



NUMERICAL AND THEORETICAL MODELLING OF URANIUM CARBONATE LEACHING

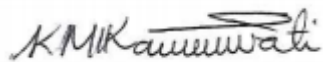
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A dissertation submitted to the Faculty of Engineering, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Engineering.

Johannesburg, 2014

DECLARATION

I declare that this dissertation is my own unaided work unless otherwise stated. It is being submitted for the degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted for any degree or examination in any other University.

A handwritten signature in black ink, appearing to read 'K M Kammwathi', is written over a light gray rectangular background.

30 May 2014

ABSTRACT

This research involved development of leaching models which characterise the carbonate leaching of a carnotite uranium ore from an industrial uranium processing facility. For confidentiality purposes, the name of the uranium processing facility was not explicitly stated. Fundamental, empirical, and linear multi-variable leaching models were developed. The fundamental model was developed from first principles and resulted in a differential equation governing the rate of disappearance of uranium from ore particles. This differential equation was solved by expressing the amount of uranium present in the particles in terms of fractional conversion. Empirical models were developed by fitting leaching data to four different exponential functions of forms analogous to the actual leaching profiles from the industrial plant. The multi-variable linear leaching model was constructed using a Microsoft excel linear regression statistical tool. All three types of models developed were found to predict the performance of a leaching process with reasonable accuracy. From the multi-variable leaching model it was found that even though the carbonate leaching of uranium is highly temperature driven, it is possible to operate the leaching process at low temperatures and still attain high leach efficiencies. This is achieved by adjusting other leach variables to compensate for reduced leach temperatures which has a potential of reducing energy costs by half, obtain high leach efficiencies and produce 20% more uranium. A mobile phone application based on the linear multi-variable model was developed as a portable process management tool. The mobile application was developed using a Livecode software and enabled easy visualisation of the effects of different values of leach variables on leaching process efficiency.

ACKNOWLEDGEMENTS

My son, Siyabonga Ngenohaame Kamati gave me the initial motivation to register for this Master's Degree and therefore, this dissertation is dedicated to him. I would then wish to thank my partner, Lungile Precious Ndlovu for continuous motivation over a number of years until today. I also wish to thank my friends, family, brothers and sisters who have tirelessly supported me in my endeavours.

I wish to thank the Namibian Graduate Scholarship and Training Program stakeholders and the Namibian government in general through the Ministry of Education, for sponsoring my postgraduate studies. I would also like to thank the University of the Witwatersrand, through the department of Chemical and Metallurgical Engineering for making this research possible.

I wish to whole heartedly thank my academic supervisor, Prof Sehliselo Ndlovu for supervising this research work. Prof Sehliselo Ndlovu set aside time from her busy schedule to give valuable inputs into my research work and thus, special thanks goes to her. I wish also to thank Dr Geoffrey Simate for valuable inputs and comments he gave towards this research.

I would like to give special thanks to the staff of the industrial carbonate uranium leaching facility for offering me the opportunity to undertake this research on their premises. Their assistance in providing me with necessary information is highly acknowledged. Determination of economic impacts of this work and consideration of exponential empirical leaching models was motivated by industrial supervisors at the industrial uranium leaching facility. Thus their valuable inputs into this research are highly appreciated.

Last but not least, I wish to thank God for the strength he has given me to pursue this work.

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CHAPTER 1

1. INTRODUCTION

1.1. BACKGROUND AND PROBLEM

Leaching is a process whereby a valuable mineral is extracted from a host ore by dissolving into a solution, known as a lixiviant or a leaching agent. Leaching belongs to a class of heterogeneous reactions in which solids are contacted by gases or liquids and get transformed into one or more products (Levenspiel, 1972). In solid-liquid leaching in particular, a liquid contacts a solid and selectively dissolves the valuable mineral. In many leaching processes, the target mineral is extracted from the ore leaving behind particles of relatively unchanged size. Particle size does not change greatly during leaching especially in ores containing large proportions of gangue materials (Levenspiel, 1972). At the industrial carbonate leaching plant studied for example, leached ore contains about 0.1% of target uranium. Levenspiel (1972) stated that particles change considerably in size when a pure solid is taking part in a solid-liquid or solid-gas reaction. This happens for example in coal combustion but not in uranium leaching. Because coal is made up primarily of carbon (with a low fraction of impurities), the coal particle disappears progressively as its carbon fraction reacts with oxygen.

The progressive conversion of uranium from solid particles can be modelled through a mathematical representation of a leaching process. The rate of leaching of a mineral from a solid particle is modelled using the shrinking core model for spherical particles, also known as the un-reacted core model. In a scenario where the reaction between a solid and liquid first occurs on the particle surface before moving into the particle interior; the rate of leaching of uranium from spherical particles is given by (Comninos, 1985; Crundwell, 1985; Dry, 1984):

$$\frac{dM_u}{dt} = -k\varphi\gamma \frac{F_o}{\rho l_o} \left(\frac{M_u}{M_{uo}} \right)^{\frac{2}{3}} \quad (1.1)$$

Where:

- k = overall reaction rate constant, hr^{-1}
- φ = factor that accounts for solution condition effects
- F_o = initial mass of solid particles, kg
- γ = average shape factor of solid particles
- ρ = density of solid particles, kg/m^3
- l_o = particles radius, m
- M_u = amount of uranium in the particle at time t , moles
- M_{uo} = initial amount of uranium present in particles, moles

Refer to section 2 (Theoretical background) for the derivation of equation 1.1.

If initial particles from which uranium is leached are not of the same size but have a certain particle size distribution $f(l_o)$, the rate of uranium leaching from the particles is given by equation 1.2 below (Comninou, 1985; Crundwell, 1985; Dry, 1984).

$$\frac{dM_u}{dt} = -k \int_0^l \varphi\gamma \frac{F_o}{\rho l_o} \left(\frac{M_u}{M_{uo}} \right)^{\frac{2}{3}} f(l_o) dl_o \quad (1.2)$$

A leaching model developed in accordance with equation 1.1 or equation 1.2 is termed a fundamental model; build from fundamental principles and describable mathematical relationships governing the leaching process. It is also possible to develop models without using fundamental principles i.e. numerical and empirical models. Fundamental models offer a high level of confidence in their use relative to empirical models. Other models such as

those developed from empirical observations rather than describable mathematical relationships are prone to failure should the system orientation change. The system orientation here refers to the number of operational leach tanks, the point of feed introduction, agitation system, leach reactants and any other components and factors making up the leach process. However, for systems where the setup is not expected to change, empirical models are powerful decision making tools, are faster to develop and simple. Levenspiel (1972) stated that a good model should give a close representation of reality without too many mathematical complexities. Therefore in constant orientation systems, fundamental and empirical models will complement each other in effective decision making.

Numerical and theoretical models describing leaching operations are of significant importance. The sudden slump of uranium prices experienced recently calls for flexibility in process operation to either reduce operating costs or to increase revenue. The slump in uranium prices is a result of the nuclear disaster that occurred in Fukushima, Japan in March 2011. As a result of the tsunami initiated nuclear accident, several countries (Germany, Switzerland, Taiwan, Italy, France, and Belgium) opted to phase out nuclear power while others even deemed it illegal (Bryndza, 2012). Some of the countries which were planning to build nuclear reactors delayed construction cycles (China) while others (Philippines, Morocco, Israel, Venezuela, Uruguay, and Kuwait) suspended their nuclear plans (Bryndza, 2012). Flexibility in process operation will enable industrial uranium plants to remain economical even in events of sudden changes in the uranium market.

The flexibility to operate differently can be facilitated by the availability of predictive tools. Mathematical tools can be used to identify new process operating philosophies, sources of process inefficiencies and can be integrated with consumables costs to minimize operating

costs. In response to difficult market conditions, a processing facility may opt to increase production or cut back on consumption of certain consumables. Mathematical models which predict the response of a process to new constraints will guide plant operators in making crucial decisions. In order to increase production, a leaching facility made up of leaching tanks in series can either increase the feed rate by increasing pumping capacity or can simply take one tank offline to shorten the residence time. Identifying the most feasible option lies in the availability of models that can accurately quantify the impacts of different operating conditions on the leaching process.

The most recent models on uranium reactive processes focus on averting and remediating environmental impacts of uranium contamination. In many of these models, the emphasis has been placed on modelling surface and ground water pollution from uranium tailings and spent fuel disposals (Haile & Merkel, 2013; Cachoir, et al., 2003; Shoesmith & Sunder, 1991; Mason, et al., 1997; Park & Lee, 1996). The dissolution of uranium into large bodies of water and soil differ considerably from industrial leaching operations (especially agitated leaching). Thus, models which have been developed for ground water dissolution and transport within soils cannot be adapted to industrial leaching operations. Separate models need to be developed for industrial leaching operations where faster leaching reactions and aggressive leaching conditions are required.

There are however several researchers who have studied uranium dissolution kinetics and developed leaching models for industrial uranium leaching processes. Different types of industrial uranium leaching models have been developed, such as solubility based dissolution model (Shoesmith & Sunder, 1991), electrochemistry based dissolution (Shoesmith & Sunder, 1991; Peper, et al., 2004), kinetic models (Vetter, et al., 1989; Shoesmith & Sunder, 1991),

and dynamic models (Vetter, et al., 1989). The application of these models to this present research is limited by the fact that they were developed for uraninite (UO_2) and not for the carnotite uranium mineralisation of interest in this research. However, the approach used in these industrial uranium leaching models can be applied to carnotite ($\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$) leaching.

1.2. RESEARCH PROBLEM

The aim of this research was to develop empirical and fundamental models that can describe the kinetics (rate) of carbonate leaching of a carnotite uranium ore, $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$, using leaching plant data from an industrial uranium carbonate leaching facility.

1.3. RESEARCH OBJECTIVES

The objectives of this research are:

- To develop empirical and fundamental models describing the rate of carbonate leaching of a carnotite uranium ore.
- To utilise developed empirical and theoretical models to predict the performance of a carbonate uranium leaching process.
- To develop predictive tools for leaching processes based on empirical and theoretical modelling of alkaline leaching reactions.

1.4. RESEARCH METHODOLOGY

Developing mathematical models require large sets of data. It is time consuming and costly to produce a large set of data from leaching experiments. Thus leach profiles as reported by on-site laboratory of an existing alkaline leaching plant were used in model development. These

leach profiles give the amount of uranium in the ore exiting from several leach tanks. If mathematical models developed in this manner are deemed accurate and reliable, their application can be tested on existing processes. However, if models developed from plant data are in-accurate or un-reliable, controlled leach experiments would need to be carried out and the results used to develop models.

1.5. REPORT LAYOUT

This dissertation comprises of 6 chapters namely; introduction, theoretical background, literature review, experimental procedures, results and discussion, conclusions, and recommendations. Chapter 1 consists of a general introduction to modelling of leaching processes and an overview of existing leaching models. Chapter 2 consists of theoretical treatments which led to the development of fundamental leaching models. Chapter 3 outlines different types of mathematical models as found in literature. Chapter 4 highlights data collection and treatment procedure used this research. Chapter 5 consists of results and discussions. Chapter 6 contains the conclusions drawn from the results in Chapter 5 while Chapter 7 consists of recommendations.

CHAPTER 2

2. THEORETICAL BACKGROUND

Leaching processes are governed by differential equations that represent mass balances (Vetter, et al., 1989) of the leaching system, combined with reaction kinetics. Differential equations governing leaching operations are developed from mathematical representation of the leaching process. These differential equations lead to the development of a fundamental leaching model. In this chapter, the necessary mathematical expressions which led to the fundamental leaching model are established.

2.1. DERIVATION OF THE LEACHING MODEL

Many authors such as Comninou (1985), Crundwell (1985) and Dry (1984) all developed leaching models based on the shrinking core particle model where leaching takes place on the particle surface only. Based on the shrinking core model, the reaction first occurs on the outer layer of a particle before moving into the interior of the particle (Levenspiel, 1972). Development of these models as found in literature assumes that reaction products do not form a layer around particles' surfaces that would affect the rate of the reaction. Levenspiel (1972) however developed equations which can be used to confirm whether products form a rate limiting layer around leached particles. Derivation of the shrinking core leaching model is illustrated below.

Considering uranium containing particles leaching in solution according to a shrinking core model with no resistance caused by diffusion through the product layer, the rate of change of uranium from a particle is given by (Levenspiel, 1972):

$$\frac{dM_u}{dt} = -k\varphi A \quad (2.1)$$

Where: k = reaction rate constant, hour⁻¹
 φ = dimensionless factor that accounts for solution condition effects
 A = surface area of the particle, m²
 M_u = Amount of uranium in the particle at time t , moles

Often the particle area is expressed in terms of the particles' shape factor (γ) and the characteristic size (ℓ). This paves way for the area of the particles to be expressed in terms of the characteristic volume (v) and thus the density of the particles (ρ) (Levenspiel, 1972).

$$\gamma = \frac{A}{\ell^2} \quad (i)$$

$$v = \ell^3 \quad (ii)$$

$$\ell = v^{1/3} \quad (iii)$$

$$v = \frac{m}{\rho} \quad (iv)$$

$$A = \gamma \ell^2 = \gamma v^{2/3} = \gamma \left(\frac{m}{\rho}\right)^{2/3} \quad (v)$$

Thus the amount of uranium, M_u left in a particle at any given time will be given by the following expression:

$$\frac{dM_u}{dt} = -k\varphi A = -k\varphi\gamma \left(\frac{M_u}{\rho}\right)^{2/3} \quad (2.2)$$

The assumption that the product layer formed around the particles does not affect the rate of reaction leads to the conclusion that the mass or molar density of uranium will remain constant during leaching (Dry, 1984). Thus;

$$\rho = \frac{M_{uo}}{l_o^3} \quad (vi)$$

Therefore;

$$\frac{dM_u}{dt} = -k\phi\gamma \left(\frac{l_o^3}{M_{uo}}\right)^{2/3} (M_u)^{2/3} \quad (2.3)$$

Now if you have an N number of particles with an average shape factor γ of total mass F_o leaching, the total rate of change of the amount of uranium in particles will be given by:

$$\frac{dM_u}{dt} = -k\phi\gamma N \left(\frac{l_o^3}{M_{uo}}\right)^{2/3} (M_u)^{2/3} \quad (2.4)$$

The number of particles can be calculated from the total mass of particles and the volume of one particle (unit volume), assuming particles are of uniform size. The unit volume of the particles is in turn calculated from the density and characteristic size of the particles according to equation (ii). Thus;

$$N = \frac{F_o}{\rho l_o^3} \quad (vii)$$

Now, the rate of leaching of uranium from the particles will be;

$$\begin{aligned}\frac{dM_u}{dt} &= -k\varphi\gamma N \left(\frac{l_o^3}{M_{uo}}\right)^{\frac{2}{3}} (M_u)^{\frac{2}{3}} \\ &= -k\varphi\gamma \frac{F_o}{\rho l_o^3} \left(\frac{l_o^3}{M_{uo}}\right)^{\frac{2}{3}} (M_u)^{\frac{2}{3}}\end{aligned}\quad (viii)$$

$$= -k\varphi\gamma \frac{F_o}{\rho l_o^3} (l_o^3)^{\frac{2}{3}} \left(\frac{1}{M_{uo}}\right)^{\frac{2}{3}} (M_u)^{\frac{2}{3}} \quad (ix)$$

$$= -k\varphi\gamma \frac{F_o}{\rho l_o^3} l_o^2 \left(\frac{M_u}{M_{uo}}\right)^{\frac{2}{3}} \quad (xiv)$$

$$= -k\varphi\gamma \frac{F_o}{\rho l_o^3} \left(\frac{M_u}{M_{uo}}\right)^{\frac{2}{3}} \quad (xv)$$

Therefore;

$$\frac{dM_u}{dt} = -k\varphi\gamma \frac{F_o}{\rho l_o^3} \left(\frac{M_u}{M_{uo}}\right)^{\frac{2}{3}} \quad (2.5)$$

The solution conditions factor (φ) changes with progression of some leaching processes such as oxidative leaching as reported by Dry (1984), Crundwell (1985), and Comninos (1985). If the solution conditions change with time, equation 2.5 is integrated iteratively using computer programs. At the industrial carbonate leaching plant studied:

- the leaching process is highly temperature driven;
- there is no significant reduction in temperature from one tank to the other;
- pH, Na_2CO_3 and NaHCO_3 concentrations are constant between tanks;

There is a possibility that the solution conditions factor can be constant. If the solutions condition factor does not change with leaching time, equation 2.5 will be an ordinary differential equation that can be integrated analytically.

