000302	-59.9994
20	0.0139	0.000113	-59.9999
25	0.0174	8.43E-07	-60
30	0.021	5.46E-09	-60
35	0.0243	5.38E-11	-60
40	0.0280	3.03E-13	-60
45	0.0310	4.54E-15	-60
50	0.0350	1.68E-17	-60

Table 5: the amount of gold in solution(x(t)) and that being adsorbed unto activated carbon phase (u(t)) after the kinetic rate of adsorption and the maximum capacity of carbon have been increased

Time		r_t is the volumetric flow rate of the activated carbón									
Minutes	(fraction of a day)	10	20	30	40	50	60	70	80	90	100
1	0.00069	2280.997	1139.998	759.6637	569.4992	455.3993	379.3324	324.9832	284.2496	252.5527	227.1997
2	0.00138	1626.347	812.6733	541.4475	405.8366	324.4693	270.2242	231.4665	202.4183	179.8145	161.7347
3	0.00208	1153.827	576.4137	383.9415	287.7068	229.9655	191.471	163.9671	143.3534	127.3129	114.4827
5	0.00347	583.4119	291.206	193.8035	145.103	115.8824	96.40189	82.48324	72.05149	63.93401	57.44119
6	0.00416	415.7582	207.3791	137.919	103.1895	82.35163	68.45962	58.5339	51.09477	45.306	40.67582
7	0.00486	294.7475	146.8738	97.58226	72.93688	58.1495	48.2912	41.24753	35.96844	31.86051	28.57475
8	0.0056	204.8003	101.9001	67.59992	50.45007	40.16005	33.30001	28.39857	24.72503	21.86647	19.58003
9	0.00625	148.666	73.833	48.88854	36.4165	28.9332	23.94431	20.37979	17.70825	15.62939	13.9666
10	0.0069	107.843	53.42148	35.2809	26.21074	20.76859	17.14047	14.54822	12.60537	11.09354	9.884296
11	0.0076	76.23912	37.61956	24.74631	18.30978	14.44782	11.87317	10.03361	8.65489	7.582039	6.723912
12	0.0083	53.81183	26.40592	17.27057	12.70296	9.962366	8.135296	6.82987	5.851479	5.090143	4.481183
13	0.009	37.89657	18.44829	11.96549	8.724143	6.779314	5.482755	4.556375	3.862071	3.321798	2.889657
14	0.0097	26.60249	12.80125	8.200808	5.900623	4.520499	3.600411	2.943016	2.450312	2.066913	1.760249
15	0.0104	18.58778	8.793892	5.529245	3.896946	2.917557	2.264627	1.798115	1.448473	1.176399	0.958778

16	0.011	13.59831	6.299157	3.866093	2.649579	1.919663	1.43305	1.085369	0.824789	0.622019	0.459831
17	0.0118	8.864141	3.932071	2.288039	1.466035	0.972828	0.644022	0.409093	0.233018	0.096005	-0.01359
18	0.0125	5.999972	2.499986	1.333318	0.749993	0.399994	0.166661	-5.4E-05	-0.125	-0.22223	-0.3
19	0.0132	3.967447	1.483724	0.655812	0.241862	-0.00651	-0.17209	-0.2904	-0.37907	-0.44807	-0.50326
20	0.0139	2.52509	0.762545	0.175027	-0.11873	-0.29498	-0.41249	-0.49644	-0.55936	-0.60833	-0.64749
25	0.0174	-0.36561	-0.68281	-0.78854	-0.8414	-0.87312	-0.89427	-0.90938	-0.9207	-0.92951	-0.93656
30	0.021	-0.89129	-0.94565	-0.96376	-0.97282	-0.97826	-0.98188	-0.98447	-0.98641	-0.98792	-0.98913
35	0.0243	-0.97842	-0.98921	-0.99281	-0.99461	-0.99568	-0.9964	-0.99692	-0.9973	-0.9976	-0.99784
40	0.028	-0.99648	-0.99824	-0.99883	-0.99912	-0.9993	-0.99941	-0.9995	-0.99956	-0.99961	-0.99965
45	0.031	-0.99919	-0.9996	-0.99973	-0.9998	-0.99984	-0.99987	-0.99988	-0.9999	-0.99991	-0.99992
50	0.035	-0.99989	-0.99994	-0.99996	-0.99997	-0.99998	-0.99998	-0.99998	-0.99999	-0.99999	-0.99999

Table 4.6: the gold on activated carbon for a variable activated carbon input

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