Furthermore, equation 2.5 gives the rate of leaching of uranium from particles of the same size. If initial particles are not of the same size but having a certain particle size distribution, equation 2.5 can be further modified to conform to this situation. If you consider particles with a size distribution given in Figure 1 being leached; the rate of uranium from particles of size l_1 , l_2 , l_3 and l_4 will be given by:

$$\frac{dM_{u1}}{dt} = -k \int_0^{l_1} \phi \gamma \frac{F_o}{\rho l_o} \left(\frac{M_u}{M_{uo}} \right)^{\frac{2}{3}} f(l_o) dl_o \quad (2.5.1)$$

$$\frac{dM_{u2}}{dt} = -k \int_{l_1}^{l_2} \phi \gamma \frac{F_o}{\rho l_o} \left(\frac{M_u}{M_{uo}} \right)^{\frac{2}{3}} f(l_o) dl_o \quad (2.5.2)$$

$$\frac{dM_{u3}}{dt} = -k \int_{l_2}^{l_3} \phi \gamma \frac{F_o}{\rho l_o} \left(\frac{M_u}{M_{uo}} \right)^{\frac{2}{3}} f(l_o) dl_o \quad (2.5.3)$$

$$\frac{dM_{u4}}{dt} = -k \int_{l_3}^{l_4} \phi \gamma \frac{F_o}{\rho l_o} \left(\frac{M_u}{M_{uo}} \right)^{\frac{2}{3}} f(l_o) dl_o \quad (2.5.4)$$

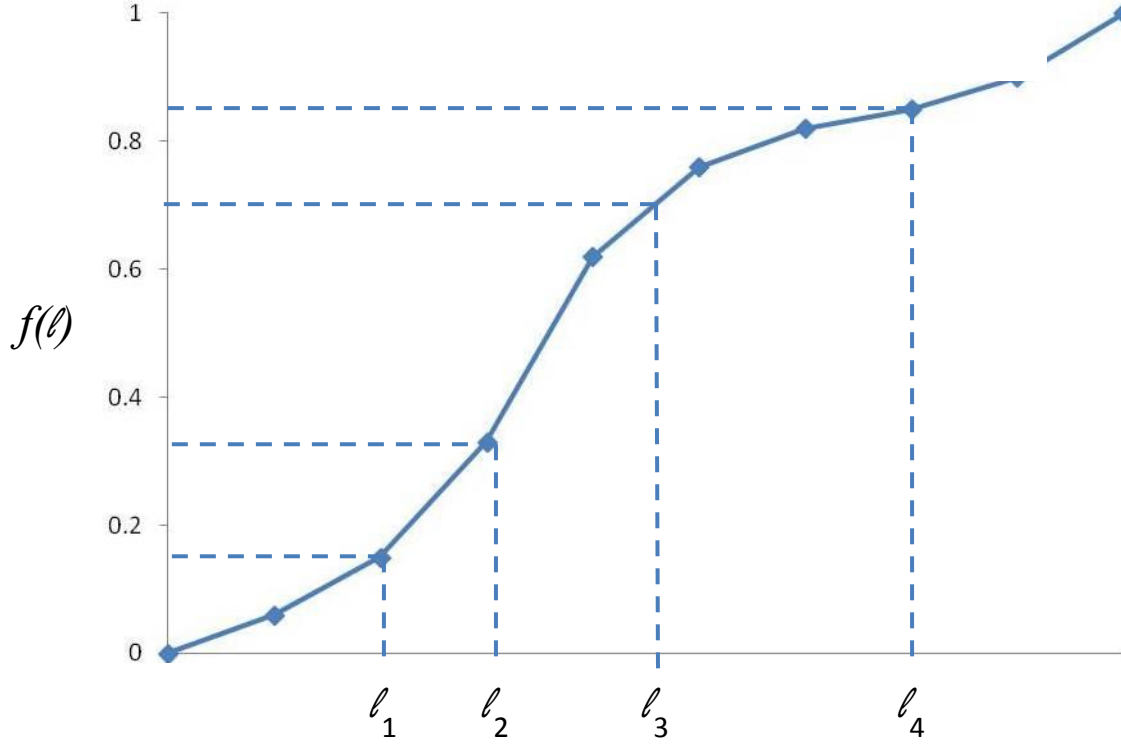


Figure 1: Typical Particle Size Distribution

If the amount of leachable uranium does not depend on particle size, the value M_{uo} will be constant in equations 2.5.1 to 2.5.4. If however the initial content of uranium in particles depends on particle size, M_{uo} values will differ between equation 2.5.1 and 2.5.4. M_{uo} values will thus be M_{uoi} for particles of size i . The total rate of leaching of uranium from all particles will be the summation of the individual particle sizes' leaching rates according to equation 2.6.

$$\sum \frac{dM_u(l_{oi})}{dt} = \frac{d}{dt} \sum M_u(l_{oi}) \quad (2.6)$$

The term $\gamma \frac{F_o}{\rho l_o}$ in equation 2.5 represents the surface area (A_o) of particles being leached. The reaction rate for non-oxidative leaching can be represented by the Arrhenius rate expression as $k = k' \exp\left(\frac{-E_a}{RT}\right)$. Thus equation 2.5 can be written as:

$$\frac{dM_u}{dt} = -k' \phi A_o \exp\left(\frac{-E_a}{RT}\right) \left(\frac{M_u}{M_{uo}}\right)^{\frac{2}{3}} \quad (i)$$

$$\therefore \frac{dM_u}{dt} = -\alpha \exp\left(\frac{-E_a}{RT}\right) \left(\frac{M_u}{M_{uo}}\right)^{\frac{2}{3}} \quad (2.7)$$

Where: E_a = activation energy, $\text{Jmol}^{-1}\text{K}^{-1}$
 k' = frequency factor
 R = universal gas constant, $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$
 T = temperature, Kelvin

Other researchers (Dry, 1984; Comninos, 1985; Crundwell, 1985) who have studied leaching kinetics used computational tools to find a solution of equation 2.7. Instead of finding a numerical solution to equation 2.7, an alternative expression has been derived in this research. The amount of uranium remaining in particles at any time can be expressed in terms of fractional conversion according to the derivations below.

$$X = \frac{M_{uo} - M_u}{M_{uo}} = 1 - \frac{M_u}{M_{uo}} \quad (i)$$

$$\frac{M_u}{M_{uo}} = 1 - X \quad (ii)$$

$$M_u = M_{uo}(1 - X) \quad (iii)$$

$$dM_u = -M_{uo}dX \quad (iv)$$

Where: X = fractional conversion of uranium

M_{uo} = Initial amount of uranium in particles (moles)

M_u = Amount of uranium in particles at any time (moles)

Substituting expressions *iii* and *iv* above into equation 2.7 yields the following expression:

$$M_{uo} \frac{dX}{dt} = \alpha \exp\left(\frac{-E_a}{RT}\right) (1 - X)^{\frac{2}{3}} \quad (2.8)$$

$$\frac{dX}{dt} = \frac{\alpha}{M_{uo}} \exp\left(\frac{-E_a}{RT}\right) (1 - X)^{\frac{2}{3}} \quad (2.8.1)$$

$$\frac{dX}{(1-X)^{2/3}} = \frac{\alpha}{M_{uo}} \exp\left(\frac{-E_a}{RT}\right) dt \quad (2.8.2)$$

Equation 8.2 can be integrated by substitution by letting $u = 1 - X$ and thus $du = -dX$.

Therefore;
$$-\int \frac{du}{u^{2/3}} = \int \frac{\alpha}{M_{uo}} \exp\left(\frac{-E_a}{RT}\right) dt \quad (i)$$

$$-\int u^{-2/3} du = \int \frac{\alpha}{M_{uo}} \exp\left(\frac{-E_a}{RT}\right) dt \quad (ii)$$

This is then evaluated between the limits $u = 0$ and $u = u$; and between $t = 0$ and $t = t$.

$$-3u^{1/3} \Big|_0^u = \frac{\alpha}{M_{uo}} \exp\left(\frac{-E_a}{RT}\right) t \Big|_0^t \quad (iii)$$

Now, substitute for $u = 1 - X$ and evaluate between the limits $X = 0$ and $X = X$

$$-3(1 - X)^{1/3} \Big|_0^X = \frac{\alpha}{M_{uo}} \exp\left(\frac{-E_a}{RT}\right) t \quad (iv)$$

$$(1 - X)^{1/3} \Big|_0^X = -\frac{\alpha}{3M_{uo}} \exp\left(\frac{-E_a}{RT}\right) t \quad (v)$$

$$(1 - X)^{1/3} - 1 = -\frac{\alpha}{3M_{uo}} \exp\left(\frac{-E_a}{RT}\right) t \quad (vi)$$

$$(1 - X)^{1/3} = 1 - \frac{\alpha}{3M_{uo}} \exp\left(\frac{-E_a}{RT}\right) t \quad (vii)$$

$$1 - X = \left(1 - \frac{\alpha}{3M_{uo}} \exp\left(\frac{-E_a}{RT}\right) t\right)^3 \quad (viii)$$

$$X = 1 - \left(1 - \frac{\alpha}{3M_{uo}} \exp\left(\frac{-E_a}{RT}\right) t\right)^3 \quad (ix)$$

$$X = 1 - \left(1 - \beta \exp\left(\frac{-E_a}{RT}\right) t\right)^3 \quad (2.9)$$

Thus equation 2.9 gives the variation of fractional conversion of uranium as a function of leaching time.

2.2. DERIVATION OF LEACHING RESISTANCE TERMS

There are several factors which limit the rate of uranium leaching from particles. Resistances to leaching are a result of different mechanisms which take place in succession (Levenspiel, 1972) during leaching. These mechanisms are summarised from Levenspiel (1972) below.

- Diffusion of liquid reactant through the liquid film surrounding the particle (Film resistance).
- Diffusion of liquid reactant through ash layer to the surface of the un-reacted particle.
- Reaction between the liquid and uranium at the particle surface.

- Diffusion of liquid or gaseous products through the ash layer to the surface of the particles.
- Diffusion of liquid or gaseous products through the liquid film into the main liquid body.

There are instances where some of these resistances do not happen. These resistances differ in magnitude and the highest resistance is classified as the rate limiting step. Again the type of rate limiting steps depends on system configuration and the type of reactions occurring. For agitated systems, often the film resistance does not limit the rate of leaching (Rao et. al, 2010). Also when there are no liquid or gaseous reaction products and for irreversible liquid-solid reactions, ash layer and liquid film diffusions do not limit the rate of leaching (Levenspiel, 1972). The reaction stoichiometry in irreversible leaching of uranium from particles can be represented according to equation 2.10 below (Levenspiel, 1972).



2.2.1. DIFFUSION THROUGH LIQUID FILM RESISTANCE

The rate of change of the amount of fluid (A) and uranium in particles (U) per unit external particle surface area is as given below (Levenspiel, 1972).

$$-\frac{1}{4\pi R^2} \frac{dN_u}{dt} = -\frac{b}{4\pi R^2} \frac{dN_A}{dt} = bk_l C_{Al} \quad (2.11)$$

Where: k_l = Mass transfer coefficient between the fluid and the solid particle, cm/s
 C_{Al} = Liquid reactant concentration in the main body of fluid, mol/cm³

N_A = Number of moles of liquid reactant

N_u = Number of moles of uranium in solid particles

The number of moles of uranium, N_u present at any time in a solid particle is;

$$N_u = \rho_u V_p$$

$$N_u = \rho_u \frac{4}{3} \pi r_c^3 \quad (2.12)$$

Where: ρ_u = Molar density of uranium in the solid particle, mol/m³

V_p = Volume of a particle, m³

r_c = Radius of the un-reacted particle core, m

Thus the rate of disappearance of uranium from the solid particle is obtained by differentiating equation 2.12 to obtain the following expression.

$$-dN_u = -\rho_u 4\pi r_c^2 dr_c \quad (2.13)$$

Substituting equation 2.11 into equation 2.13 yields (Levenspiel, 1972):

$$-\frac{1}{4\pi R^2} \frac{dN_u}{dt} = bk_l C_{Al} \quad (2.14)$$

$$-\frac{\rho_u r_c^2}{R^2} \frac{dr_c}{dt} = bk_l C_{Al} \quad (2.15)$$

Integration of equation 2.15 gives the variation of the un-reacted core of a solid particle radius with time as follows:

$$-\frac{\rho_u}{R^2} \int_R^{r_c} r_c^2 dr_c = bk_l C_{Al} \int_0^t dt \quad (i)$$

$$-\frac{\rho_u}{3R^2} r_c^3 \Big|_R^{r_c} = bk_l C_{Al} t \quad (ii)$$

$$-\frac{\rho_u}{3R^2} (r_c^3 - R^3) = bk_l C_{Al} t \quad (iii)$$

$$-\frac{\rho_u}{3R^2} R^3 \left(\frac{r_c^3}{R^3} - 1 \right) = t \quad (iv)$$

$$\frac{\rho_u R}{3bk_l C_{Al}} \left[1 - \left(\frac{r_c}{R} \right)^3 \right] = t \quad (2.16)$$

Equation 2.16 gives the variation of the un-reacted core particle radius with time. The time required for complete reaction and thus disappearance of the particle (t^*) can be obtained by letting $r_c = 0$ in equation 2.16 to get (Levenspiel, 1972):

$$\frac{\rho_u R}{3bk_l C_{Al}} = t^* \quad (2.17)$$

By dividing equation 2.16 with equation 2.17 yields the relationship between the un-reacted particle core radius with fractional time for complete conversion according to equation 15 (Levenspiel, 1972).

$$\frac{t}{t^*} = 1 - \left(\frac{r_c}{R} \right)^3 \quad (2.18)$$

Levenspiel (1972) has shown how the right hand side of equation 2.18 can be converted to a function of fractional conversion. If X_u is the fraction of converted particle, then $1 - X_u$ is the fraction of un-converted particle. This can be expressed in terms of particle volume as:

$$1 - X_u = \frac{\text{Volume of un-reacted core}}{\text{Initial volume of particle}} \quad (i)$$

$$1 - X_u = \frac{\frac{4}{3}\pi r_c^3}{\frac{4}{3}\pi R^3} \quad (ii)$$

$$1 - X_u = \left(\frac{r_c}{R}\right)^3 \quad (2.19)$$

Substituting $\left(\frac{r_c}{R}\right)^3$ from equation 2.19 into equation 2.18 gives the relationship between fractional conversion and the fractional time for complete conversion as shown below.

$$\frac{t}{t^*} = X_u \quad (2.20)$$

Thus, if the rate limiting mechanism is diffusion of liquid reactants through the liquid film surrounding the particle, a plot of fractional conversion versus time will yield a straight line.

2.2.2. DIFFUSION THROUGH ASH LAYER RESISTANCE

When diffusion of the liquid reactant through the layer of ash to the particle's un-reacted core is the rate limiting step, the rate of reaction depends on the rate of diffusion of the liquid to the un-reacted core (Levenspiel, 1972). The flux of the liquid reactant at any location namely the reaction surface, the ash layer and exterior of the particle is constant (Levenspiel, 1972) and is represented mathematically as follows:

$$-\frac{dN_A}{dt} = 4\pi r^2 J_A = 4\pi R^2 J_{As} = 4\pi r_c^2 J_{Ac} \quad (2.21)$$

Where: J_A = diffusion flux of liquid reactant anywhere in the particle, mol/cm²s
 J_{As} = diffusion flux of liquid reactant through the particle's exterior
 J_{Ac} = diffusion flux of liquid reactant through the un-reacted core, mol/cm²s

The diffusion flux of the liquid reactant is given by Fick's laws of diffusion. Miles (2008) described diffusion as a phenomenon in which species move into or through a specie in order to minimise the chemical potential. Fick's first law of diffusion applies to scenarios where two species diffuse in opposite directions in same amounts and is given by:

$$J = -D \frac{dC_A}{dr}$$

Where: D = Diffusion coefficient of the liquid in the ash layer, cm²/s
 C_A = Concentration of the liquid reactant in the ash layer, mol/cm³

Substituting the expression of Fick's first law of diffusion into equation 2.21 yields the rate of disappearance of the liquid reactant as:

$$-\frac{dN_A}{dt} = 4\pi r^2 D \frac{dC_A}{dr} \quad (2.22)$$

Equation 2.22 is integrated with the following boundary conditions:

$$\text{At } r = R \quad C_A = C_{As}$$

$$\text{At } r = r_c \quad C_A = C_{Ac} = 0$$

Where: C_{As} = Concentration of liquid reactant at the particle surface, mol/cm³

C_{Ac} = Concentration of liquid reactant at the reaction surface, mol/cm³

The integration of equation 2.22 is carried out below, after separating necessary variables.

$$-\frac{dN_A}{dt} \int_R^{r_c} \frac{dr}{r^2} = 4\pi D \int_{C_{As}}^0 dC_A \quad (i)$$

$$-\frac{dN_A}{dt} \left[-\frac{1}{r} \right]_R^{r_c} = -4\pi D C_{As} \quad (ii)$$

$$-\frac{dN_A}{dt} \left[\frac{1}{r} \right]_R^{r_c} = 4\pi D C_{As} \quad (iii)$$

$$-\frac{dN_A}{dt} \left(\frac{1}{r_c} - \frac{1}{R} \right) = 4\pi D C_{As} \quad (2.23)$$

Now using equation 2.14 and equation 2.15, equation 2.23 can be transformed to give the rate of change in the amount of uranium present in the particles as given below.

$$-\rho_u 4\pi r_c^2 \left(\frac{1}{r_c} - \frac{1}{R} \right) \frac{dr_c}{dt} = 4b\pi D C_{As} \quad (i)$$

$$-\rho_u \int_R^{r_c} \left(\frac{1}{r_c} - \frac{1}{R} \right) r_c^2 dr_c = bD C_{As} \int_0^t dt \quad (ii)$$

$$-\rho_u \int_R^{r_c} \left(r_c - \frac{r_c^2}{R} \right) dr_c = bD C_{As} \int_0^t dt \quad (iii)$$

$$-\rho_u \left(\frac{r_c^2}{2} - \frac{r_c^3}{3R} \right) \Big|_R^{r_c} = bD C_{As} t \quad (iv)$$

$$-\rho_u \left[\left(\frac{r_c^2}{2} - \frac{r_c^3}{3R} \right) - \left(\frac{R^2}{2} - \frac{R^3}{3R} \right) \right] = bDC_{As}t \quad (v)$$

$$-\rho_u \left[\frac{r_c^2}{2} - \frac{r_c^3}{3R} - \frac{R^2}{2} + \frac{R^2}{3} \right] = bDC_{As}t \quad (vi)$$

$$-\rho_u \left[\frac{r_c^2}{2} - \frac{r_c^3}{3R} - \frac{R^2}{6} \right] = bDC_{As}t \quad (vii)$$

$$-\frac{\rho_u R^2}{6} \left[\frac{3r_c^2}{R^2} - \frac{2r_c^3}{3R^3} - \frac{R^2}{6R^2} \right] = bDC_{As}t \quad (viii)$$

$$-\frac{\rho_u R^2}{6} \left[3 \left(\frac{r_c}{R} \right)^2 - 2 \left(\frac{r_c}{R} \right)^3 - 1 \right] = bDC_{As}t \quad (ix)$$

$$-\frac{\rho_u R^2}{6} \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right] = bDC_{As}t \quad (x)$$

Thus, the variation of the un-reacted core of a solid particle radius with time is as follows:

$$\frac{\rho_u 6R^2}{bDC_{As}} \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right] = t \quad (2.24)$$

The time required for complete reaction and thus disappearance of the particle (t^*) can be obtained by letting $r_c = 0$ in equation 2.24 to get:

$$t^* = \frac{\rho_u R^2}{6bDC_{As}} \quad (2.25)$$

By dividing equation 2.24 with equation 2.25 yields the relationship between the un-reacted particle core radius with fractional time for complete conversion (equation 2.26).

$$\frac{t}{t^*} = 1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \quad (2.26)$$

Now, recall that the fractional conversion is given by equation 16 as:

$$1 - X_u = \left(\frac{r_c}{R}\right)^3$$

Substituting $\left(\frac{r_c}{R}\right)^3$ from equation 2.19 into equation 2.26 gives the relationship between fractional conversion and the fractional time for complete conversion (Levenspiel, 1972) as shown below.

$$\frac{t}{t^*} = 1 - 3(1 - X_u)^{2/3} + 2(1 - X_u) \quad (2.27)$$

Thus, if the rate limiting mechanism is diffusion of liquid reactants through the layer of ash surrounding a particle's un-reacted core, a plot of the right hand side of equation 2.27 versus time will yield a straight line.

2.2.3. CHEMICAL REACTION RESISTANCE

When chemical reaction is the rate limiting step, the concentration of the liquid reactant at the reaction surface is the same as in the bulk fluid (Levenspiel, 1972). Also, the liquid reactant's concentration is not affected by the presence of a liquid film or by the layer of ash (Levenspiel, 1972). The rate of disappearance of the liquid reactant and uranium in the particles per unit surface area of the particle is given by (Levenspiel, 1972):

$$-\frac{1}{4\pi r_c^2} \frac{dN_u}{dt} = -\frac{b}{4\pi r_c^2} \frac{dN_A}{dt} = b k_s C_{Al} \quad (2.28)$$

Where: k_s = First order rate constant for the surface reaction, cm/s

C_{Al} = Liquid reactant concentration in the main body of fluid, mol/cm³

Thus, substituting dN_u from equation 2.13 into equation 2.28 yields the following expression:

$$-\frac{1}{4\pi r_c^2} - \rho_u 4\pi r_c^2 \frac{dr_c}{dt} = bk_s C_{Al} \quad (i)$$

Thus; $-\rho_u \frac{dr_c}{dt} = bk_s C_{Al}$ (2.29)

Integration of equation 2.29 results in the following expressions:

$$-\rho_u \int_R^{r_c} dr_c = bk_s C_{Al} \int_0^t dt \quad (i)$$

$$-\rho_u r_c \Big|_R^{r_c} = bk_s C_{Al} t \quad (ii)$$

$$-\rho_u (r_c - R) = bk_s C_{Al} t \quad (iii)$$

Thus, the variation of the un-reacted core of a solid particle radius with time as follows:

$$\rho_u (R - r_c) = bk_s C_{Al} t \quad (2.30)$$

The time required for complete reaction and thus disappearance of the particle (t^*) can be obtained by letting $r_c = 0$ in equation 2.30 to get:

$$\frac{\rho_u R}{bk_s C_{Al}} = t^* \quad (2.31)$$

By dividing equation 2.30 with equation 2.31 yields the relationship between the un-reacted particle core radius with fractional time for complete conversion (equation 2.32).

$$\frac{t}{t^*} = 1 - \left(\frac{r_c}{R}\right) \quad (2.32)$$

Substituting $\left(\frac{r_c}{R}\right)^3$ from equation 16 into equation 2.26 gives the relationship between fractional conversion and the fractional time for complete conversion as shown below.

$$\frac{t}{t^*} = 1 - (1 - X_u)^{1/3} \quad (2.33)$$

Thus, if the rate limiting mechanism is the chemical reaction, a plot of the right hand side of equation 2.33 versus time will be a straight line.

2.2.4. REMARKS

Expressions for time versus conversion relationship for the various resistances to leaching developed in section 2.2 accounted for a single resistance occurring at a time. In reality, sometimes these resistances happen simultaneously or one after the other. When resistances occur simultaneously, the overall resistance to leaching is the summation of the individual leaching resistances. It can also happen that during leaching, one resistance controls the leaching rate and as time progresses another resistance comes into play. The above statements corroborate Levenspiel (1972) who stated that:

- For a constant size particle the liquid film resistance remains unchanged.

- Resistance due to reaction increases with decreasing un-reacted core radius.
- Resistance due to the presence of an ash layer does not exist at the start but surfaces and progress more and more with time as the ash layer builds up.

Resistances to leaching are all linear in concentration and act in series (Levenspiel, 1972). Thus the time taken to reach a certain conversion with multiple resistances limiting the rate of leaching is given by equation 2.34. The time required to reach complete conversion of the particle with multiple resistances is given by equation 2.35.

$$t_{total} = t_{film} + t_{ash} + t_{reaction} \quad (2.34)$$

$$t^*_{total} = t^*_{film} + t^*_{ash} + t^*_{reaction} \quad (2.35)$$

2.3. REACTION RATE AND ACTIVATION ENERGY

The temperature dependence of chemical reaction is modelled through an Arrhenius equation, which is an empirical correlation of the temperature effect in chemical reactions. It is named after Svante August Arrhenius, a Swedish scientist who proposed the equation from the work of a Dutch Chemist, Jacobus Van't Hoff in 1889 (the Nobel prize, 2013). The reaction rate constant is given by equation 2.36.

$$k = k' e^{-E_a/RT} \quad (2.36)$$

Where: k = reaction rate constant, s^{-1}

k' = frequency factor

R = universal gas constant, $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$

T = absolute temperature, Kelvin

E_a = activation energy, Jmol^{-1}

The frequency factor gives an indication of the probability of molecules to overcome the activation energy and thus have a successful reaction, while the exponential term gives an indication of the number of molecules with sufficient energy to react (Smith, 2010). For a reaction to occur reactants need to collide and collisions which result in a reaction are much fewer than the total number of collisions (Pall, 2013). The rate of collisions increases with increase in temperature and the temperature effect on reaction rate is modelled through the Arrhenius equation. Reactions with large values of activation energies have small rate constants and are thus slow (Pall, 2013).

Equation 2.36 is transformed by applying natural logarithm on both sides to yield equation 2.37. A plot of $\ln k$ versus $\frac{1}{T}$ in equation 2.37 yields a straight line with a slope $-E_a/R$ and a y-intercept $\ln k'$. This allows for graphical determination of the activation energy and the reaction frequency factor.

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln k' \quad (2.37)$$

CHAPTER 3

3. LITERATURE REVIEW

The literature review is grouped into different sections namely; uranium extraction aspects, uranium leaching reactions, aspects of predictive numerical modelling, and application of theoretical models in leaching processes. Uranium extraction aspects will specifically be discussed with reference to uranium deposits of Namibia.

3.1. URANIUM EXTRACTION ASPECTS

Uranium ores are divided into three main categories, namely; primary ores, secondary ores, and refractory ores (Connelly, 2008). The type of ore influences the processing steps to be employed. For example according to Connelly (2008), refractory ores such as davidite, brannerite and betafite are difficult to treat. The chemical formula of davidite is $(\text{La,Ce,Ca})(\text{Y,U})(\text{TiFe}^{3+})_{20}\text{O}_{38}$ while that of brannerite is $(\text{U,Ca,Ce})(\text{Ti,Fe})_2\text{O}_6$ and that of betafite is $\text{U,Ca,Ce}(\text{Ti,Fe})_2\text{O}_6\text{OH}$ (Weinrich, 2013). In order to be leached, refractory ores require higher leaching temperatures, greater free acid and oxidant concentrations, and longer leaching times (Reptile Uranium, 2012). The commonly mined uranium ores are uraninite (UO_2) and pitchblende which are primary ores (Connelly, 2008). Pitchblende is a non-crystallized type of uraninite associated with silver and is interchangeably referred to as uraninite (Rogers, 1946) with a chemical formula UO_2 .

Uranium is extracted from its ores by dissolution (leaching) using either an acid or an alkaline solution as a complexing agent prior to downstream concentration and purification.

This is applicable to all three main categories of uranium ores (primary, secondary and refractory ores). A complexing agent is simply a substance that forms soluble complex compounds with other substances. The choice of using acidic or alkaline leaching is dictated by the carbonate content of the ore and each choice has its own advantages and disadvantages. Uranium ores with high carbonate content are associated with unfavorable acid consumptions (International Atomic Energy Agency, 2001) and thus the use of alkaline leaching is favored. Acid leaching commonly makes use of sulphuric acid to dissolve uranium from its typical ores. It produces rapid dissolution kinetics but at the same time is less selective (Lunt, 2006) and thus requiring more downstream purification steps. Alkaline leaching on the other hand makes use of a carbonate (sodium carbonate, sodium bicarbonate, sodium hydrogen carbonate or carbon dioxide) to dissolve uranium (International Atomic Energy Agency, 2001; Connelly, 2008). Alkaline leaching has slower dissolution kinetics requiring long leaching times but is more selective to uranium (Weil, 2012) and less upfront purification steps are required.

Uranium as found in commonly mined ores occurs in different oxidation states, mostly the tetravalent and hexavalent state. Uranium in the hexavalent state (U^{6+}) is directly soluble in an acidic or alkaline medium but uranium in a tetravalent state (U^{4+}) is not directly soluble. The hexavalent uranium in the ore can be UO_3 or a combination of uranium oxides with other compounds, while the tetravalent uranium is UO_2 and the relative proportions of the two vary. Figure 2 shows an Eh-pH diagram of a U-O-H system at 25°C and 1 atm, using different methods of constructing Eh-pH diagrams (Takeno, 2005). Eh-pH diagrams depict the dominant aqueous species and stable solid phases on a plane defined by the redox potential and pH axes (Takeno, 2005). Uranium deposits with tetravalent uranium include

uraninite, uranothorite and coffinite while those with hexavalent uranium include carnotite (Venter & Boylett, 2009; Lunt, et al., 2007).

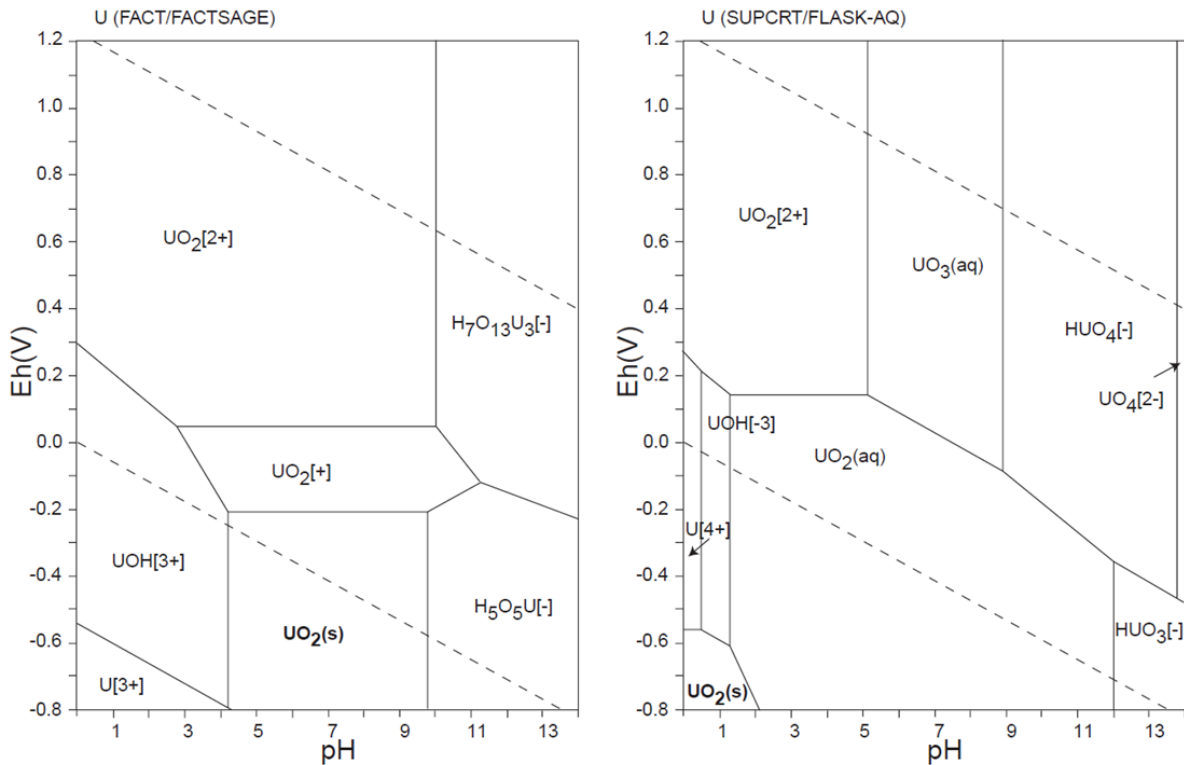


Figure 2: Eh-pH diagram of a U-O-H system at 25°C and 1 atm (Takeno, 2005)

In order to attain significant uranium recoveries from the ore, uranium in the tetravalent form is converted to a hexavalent form using an oxidant. Each type of oxidant has its advantages and disadvantages and its application depends on the type of ore to be treated, availability and cost effectiveness of using that particular oxidant. Oxidants that have been commercially applied to acidic uranium leaching include ferric ions ($\text{Fe}_2(\text{SO}_4)_3$), manganese dioxide (MnO_2), sodium chlorate (NaClO_3), hydrogen peroxide (H_2O_2), oxygen, and sulfur dioxide-air mixtures (Venter & Boylett, 2009). An extensive list of advantages and disadvantages of these oxidants is outlined by Venter and Boylett (2009) and are beyond the scope of this literature review. Hydrogen peroxide, gaseous oxygen, and chlorine base salts (Hunter, 2013) are common oxidants used in alkaline leaching of uranium. Chlorine base salts such as

sodium hypochlorite and sodium chlorate however create environmental problems and negatively affect the efficiency of solvent extraction and ion exchange (Hunter, 2013).

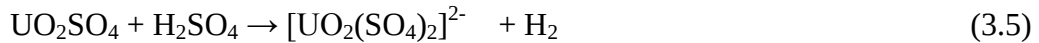
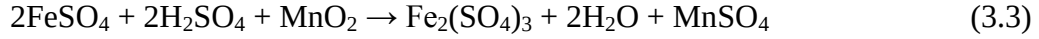
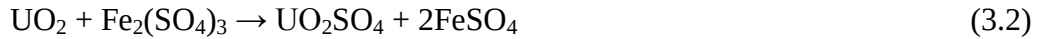
Current and future uranium mines in Namibia have various uranium mineralizations. Rossing Uranium deposits are made up of 55% of uraninite (UO_2) and 40% of beta-uranophane, $(\text{Ca}(\text{UO}_2)\text{Si}_2\text{O}_7 \cdot 6\text{H}_2\text{O})$ (Rossing Uranium, 2012; Roesener & Schreuder, 1997; Schreiber, 1996) with tetravalent uranium requiring usage of an oxidant. Rossing Uranium deposits are also made up of small quantities (<5%) of betafite, $(\text{U,Ca,Ce})(\text{Ti,Fe})_2\text{O}_6\text{OH}$ which is insoluble in acid based solutions often employed in uranium extraction (Roesener & Schreuder, 1997; Schreiber, 1996).

The Valencia Uranium deposit is made up of uranophane, $(\text{Ca}(\text{UO}_2)_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O})$ with tetravalent uranium requiring usage of an oxidant (Roesener & Schreuder, 1997; Schreiber, 1996). The Valencia deposit is also made up of uranothallite, $(\text{Ca}_2\text{U}(\text{CO}_3)_4 \cdot 10\text{H}_2\text{O})$ which cannot be dissolved in acid solutions (Roesener & Schreuder, 1997). The Langer Heinrich's uranium deposits are made up mainly of carnotite, $(\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O})$ (Venter & Boylett, 2009; Lunt, et al., 2007; Roesener & Schreuder, 1997; Schreiber, 1996) with hexavalent uranium not requiring usage of an oxidant. Trekkopje which was initially scheduled to start production in 2013 also has uranium deposits mostly made up of carnotite (Venter & Boylett, 2009; Roesener & Schreuder, 1996).

3.2. URANIUM LEACHING REACTIONS

3.2.1. ACIDIC LEACHING REACTIONS

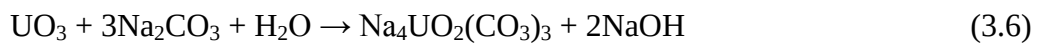
The following reactions are associated with acid based uranium leaching (International Atomic Energy Agency, 2001).

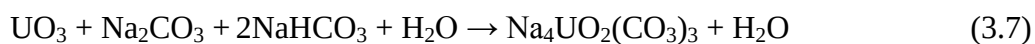


Reaction 3.1 is the dissolution of the hexavalent uranium (U^{6+}) using sulphuric acid. Reaction 3.2 involves the conversion or oxidation of tetravalent uranium (U^{4+}) to a soluble hexavalent form using ferric ions. After oxidising the tetravalent uranium, ferric ions are reduced to ferrous ions but the ferrous ions are in turn re-oxidised back to ferric ions using manganese dioxide (MnO_2) according to reaction 3.3. The primary source of iron in the leach circuit is haematite (Fe_2O_3) which is reacted with sulphuric acid to form ferric ions according to reaction 3.4. Finally reaction 3.5 is the formation of a stable soluble uranyl sulphate complex which enables downstream purification as it can be absorbed and desorbed by ion exchange resin (International Atomic Energy Agency, 2001). Rossing Uranium in Namibia operates according to reactions 3.1 to 3.5.

3.2.2. ALKALINE LEACHING REACTIONS

The following reactions describe the process of uranium extraction using sodium carbonate and sodium bicarbonate (alkalis) as leaching or complexing agents (Weil, 2012).





Reaction 3.6 is the dissolution of hexavalent uranium using sodium carbonate. Reaction 3.7 shows the dissolution of the hexavalent uranium using a combination of sodium carbonate and sodium bicarbonate. From reaction 3.6 and 3.7, it can be seen that in alkaline leaching, sodium carbonate or its combination with sodium bicarbonate react with hexavalent uranium (UO_3) to form the soluble complex $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$. Just like in acidic leaching, the tetravalent uranium compounds cannot be recovered by carbonate reactants without adding an oxidant (International Atomic Energy Agency, 2001). The tetravalent uranium (UO_2) is sometimes converted to hexavalent uranium (UO_3) using oxygen according to reaction 3.8 with subsequent dissolution into sodium carbonate.

In carnotite uranium mineralization where uranium occurs in a hexavalent state (U^{6+}), use of an oxidant is not required. Thus reaction 3.8 is not applicable to carnotite uranium ores. Leaching of uranium from carnotite occurs according to reaction 3.9 and 3.10 (Mason, et al., 1997; Dry, 2009).



Reaction 3.9 produces hydroxyl ions which increase the solution pH. When the pH of the solution rises to excessive levels, leached uranium begins to precipitate. Addition of sodium

bicarbonate (reaction 3.10) prevents the formation of hydroxyl ions and hence buffers the pH (Mattus & Torma, 1980; Nicol, 2013).

3.3. PREDICTIVE NUMERICAL MODELS

Predictive numerical models can be deemed as statistical models because they use process or observation data to build models which can be used to predict the performance of a particular system. There are at least 10 different techniques used to develop predictive models based on a system's data as observed by Gray & MacDonell (1997) in the comparison of these techniques. Table 1 gives the different techniques of developing predictive models and their applications (Gray & MacDonell, 1997).

Table 1: Numerical predictive techniques and their applications (Gray & MacDonell, 1997)

Technique	Applications for Software Metrics
Least Squares Regression	Simple models involving a small number of variables, where the relationships are linear or linear after transformation.
Robust Regression	Where the data contains a number of influential outliers and a general model that fits the "normal" projects is most desirable.
Neural Networks (Multi-layer perceptron)	Metrics where accuracy is much more important than understanding the relationships.
Neural Networks	Can be used to cluster systems in similar groups. This can help when modelling very different systems, and separate models need to be developed using other techniques.
Fuzzy Systems	Early estimation where sufficient information for more detailed models is not available. Can also be useful where data is only available in small quantities or not at all.

Technique	Applications for Software Metrics.
Hybrid Neuro-Fuzzy Systems	Provides a data-driven process for developing accurate fuzzy models and allows for the insertion and extraction of rules. This can assist with gaining understanding of the development process. Requires more data than a fuzzy system, but may operate better than a neural network.
Rule Based Systems	Deterministic systems where relationships exhibit very little stochastic behaviour.
Case-Based Reasoning	Situations where projects with similar independent variables tend to be similar in terms of dependent variables, but the relationship is very complex.
Regression Trees	As with Kohonen networks, regression trees allow different models to be used in a piecewise fashion for different types of system. Provides good explanation facilities.
Classification and Decision Trees	Suitable for non-numeric variables. Can be used to generate theory as well as models.

Predictive techniques given in Table 1 have their own intrinsic characteristics and unique approaches to model development. Least Squares Regression, Robust Regression, and Neural Networks will be used for model development in this research and thus only their characteristics and approaches as appearing in literature will be further discussed. According to Grey and MacDonell (1997); once an estimation model has been derived it is important that the limitations of the techniques used to develop and implement the model are understood in order to ensure that it is only used within its limitations. Thus, the limitations of the above techniques as well as their advantages will be considered from literature. General comments on predictive models from literature will also be looked at.

3.3.1. LEAST SQUARES REGRESSION TECHNIQUE

Linear least squares regression (LSR) technique is the simplest and most common of statistical methods (Bhar, 2008; Gray & MacDonell, 1997). Least squares regression generates a linear equation with coefficients of independent variables to give a predicted value of the dependent variable. Least squares regression operates by estimating the coefficients of independent variables by minimizing the squares of residuals (r_i) between the observed data and the model's prediction for the i^{th} observation (Gray & MacDonell, 1997; Courtney & Gustafson, 1993; Lovell, 1983). That is;

$$\text{Minimize } \sum_{i=1}^n r_i^2 \quad (3.11)$$

The least squares method is well suited for situations where there are many degrees of freedom (many observations than parameters to be estimated) but is susceptible to data sets containing outlier observations (Gray & MacDonell, 1997). Relying on coefficients predicted by linear regression has been deemed problematic especially in cases where small data is available and where hypotheses have not been proposed in advance (Courtney & Gustafson, 1993; Gray & MacDonell, 1997). This is because linear combinations of independent variables can be attained and correctly predict the output variable but at the same time violates common sense (Courtney & Gustafson, 1993; Gray & MacDonell, 1997). This can include a slope being of a different magnitude than expected, especially in relation to other variables, or a slope may even have the opposite sign to what common-sense would suggest (Gray & MacDonell, 1997).

As an example, decreasing the ore grade to a leaching process lowers efficiency. A predictive model could be found that fits the data well but with a positive coefficient for ore grade

(suggesting low grade favour efficiency) which is illogical. Another important aspect of linear regression is data splitting, where data is divided into three sets; one set for developing models, one for selecting the best model and one to test the model's best fit (Picard & Berk, 1990; Snee, 1977). Testing the performance of a model on data that has not been withheld for validation provides a biased estimate and exaggeration of the predictive capabilities of the final model (Gray & MacDonell, 1997). Problems outlined above are not limited only to linear regression but to any regression analysis such as quadratic regression because data extraction and preparation steps are the same.

3.3.2. ROBUST REGRESSION ANALYSIS

Robust regression analysis was developed to provide an improvement to the least squares regression in the presence of outliers in data sets (Bhar, 2008), and can be used to screen for outliers in data sets (Miyazaki, et al., 1994; Massart, et al., 1986; Rousseeuw & Leroy, 1987). An outlier is interpreted as an observation whose dependent variable is unusual (Bhar, 2008), or when an observation has a large value where such a value would indicate that the observation is a large number of standard deviations from the mean (Gray & MacDonell, 1997). The source of outliers in data can be attributed to operational mistakes (Bhar, 2008), or error in measurements and can have considerable impacts on the efficacy of estimation models.

A single outlier in data can destroy the least squares regression (Bhar, 2008; Gray & MacDonell, 1997) and hence the emergence of robust regression as an alternative to least squares regression. Robust regression is not affected by up to 50 percent of outliers or data values that do not reflect the underlying system being modelled (Gray & MacDonell, 1997). The improvement given by robust regression is achieved by using the following method to

estimate model coefficients; with r_i being residuals between model prediction and observed data as with least squares.

$$\text{Minimize } \sum_{i=1}^{median} r_i^2 \quad (3.12)$$

In order to improve prediction capability of the least squares approximation without using robust regression, outliers in data sets are often rejected and are not used in model development. The practice of outliers rejection though a common practice is however not always justifiable. According to Garry & MacDonell (1997), the fact that a data point qualifies as an outlier is not sufficient justification to remove it from a sample as it is important to ensure that data populations being studied are properly defined.

These problems with data removal in improving model fits of least squares regression estimates deems it necessary and critical to revert to robust regression analysis in data sets containing outlier observations. It is equally important to ensure that data sets have minimum outliers as possible especially if observations are obtained experimentally. In cases where data sets are obtained from plant operational data, it is unlikely to avoid the presence of significant amounts of outliers.

3.3.3. NEURAL NETWORKS

The most common model-building technique used in the literature as an alternative to least mean squares regression is back-propagation trained feed-forward neural networks (Gray & MacDonell, 1997). Neural networks are computational models and are an artificial representation of biological neurons in the human brain and try to imitate its learning and adapting process (Chakraborty, 2010; Krose & van der Smagt, 1996). Artificial neurons are

composed of processing units (interconnecting artificial neurons) which communicate by sending signals to each other over a large number of weighted connections and exhibit complex behaviour which is determined by the interconnections between these processing units (Chakraborty, 2010; Krose & van der Smagt, 1996).

In designing neural network computational structures, an appropriate architectural network of neurons is build first as depicted in Figure 3 (Cheung & Cannons, 2002). After building the suitable architecture of neurons, the network is presented with training data consisting of various inputs and the desired output (Gray & MacDonell, 1997). The neural network learns by adjusting the weighted sums of inputs to its several neurons that generate an output to decrease the difference between the predicted output and the actual output (Gray & MacDonell, 1997). The neural network then transforms the various inputs into outputs to the best of its ability (Cheung & Cannons, 2002). The learning process is referred to as the training of neural networks and goes on until the “neural network's ability to generalise, as measured by its predictive performance on new data, is optimal” (Gray & MacDonell, 1997).

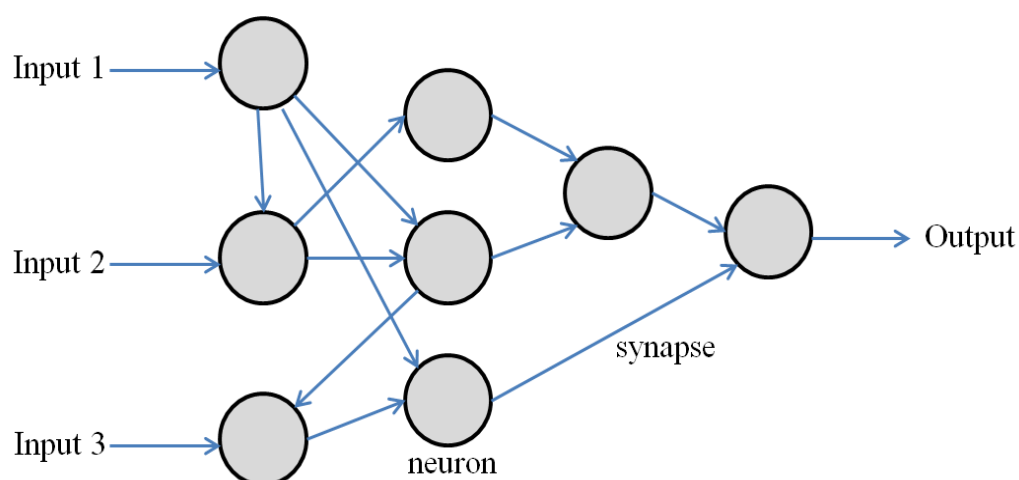


Figure 3: An architecture of Neurons

Neural networks are made up of several layers or groups of neurons. In Figure 3 for example, there are three layers of neurons namely; the input layer (single-input- multi-output), intermediate layer (multi-input-single output) and finally the output layer which is also a multi-input-single-output layer. The output of each multi-input-single-output (MISO) neuron is a function of the weighted sum of inputs plus a bias as shown in Figure 4 (Cheung & Cannons, 2002). A strong point of neural networks is their ability to capture any relationship that may exist between variables but their short-coming is that they do not provide information about how outputs are reached (Gray & MacDonell, 1997). Thus neural networks' predictions cannot be tested to ensure that the predictions are consistent and do not violate common sense.

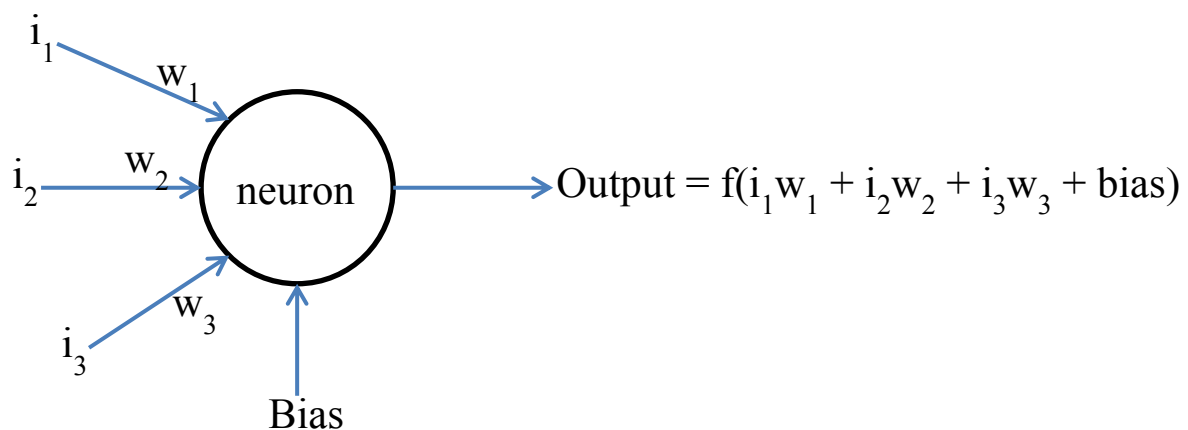


Figure 4: multi-input-single-output neuron (Gray & MacDonell, 1997)

3.3.4. REGRESSION TREES

Regression trees are directed graphs which begin at a single point called a node and branch out into many other nodes (Wilkinson, 1992). Regression trees are represented by a set of yes or no questions which split data sets into smaller and smaller parts (Timofeev, 2004). A hierarchy of questions are asked and the final decision or answer depends on answers to all the previous questions (Zhang, 2013). A regression tree is built to predict the response y from

a set of predictor variables $X_1, X_2, \dots, X_N$. At each internal node of the tree, a yes or no question is asked about the predictor variables and depending on the answer, a right or left branch is followed (Berk, 2009). A series of branches is then followed until a terminal node, called a leaf node is reached where a prediction of the output y is made (Berk, 2009). The leaf node in which a prediction of the output variable y is made, computes an average of responses y_i of all training data that reach that particular leaf node (Berk, 2009). Figure 5 is an example of a regression tree that predicts the outcome y based on temperature and density values.

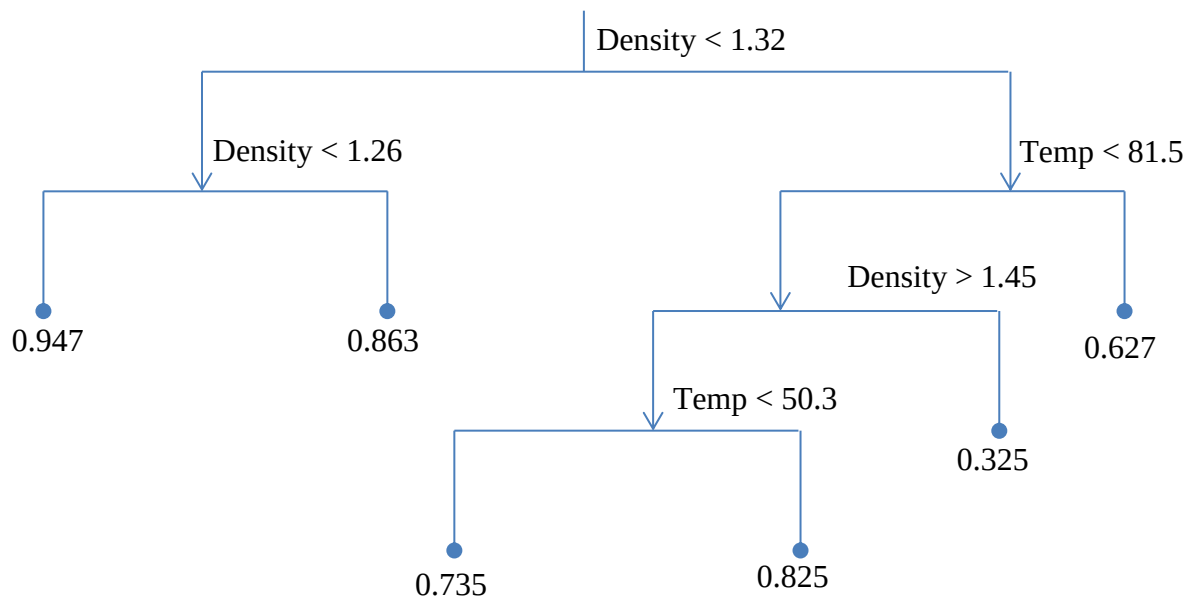


Figure 5: Typical regression tree

Regression trees are discrete functions (Rokach & Maimon, 2007) and are alternatives to linear and non-linear regression, discriminant analysis, and other procedures based on algebraic models (Wilkinson, 1992). Predictors such as linear and polynomial regression are global models which hold over the entire data set (Berk, 2009). The discrete nature of regression trees is useful for data sets with lots of complicated interacting features, where

assembling a single global model is difficult (Berk, 2009). The drawback of regression trees is that a certain range of input variables are associated with a single average value of the output variable y at each terminal node (Berk, 2009). This can result in a model with low prediction accuracy. Another shortcoming of regression trees is their instability, where a small change in a data set can lead to a tree with a completely new and different anatomy (Breiman, et al., 1984).

It is possible to construct regression trees by hand for single predictor data sets by arranging variables in an increasing or decreasing order, group then according to a pre-determined criterion, and determine the average response for each group. Though this can be done with ease for small data sets, it would be time consuming for large data sets. Constructing regression trees is virtually impossible for data sets containing multiples of predictor variables. As a result, there are several algorithms developed to induce regression trees. Regression tree inducers are recursive algorithms that automatically construct regression trees from data sets (Rokach & Maimon, 2007). Regression tree inducers builds regression trees to either render them optimum (minimize prediction error), minimise the number of nodes, or to minimise the average depth of regression trees (Rokach & Maimon, 2007). A typical regression tree inducing algorithm is shown in Figure 6 ((Rokach & Maimon, 2007; Breiman, et al., 1984).

As can be seen in Figure 6, recursive regression tree inducing algorithms first splits the set of predictor variables into two regions and determine the average response y in each region (Rokach & Maimon, 2007). After that, one or both of the regions are further split into two or more regions and the process is continued until some stopping rule is applied (Berk, 2009). The stopping rule determines the length and complexity of the resulting regression tree

(Moisen, 2008). The stopping rule or criterion includes but is not limited to the following scenarios (Rokach & Maimon, 2007; Zhang, 2013; Berk, 2009; Moisen, 2008; Wilkinson, 1992):

```

Function RegressionTree = TreeGrowing(T,X,y)
TL = Tree_Length;
i = 1
DO WHILE i < TL + 1
T = Training set;
X = Input set (Predictor variables)
y = Target feature (output)

Create a new tree with a single root node

If stopping criteria met THEN
    Create a leaf node and assign it the average y value
    of n data points of that node.
ELSE
    S* = Arbitrary split
    BestSplit = Try_All_Numeric_Splits(Xi,yi)
    IF BestSplit is better than S*
        S* = BestSplit
    END IF
    Create node with S*
    Left_branch(i) = TreeGrowing(T,Xi,yi : (Xi,yi) ∈ S*)
    Right_branch(i) = TreeGrowing(T,Xi,yi : (Xi,yi) ∉ S*)
END IF
i = i + 1
END WHILE

```

Figure 6: Regression tree inducing algorithm (Rokach & Maimon, 2007; Breiman, et al., 1984)

- If the resulting sum of squared differences between actual responses and predictions of the regression tree is less than a pre-determined value, stop splitting and make that node a terminal (leaf) node.
- If the length of the tree reaches a certain pre-determined value, stop splitting and make that node a terminal node.
- Keep splitting until each node contains a minimum of a pre-determined number of data points.

The tree growing stopping criteria given above with the exception of the sum of squared differences have various shortcomings. Applying a stopping criterion to regression tree building can result in an early stoppage (Zhang, 2013; Berk, 2009). There are some variables which are not informative themselves but which lead to informative subsequent splits (Zhang, 2013; Berk, 2009). Growing very large regression trees to avoid early stopping however leads to nodes with few data points, over-fit the data, and result in poor predictions on independent data sets (Moisen, 2008).

A solution to prevent early stopping in building regression trees and to reduce the size and complexity of a regression tree while retaining accuracy involves pruning (Rokach & Maimon, 2007; Zhang, 2013; Berk, 2009; Moisen, 2008; Wilkinson, 1992). Pruning entails building an overly large regression tree until some minimum node size is reached (Moisen, 2008) and then collapse some branches back together (Zhang, 2013). In pruning a regression tree, an evaluation of the sum of squares of differences on testing data is done at each pair of leaf or terminal nodes (Berk, 2009). This is done to see whether the sum of squared differences would shrink when these nodes are removed and made a single node, and if it does shrink the tree is pruned (Berk, 2009).

3.4. THEORETICAL MATHEMATIC MODELS

The disadvantage of using statistical based numerical models discussed in section 3.3 is their dependency on system data. As a result, it is difficult to use such numerical models to pre-determine the performance of new systems with different orientations or operation philosophies. This problem is minimized by developing predictive methods from first principles using relevant theories. Theory based models do not require system data for development but for validation purposes. When appropriate theories have been utilised with no over-simplification in the assumptions, developed models will give an accurate prediction of the system being modelled.

Theory based models have been used successfully to predict the performance of a number of leaching operations (Crundwell, 1985; Dry, 1984; Levenspiel, 1972; Comninos, 1985). Theoretical models have been used to predict the performance of both column and heap leaching processes using various leaching methods such as acidic or bacterial leaching. These models use reactants mass balance in solid beds and particles, energy balances and momentum balances (de Andrade Lima, 2004). Liu et. al. (2004) for example developed a semi-empirical model for the bacterial growth and bioleaching of *Acidithiobacillus* using the concept of transport phenomena. Shoesmith & Sunder (1991) developed a model for the dissolution of UO_2 based on electro-chemistry and on solubility.

Common assumptions in the use of theoretical models, which do not always hold are (Villas Bôas, et al., 2003; de Andrade Lima, 2004; Srithammavut, 2008):

- The axial and radial dispersions of the liquid flow throughout the solid bed is negligible.

- The reaction between the solid and leaching agent is controlled by diffusion of the reactant species through the solid particles.
- The average residence time of the solution inside the heap or column does not change with time or position.
- The amount of leachable species and the size of solid particles are homogeneously distributed in the heap or column.
- The temperature is constant, the system is well mixed and particles are assumed to be spherical.

3.5. SUMMARY

The most important findings from literature review pertain to fundamental mathematical models and predictive numerical models. Fundamental models are of significant importance in process modelling because they are capable of explaining the behaviour of the process mathematically. Thus, the first priority of this research was to develop a fundamental model of the carnotite carbonate leaching process. Literature review identified different types of predictive numerical models which can be used to model the uranium leaching process. These were least squares regression, robust regression, neural networks, and regression trees.

Regression based models are the easiest of numerical models to develop and can be developed with widely accessible software such as Microsoft excel and Matlab. It was found from literature review that the accuracy of least squares regression estimations can be negatively affected by the presence of outliers in data sets. However, it was found that this problem can be averted by the use of robust regression. Literature review found neural networks to be undesirable for use in this research because they do not provide information

about how their outputs are reached. This makes it difficult to assess whether the model obeys common sense. Neural networks would also require speciality skills to develop.

Regression trees were also found to be undesirable to model the leaching process because they group data sets into different categories and assign a single model output to data points within each category. The single value assigned to each category is the average process response of all data points in each category. When categories are made up of large data sets, this single average value will not be a good representation of process behaviour. Thus, regression trees would not be used to develop models in this research.

CHAPTER 4

4. EXPERIMENTAL PROCEDURES

4.1. DATA COLLECTION

Due to a large quantity of data required to develop and test leaching models (particularly multi-variable models), it would have taken a long time to collect primary information required to achieve objectives of this research if data was collected through experimentation. In order to develop multi-variable linear models of a leach circuit, variables need to be varied over certain ranges and simultaneously. This would require many experimental runs and deplete the time available to construct leaching models and it would be expensive. Therefore, data used in construction of leaching models in this research was extracted from a database of daily laboratory analyses, results of special metallurgical testing and daily plant performance data of an industrial carbonate uranium leaching plant. Industrial data was collected over a long period of time and all parameters have during that time varied either on purpose or due to operational difficulties. These variations though not beneficial presented an opportunity for model development and understanding of process response to changes in leaching variables. Methods through which data is collected at the industrial carbonate uranium leaching plant (sampling and analysis) will be discussed.

The leaching circuit at the industrial plant consists of 6 leach tanks arranged in series. The leaching circuit is fed with underflow slurry from a pre-leach thickener at a density of 1.45 g/cm³. The high density feed is diluted with process water in a conditioning tank prior to entering leach tank 1. Slurry gravitates from one tank to the other e.g. tank 1 through to tank 6. Leached slurry is pumped from tank 6 to upstream process units.

4.1.1. PARTICLE SIZE DISTRIBUTION

Daily plant performance data and daily laboratory analyses do not include data of complete particle size distribution. Daily laboratory analyses only report on the percentage of particles less than 500 microns. Complete particle size distributions are often carried out during special metallurgical tests. During analysis of the particle size distribution to the leach circuit, multiple grab samples were collected from the leach feed stream. These multiple samples were combined to form a composite sample and thoroughly mixed for homogeneity. A smaller sample was then withdrawn from the composite sample and its size distribution analysed. The sample was first subjected to wet screening to remove fine particles which would blind screens. This was achieved by washing off fine particles by spraying water onto the sample in a screen of 38 microns aperture size.

The undersize and oversize particles from wet screening were collected separately and dried overnight in an oven at 110°C. The weight of dried fine particles (< 38 microns) was determined using a weighing scale. Oversize particles (>38 microns) from wet screening were screened using a series of screens. Screens containing a sample were placed on an automatic dry screening machine that shakes the screens at a chosen frequency and time frame. Masses retained by each screen were weighed using an analytical balance and the percentage of a sample retained by each screen was calculated. The cumulative percent particles retained and thus the cumulative percent passing were determined.

4.1.2. PARTICLE GRADE DISTRIBUTION

After wet and dry screening, particles of different sizes were ground into powder and placed separately in an XRF machine to analyse for the uranium content (U_3O_8).

4.1.3. URANIUM EXTRACTION PROFILES

Uranium extraction profiles giving the amount of uranium in the leach feed and in discharge streams from each leach tank were obtained from onsite operations laboratory tests. These profiles are composed of results of uranium content in solid particles as well the quantity of uranium loaded onto the leach solution in each leach tank.

The uranium content in solid particles in the leach feed and leach tails is analysed for on a daily basis and reported for each of the three shifts (morning, afternoon and night shift). In each shift, samples are taken from dedicated sampling points in the plant at intervals over the duration of the shift. The composite sample for each shift is then taken to the laboratory for analysis. The samples are washed in the laboratory, filtered and dried to enable analysis of both solids and liquids. Complete leach profiles (uranium content in solids and solution) across all leach tanks on the other hand are done twice a week. However, the analytical procedures are the same as those of daily samples.

Data for leach profiles were extracted from a collection of excel documents containing daily laboratory results. Results were collected for days on which leach profiles were taken (twice a week) for all three shifts. Average leach profile results of the three shifts were calculated to obtain average daily leach profile values. This was done to ensure that all results used in the development of mathematic models are daily values.

4.1.4. LEACH SOLUTION CONDITIONS

Leach solution conditions consists of concentrations of sodium carbonate and sodium bicarbonate, the solution pH, leach pulp density and leach temperature. Sodium carbonate

and sodium bicarbonate concentrations, solution pH and the leach pulp density are taken from samples which are analysed for uranium content. Thus they are analysed from composite samples collected at intervals over the duration of each shift. Sodium carbonate and sodium bicarbonate concentrations are determined through titrations. The pulp density is determined from a mass of a known volume of the leach pulp. Analyses of the above mentioned data is carried out on a daily basis. These data were extracted from a collection of daily laboratory results for each shift for days on which complete leach profiles were determined. Averages of these results (Na_2CO_3 , NaHCO_3 , and density) were calculated from results of each shift to obtain a daily average. The leach temperature on the other hand is monitored using online temperature transmitters. Values of leach temperatures are displayed on a SCADA system and daily average temperatures collected in a daily plant production database. Daily leach temperatures for days on which leach profiles were taken, were extracted from the database.

4.1.5. LEACH FEED PROPERTIES

Leach feed properties consists of the leach feed density, the uranium content in the solids and the vanadium content in the ore. Uranium and vanadium contents in the feed are analysed in the same manner as in the analysis of leach profiles (XRF analysis) and samples are collected in the same manner. The density of the leach pulp is determined from the mass of a known sample volume. Data were extracted from a collection of daily laboratory results for each of the three shifts and average values were calculated for each day.

4.1.6. LEACH RESIDENCE TIMES

The leach residence times were calculated from the mass flow rates to the co-current leach circuit, the leach feed density and the combined volume of the leach tanks. The feed rate to

the leach circuit is measured using online flow metres which display values on a SCADA system. Daily values of dry mass feed rates (tons/hour) to leaching are collected in a daily production database from which they were extracted. The total leach feed mass flow rates (tons/hour) for each day were calculated by dividing dry tonnage feed rate by the mass fraction of solids in the leach feed. Daily average mass flow rates were divided by the leach feed density to obtain volumetric flow rates. The volumetric flow rates were divided by the total volume of leach tanks in a leach circuit to obtain daily values of residence times, assuming negligible particle segregation in leach tanks. An assumption of negligible particle segregation implies that all particles spend the same amount of time in leaching tanks. Due to long residence times, leach samples analysed on a particular day entered the leach circuit up to two days earlier. Thus, leach residence times of previous two days were recorded against values of a particular date.

4.1.7. DATA SPLITTING

Data collected for uranium extraction profiles, leach solution conditions, leach feed properties and feed rates were collected from the 1st of January 2013 to the 30th of July 2013. The data was split into two halves and one half was used for model development while the other half was used to validate the model.

4.1.8. OUTLIER IDENTIFICATION AND REJECTION

In order to identify the presence and location of outliers (abnormal observations) in data sets, all variables were plotted on a graph to enable easy visualisation. An acceptable range in a particular parameter was determined and once a data point was classified as an outlier, it was deleted from the data set. Because relationships between variables were of central importance

in this work, all variables of a day in which an outlier observation was present (in any of the variables) were deleted. An example of outlier observations is depicted in Figure 7.

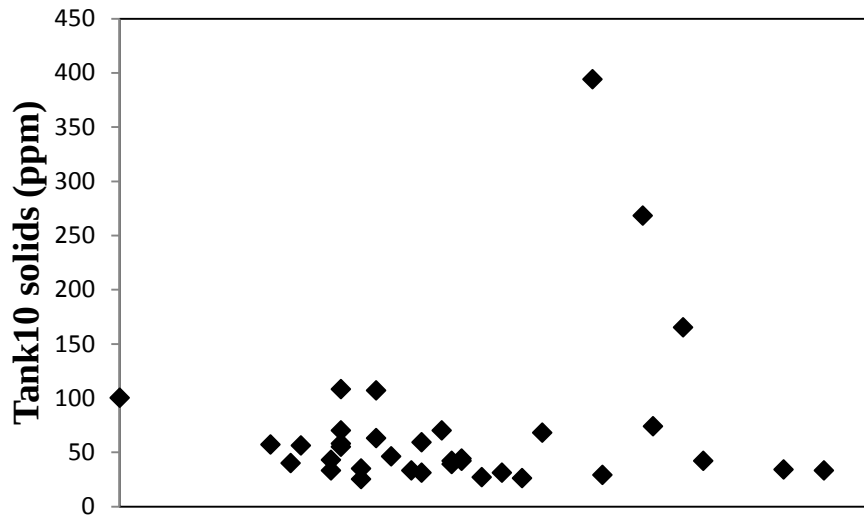


Figure 7: Presence of outliers in a data set

4.2. FUNDAMENTAL LEACHING MODEL CONSTRUCTION

4.2.1. DETERMINATION OF ACTIVATION ENERGY

The activation energy was determined from the gradient of an $\ln(k)$ versus $1/T$ plot, where k is the overall reaction rate constant and T is temperature in Kelvins. The overall rate constant was determined from resistances to the leaching rate. The rate of leaching was found to be controlled by resistances acting in series namely; chemical reaction and diffusion through the layer of ash. Thus the overall reaction rate was calculated from plots of combined chemical reaction and ash layer diffusion resistances at different temperatures. From equation 2.27 and 2.33 of section 2.2, the combined resistance to the rate of leaching is given by the following expression:

$$1 - 3(1 - X_u)^{2/3} + 2(1 - X_u) + \omega[1 - (1 - X_u)^{1/3}] = kt \quad (4.1)$$

This expression was re-arranged into a straight line equation of the form $y = \mathbf{m}x + \mathbf{c}$ (a technique that was used by Rao et. al. (2010) in determining the activation energy of alkaline leaching of uranium from dolomitic limestone ore) as follows:

$$\frac{1-3(1-X_u)^{2/3}+2(1-X_u)}{t} = \omega \frac{1-(1-X_u)^{1/3}}{t} + k \quad (4.2)$$

x and y values were calculated from $x = \frac{1-(1-X_u)^{1/3}}{t}$ and $y = \frac{1-3(1-X_u)^{2/3}+2(1-X_u)}{t}$. x and y values were then plotted and the value of the overall rate constant determined from the y-intercept of the plot.

4.3. EXPONENTIAL EMPIRICAL LEACHING MODEL CONSTRUCTION

Appropriate exponential function forms were identified (Joseph, 2007) and fitted to uranium leach profiles of the industrial carbonate uranium leaching plant. These functions were of the forms;

$$X = 1 - a^t \quad (4.3)$$

$$X = 1 - e^{-at} \quad (4.4)$$

$$X = a(1 - e^{bt}) \quad (4.5)$$

$$X = 1 - \frac{1}{(1+at)^b} \quad (4.6)$$

Where: X = approximate of uranium fractional conversion

t = leaching time (hours)

a, b = dimensionless constants

Constants in equations 4.3 to 4.6 above were assigned initial random values. Errors between actual and approximated uranium conversions were calculated as the difference between the predictions above and the actual uranium conversions from plant data. These errors were then squared and an excel solver minimisation technique was applied to find values of the constants a and b which minimises the sum of the squared differences and thus obtain an accurate prediction of uranium conversions.

4.4. MULTI-VARIABLE LINEAR LEACHING MODEL CONSTRUCTION

The multi-variable linear leaching model was constructed using Microsoft excel's linear regression statistical tool. Data of uranium conversion and independent variables which affect performance of the leach circuit were arranged in a vertical order in an excel worksheet. Uranium conversion data points were selected as an output range (Y) and independent variables as input range (X). The value of the constant term of the resulting linear regressed equation was chosen to be zero. A regression analysis was then performed to determine the values of coefficients of all independent variables to give a linear function $X_i = \theta_i \cdot Var_i$.

4.5. MULTI-VARIABLE LINEAR MODEL INTERFACE

A user interface was developed using LiveCode software to enable easy visualisation of outputs of a multi-variable leaching model and to enable testing of various combinations of leach parameters. Programming languages of LiveCode, Matlab, and Java were compared

and it was found that the LiveCode software language is more robust and allows real time development. The user interface was designed to consist of text entry fields (for user input of process parameters) and toggle buttons to perform calculations. A separate screen called a card was built onto the user interface where a user can input properties of steam used to elevate leaching temperature. This was to determine the enthalpy of steam at that particular temperature and pressure, and depending on the desired leaching temperature to calculate the amount of steam required to raise the temperature.

4.6. STEAM ENTHALPY FUNCTION

A function that determines the enthalpy of steam at a certain temperature and pressure was determined using linear regression in Microsoft Excel. Data from steam tables (Rogers & Mayhew, 1995) were used in constructing the two variable dependence of steam enthalpy. This was necessary because the program cannot read values from steam tables and perform interpolations or extrapolations.

CHAPTER 5

5. RESULTS AND DISCUSSION

Results presented here have been calculated from data collected from a database of daily laboratory analysis, results of special metallurgical testing and daily plant performance data from an industrial carbonate leaching plant.

5.1. PARTICLE SIZE DISTRIBUTION

The particle size distribution of the ore fed to the leaching circuit at the studied industrial carbonate leaching plant is given in Figure 8. According to Figure 8, uranium bearing ore fed to the leaching circuit is relatively fine with more than 90% of particles less than 600 microns. The particle's size d80 and d50 of the feed to the leaching circuit is approximately 400 and 100 microns respectively. The feed size distribution affects the approach used in developing fundamental leaching models. This is because leaching models for particles of uniform sizes are derived differently from those of particles of varying sizes according to equations 2.5 and 2.6 of section 2.1.

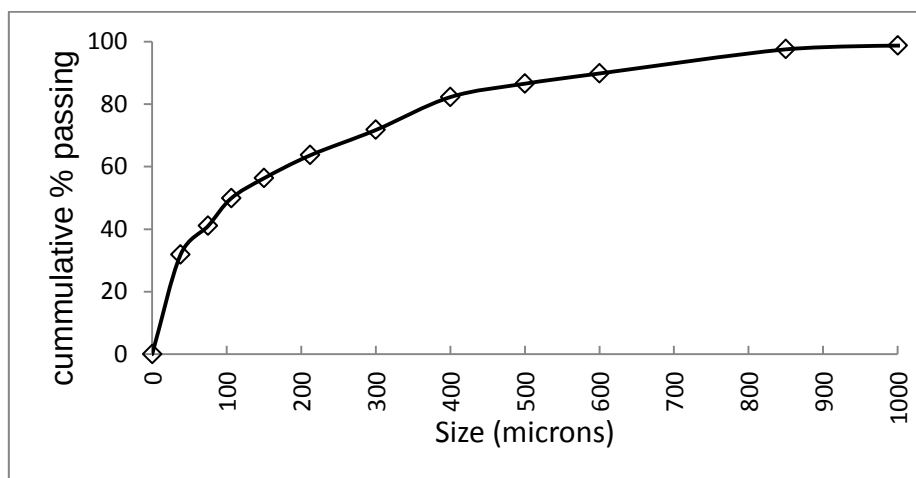


Figure 8: Leach feed particle size distribution

5.2. PARTICLE GRADE DISTRIBUTION

Figure 9 shows the particle grade distribution of a leach circuit feed sample. It is evident from Figure 9 that there is a large range of particles' grade (between 40 and 9000 parts per million of uranium). Up to 87 percent of particles have a grade less than 1000 parts per million (ppm) of uranium while 12 percent of particles have a grade larger than 1000 ppm of uranium. A plot of the leach circuit feed particles' grade distribution versus particle size reveals that most of uranium mineralization is concentrated in the fine particles (Figure 10). Particles larger than 600 microns have low uranium content of less than 250 ppm while particles smaller than 100 microns have a grade higher than 5000 ppm.

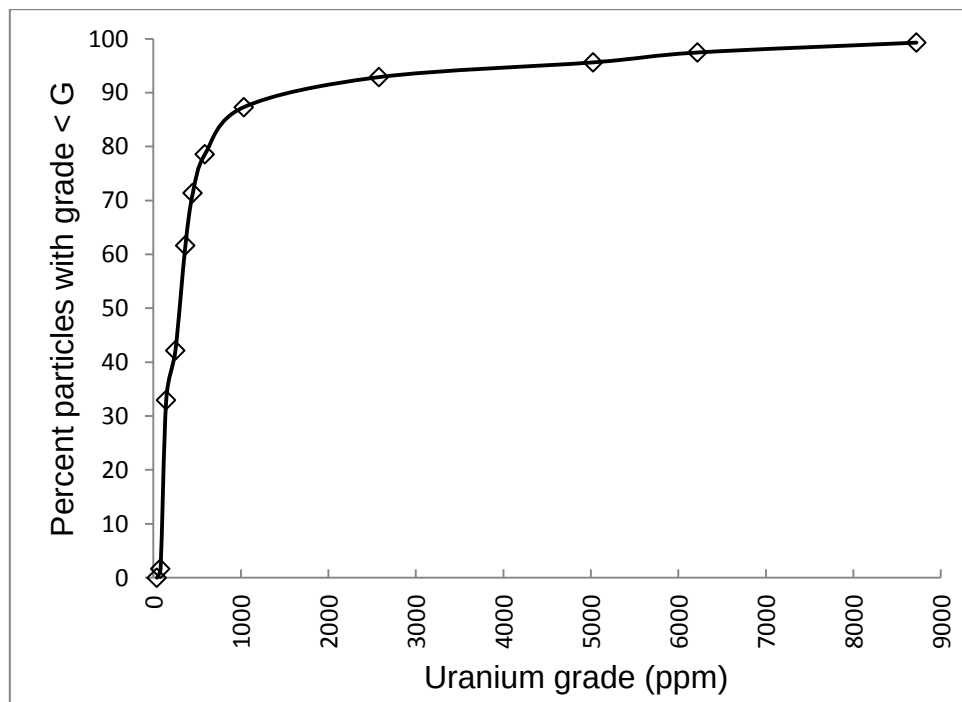


Figure 9: Leach feed particle grade distribution

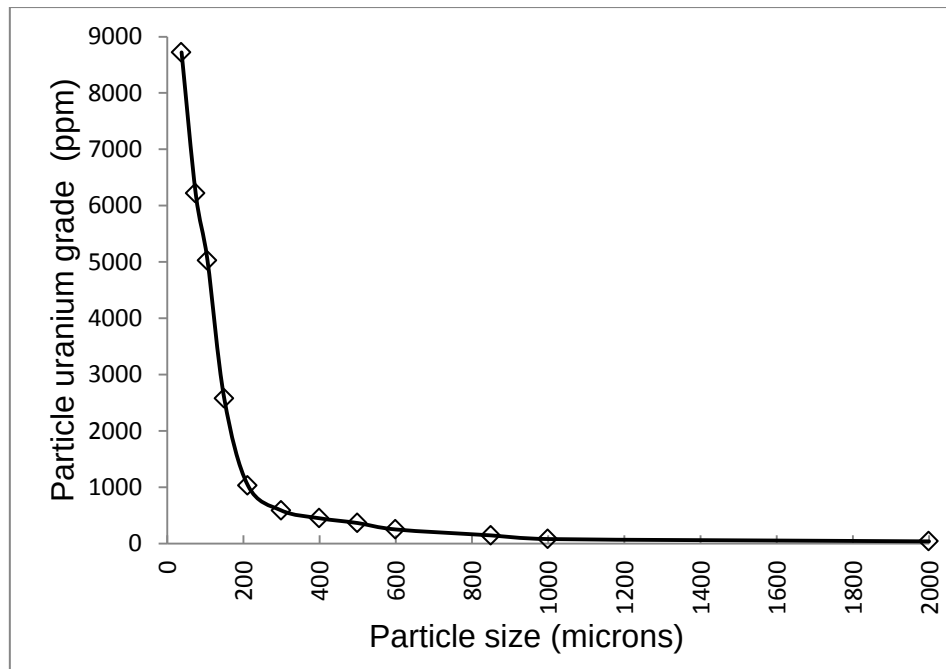


Figure 10: Leach feed particles grade per size class

5.3. RATE LIMITING MECHANISMS

To determine which resistance limits the rate of leaching and thus to aid the development of a fundamental model, the right hand sides of equation 2.19 to 2.33 were plotted against leaching time. If the right hand side of an equation governing a particular resistance yields a straight line, then that resistance limits the rate of leaching. If two or more resistance plots are straight lines, there are two or more resistances to leaching acting in series and thus the total resistance is the sum of the individual resistances.

5.3.1. PARTICLES OF SHRINKING SIZE

The right hand sides of equation 2.20 and 2.33 are plotted in Figure 11 to determine if chemical reaction or film diffusion for shrinking particles are the rate limiting mechanisms for leaching at the studied industrial carbonate leaching plant. None of these plots resulted in a

straight line suggesting that the particles are not progressively converted or consumed during reaction. Thus the radius of each particle as a whole did not shrink with progression of leaching reaction. The non-shrinking nature of ore particles as demonstrated by Figure 11 is different from other physical changes that particles can undergo such as fragmentation and attrition occurring in agitated tanks or particle segregation due to different particle sizes.

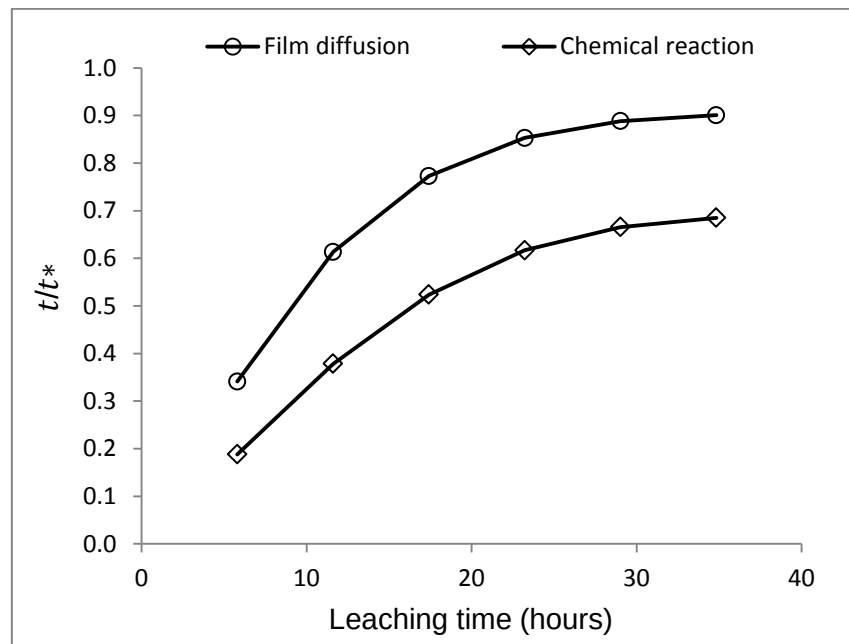


Figure 11: Resistances to leaching for particles of changing size

5.3.2. PARTICLES OF CONSTANT SIZE

The right hand sides of equation 2.20, 2.27 and 2.33 are plotted in Figure 12. Resistances for which the lines are straight are limiting or contribute to the overall resistance to leaching. From Figure 12 it can be seen that there is no film resistance present in the early stages of leaching but appears after 34 hours (leach tank 4 onwards). Furthermore, both diffusion of lixiviant through the layer of ash and chemical reaction control the rate of leaching from the start. After 34 hours there is a distinct point where the contributions of chemical reaction and

ash layer diffusion resistances to the overall resistance change in magnitude. At that point, the plot representing the film diffusion resistance becomes straight demonstrating appearance of film resistance. That causes relative magnitudes of ash layer diffusion and chemical reaction resistances to decrease relative to the overall leaching resistance.

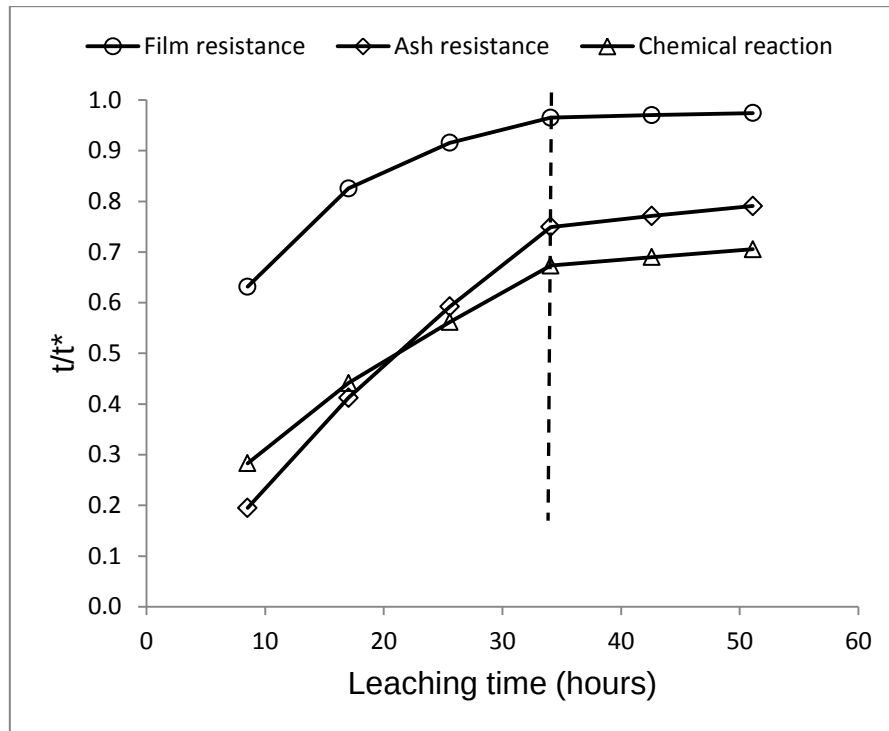


Figure 12: Resistances to leaching for particles of constant size

5.4. FUNDAMENTAL LEACHING MODEL

The equation governing the rate of leaching of a mineral from ore particles as given by equation 5.1 has been developed in section 2.1. This equation gives the variation of the amount of uranium in particles with leaching time. Several researchers (Dry, 1984; Comninos, 1985; Crundwell, 1985) who have studied leaching kinetics of ferric sulphate used computational tools to solve this expression.

$$\frac{dM_u}{dt} = -k_0 \phi \gamma \frac{F_o}{\rho l_o} \left(\frac{M_u}{M_{uo}} \right)^{\frac{2}{3}} \quad (5.1)$$

An alternative way of solving this expression has been identified in this research by expressing the amount of uranium in the particles as a function of fractional conversion. Fractional conversion as a function of leaching time is given by equation 5.2. Derivation of this equation from equation 5.1 is given in section 2.1 and was used in section 5.4.2.

$$X = 1 - \left(\left(1 - \beta \exp \left(\frac{-E_a}{RT} \right) \right) t \right)^3 \quad (5.2)$$

Where: $X =$ fractional uranium conversion

$E_a =$ activation energy, $\text{Jmol}^{-1}\text{K}^{-1}$

$R =$ universal gas constant, $\text{Jmol}^{-1}\text{K}^{-1}$

$T =$ temperature, K

$\beta = k_0 \phi A o = \text{constant}$

5.4.1. ACTIVATION ENERGY OF URANIUM LEACHING

Activation energies of chemical reactions are determined from Arrhenius plots which plot the natural logarithms of overall rate constants versus the inverse of absolute temperatures. The overall rate constants of the carbonate leaching of uranium covered in this research are given at various temperatures in Table 2. To off-set the effects of inconsistent leach operations, rate constants were calculated and grouped according to their temperatures. Average temperatures and rate constants were calculated for different temperature groups. These averages were then used to construct an Arrhenius plot to determine the activation energy of uranium leaching.

The Arrhenius plot is given in Figure 13 and the slope of the Arrhenius plot was found to be -7968. Therefore, the activation energy of the rate of uranium leaching at this industrial carbonate leaching plant was found to be 66.3 kJmol⁻¹ (15.8 kcalmol⁻¹). Because the activation energy is greater than 5 kcalmol⁻¹, it can be concluded that leaching at the studied industrial plant does not predominantly follow diffusion control mechanism (Rao, et al., 2010).

Table 2: Overall leaching rate constants at various temperatures

T	k	T _{avg}	k _{avg}	T _{avg} (K)	1/T _{avg} (K ⁻¹)	ln(k)
82.2	0.0163					
83.3	0.0274	82.8	0.02185	355.9	0.00281	-3.824
85.1	0.0275					
87.3	0.0280	86.2	0.02775	359.4	0.00278	-3.585
88.3	0.0322					
88.5	0.0288	88.4	0.03050	361.5	0.00277	-3.446
90.4	0.0528					
90.8	0.0374	90.5	0.035475	363.6	0.00275	-3.339

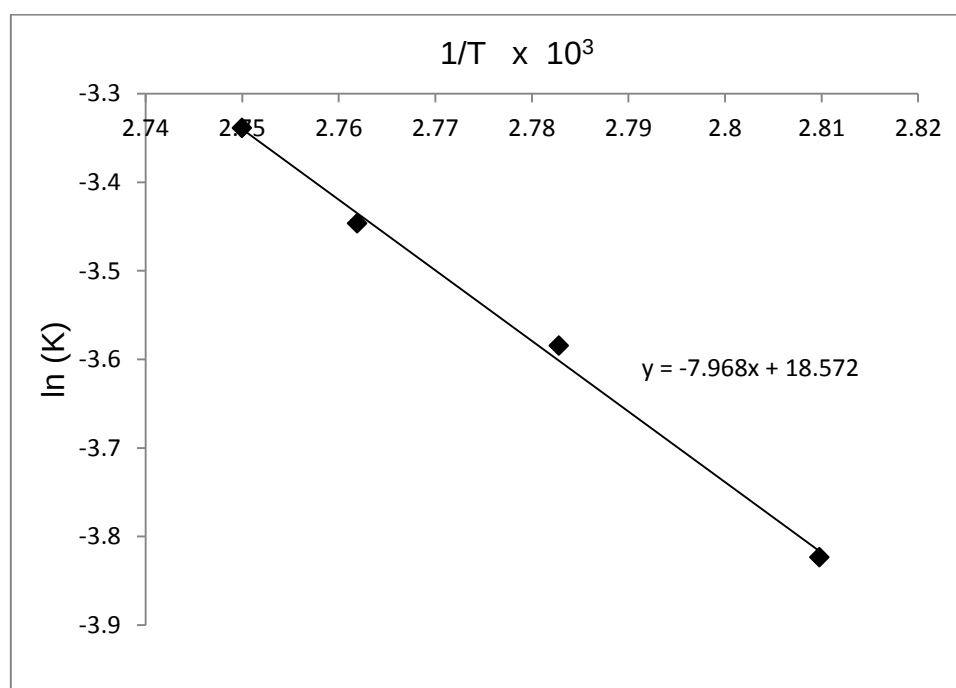


Figure 13: Arrhenius plot of carbonate uranium leaching

5.4.2. SOLUTION CONDITIONS FACTOR

The fundamental leaching model was developed for both constant and variable solution conditions factor. The results of both scenarios are given below.

5.4.2.1. Constant solutions conditions factor

The constant β in equation 5.2 is given by $\beta = k' \varphi A_o$, where k' is the frequency factor in the Arrhenius rate equation, φ is the solution conditions factor, and A_o is the surface area of the particles. Because the sodium carbonate and sodium bicarbonate concentrations and the solution pH remain constant between the first and last leaching tank, it was assumed that the solution conditions factor in the carbonate leaching of uranium at the industrial plant studied does not vary with leaching time. Thus, the value of the constant β was determined using a Microsoft Excel solver tool by minimising the squares of differences between the model and actual uranium conversions from plant data. The value of the constant β was found to be 8.37×10^7 . Figure 14 shows the difference between leaching profiles predicted by the fundamental leaching model (constant solution conditions factor) and plant data. Percentage residuals, which are differences between values predicted by the fundamental model and actual plant data, are given in Table 3.

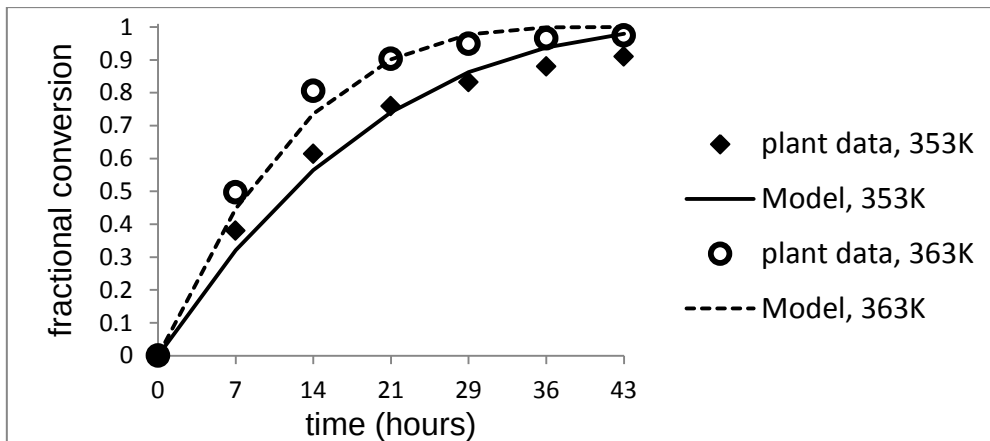


Figure 14: Fundamental leaching model versus plant scale leach profile at 80°C and 90°C

Table 3: Residuals between model and observed percent uranium conversion values

Observation #	1	2	3	4	5	6	7	8
X1	33.0	28.4	13.94	5.86	20.4	14.03	20.1	46.6
X2	20.6	17.2	-8.86	8.00	11.43	10.01	8.72	19.9
X3	9.92	5.03	0.32	0.98	3.44	1.75	0.86	4.99
X4	1.01	1.00	2.83	2.45	0.15	2.50	3.47	0.65
X5	1.04	1.89	2.55	3.26	2.62	3.87	3.37	1.72
X6	1.67	1.88	2.37	2.54	2.55	3.32	4.02	1.81

Table 3 Continued

Observation #	9	10	11	12	13	14	Average
X1	12.66	4.40	20.1	2.07	19.5	27.9	11.40
X2	12.38	0.30	15.88	2.72	15.83	15.01	
X3	0.29	4.19	10.53	0.67	8.30	4.38	
X4	4.07	4.29	5.05	3.23	2.95	1.63	3.03
X5	3.16	5.48	0.86	3.60	5.29	3.51	
X6	2.56	15.19	2.22	3.15	2.95	3.42	

From Figure 14 and Table 3 above, the fundamental leaching model over-predicted the final uranium conversions (leach tank 4 to 6) and under-estimated conversions for tank 1 to 3. The tanks are arranged in series and the tank numbers are thus related to the leaching time in Figure 14. The residence time of the ore in each tank is given by the total leaching time divided by the number of tanks (six). The over-prediction of uranium conversions especially

in tank 6 (the last tank) are problematic because that is the final uranium extraction attained from the leaching circuit. It is important to correctly predict the final uranium conversion of the leach circuit because any uranium not extracted in leaching is lost forever and reports to the tailings sections. There is no recycle stream of uranium from tailings back to the leaching circuit. The under and over-prediction of uranium conversions between early and later stages of leaching indicates that the solution conditions factor does not remain constant as leaching progresses. This is also evident from Figure 12 of section 5.3.2 which showed an appearance of film resistance after 34 hours of leaching. It is also important to note that an assumption of a constant solution conditions factor only affected the accuracy of the fundamental model for leaching at low temperatures.

In order to improve the accuracy of the fundamental leaching model, two different values of the solution conditions factor (8.37×10^7 and 6.87×10^7) were used for leach tank 1 to 3 and for leach tank 4 to 6. This reduced the absolute error of the fundamental model from 11.4% to 10.5% for tank 1 to 3 and 3% to 0.1% for tank 4 to 6. This implies that there exists a function of time which describes the variation of the solution conditions factor.

5.4.2.2. Variable solutions conditions factor

It was indicated earlier that an assumption of a constant solution conditions factor in equation 5.2 lowered the accuracy of the fundamental leaching model, especially at low temperatures. The fundamental model's accuracy was less affected during early stages of leaching but was found to be low as leaching time increased. This indicates that the solution conditions factor changes with progression of leaching and depends on temperature. Determining the time and temperature dependence of this factor is however difficult to ascertain from first principles. As an alternative, a semi-fundamental model was proposed consisting of the fundamental

leaching model (equation 2.9) with an empirical correlation for the solution conditions factor. The solution conditions factor was chosen to be governed by an exponential empirical function of time and temperature. The modified fundamental leaching model predicting fractional uranium conversion as a function of leaching time is given by equation 5.1.1. Because the solution conditions factor is now represented by an arbitrary empirical function, the activation energy term also needed to be modified to render the model accurate.

$$X = 1 - \left(\left(1 - \phi \cdot \exp\left(\frac{-\epsilon}{RT}\right) \right) t \right)^3 \quad (5.1.1)$$

Where: X = Fractional uranium conversion

$$\epsilon = 31159 - 247(T - 273.15), \text{ Jmol}^{-1}\text{K}^{-1}$$

$$\phi = t(0.0014(T - 273.15) - 0.098)$$

$$R = \text{Universal gas constant, } 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$$

$$T = \text{Temperature, K}$$

$$t = \text{Leaching time, hours}$$

Figure 15 shows the difference between leaching profiles predicted by a modified semi-fundamental leaching model (variable solution conditions factor) and plant data. Absolute differences between values predicted by the modified fundamental model and actual plant data are given in Table 3. As can be seen from Figure 15, the modified fundamental leaching model with a varying solution conditions factor predicts uranium conversions from the start to the end of leaching and at all temperatures. This improved the accuracy of the model

remarkably as evident from Table 4. The average absolute error of the fundamental leaching model with a constant solution conditions factor was found to be 7.2%. On the other hand, the average error of the modified semi-fundamental model with a variable solution conditions factor was found to be only 4%. However, the modified model resulted in an increased residual at higher temperature because despite reduced error, the chosen functional form of the variable solution conditions factor is not precise.

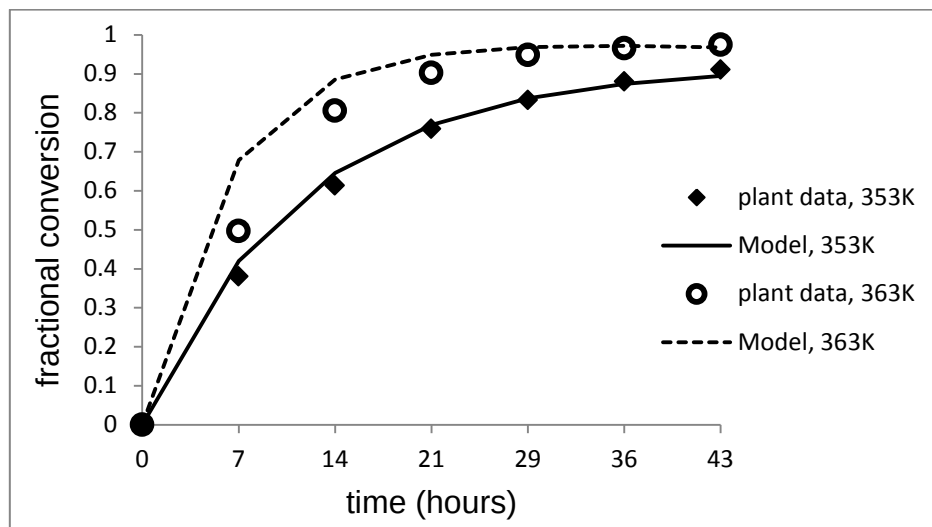


Figure 15: Modified fundamental leaching model versus plant scale leach profile at 80°C and 90°C

Table 4: Residuals between modified fundamental model and observed percent uranium conversion values

Observation #	1	2	3	4	5	6	7	8
X1	9.3	5.3	10.50	18.17	3.5	7.30	2.1	25.7
X2	1.7	3.3	4.96	7.97	5.22	2.25	2.75	8.9
X3	0.66	1.40	3.62	4.61	2.94	0.55	2.31	3.90
X4	1.09	0.72	1.35	1.98	0.17	0.35	0.56	2.87
X5	0.47	1.40	0.04	0.68	0.17	0.56	0.62	3.07
X6	1.02	2.37	1.62	0.69	0.56	2.27	2.09	4.76

Table 4 continued

Observation #	9	10	11	12	13	14	Average
X1	1.52	14.23	6.9	14.77	3.0	4.9	5.59
X2	9.81	4.78	4.68	6.32	3.99	2.24	
X3	5.62	0.83	5.66	0.57	3.08	3.16	
X4	4.72	0.89	6.27	2.10	1.05	2.36	2.44
X5	6.44	3.30	6.37	3.65	4.68	1.05	
X6	8.74	8.18	5.68	5.20	0.22	0.02	

5.5. EMPIRICAL LEACHING MODEL

Empirical models which have been covered in this work are;

- (a) Models with exponential functions which increase exponentially to a limit. Plots of conversion versus leaching time have the same form as these functions types.
- (b) Multi-variable linear models which fit data to a model defining the output y as a linear combination of two or more independent x variables (Billo, 2007);

5.5.1. EXPONENTIAL EMPIRICAL MODEL

A simplified approach to develop mathematical models representing a leaching process is to fit leaching data to functions whose form is analogous to the variation of uranium conversion with leaching time. This approach does not use mathematical treatments that are based on theory and physical principles (McConville, 2008) but rather uses empirical relationships to

develop models. The amount of uranium remaining in solid particles at any time is in the form of an asymptotic exponential function that terminates to a certain value. Common asymptotic exponential functions which can be fitted to leaching data (conversion, X versus leaching time, t) are given below (McConville, 2008).

$$X = 1 - a^t \quad (5.3)$$

$$X = 1 - e^{-at} \quad (5.4)$$

$$X = a(1 - e^{bt}) \quad (5.5)$$

$$X = 1 - \frac{1}{(1+at)^b} \quad (5.6)$$

An initial fit of exponential functions given in equations 5.3 to 5.6 to leaching data revealed that all functions above predicts leach profiles well. Thus, any function can be chosen from above given exponential functions and yield high prediction accuracy. Average errors between percent uranium conversion predicted by the above exponential functions and actual conversion are given in Table 5.

Table 5: Average error between actual and model predicted conversion

Equation	5.3	5.4	5.5	5.6
Average error (%)	0.28	0.28	-1.76	-1.59

Empirical exponential functions given above with exception of equation 5.5 terminate to a value of 1 as leaching time tends to infinity. That characteristic is undesirable because in

reality, the fractional conversion of uranium does not reach unity (100% conversion) in all cases. Leaching of uranium at the industrial carbonate leaching plant studied is highly temperature dependent and thus at lower temperatures, the final fractional conversion will be much lower than 1. It was therefore necessary to modify exponential functions above to yield fractional conversions of less than 1, decreasing with reduction in temperature. The modified equations are given below and are plotted in Figure 16 to Figure 18 while their average percent errors are given in Table 6.

$$X = \left(\frac{T}{89.56} \right) - 1.13^{-t} \quad (5.7)$$

$$X = \left(\frac{T}{89.56} \right) - e^{-0.12t} \quad (5.8)$$

$$X = \left(\frac{T}{91.03} \right) (1 - e^{-0.13t}) \quad (5.9)$$

$$X = \left(\frac{T}{86.40} \right) - \frac{1}{(1+0.0674t)^{2.24}} \quad (5.10)$$

Where: $X =$ fractional uranium conversion

$t = \frac{V_T}{Q} i$ leaching time, hours

$T =$ temperature, °C

$V_T =$ volume of one leach tank, m³

$i =$ i^{th} leach tank

Table 6: Average error between actual and model predicted conversion

Equation	5.7	5.8	5.9	5.10
Average error (%)	0.19	0.19	-0.53	-0.37

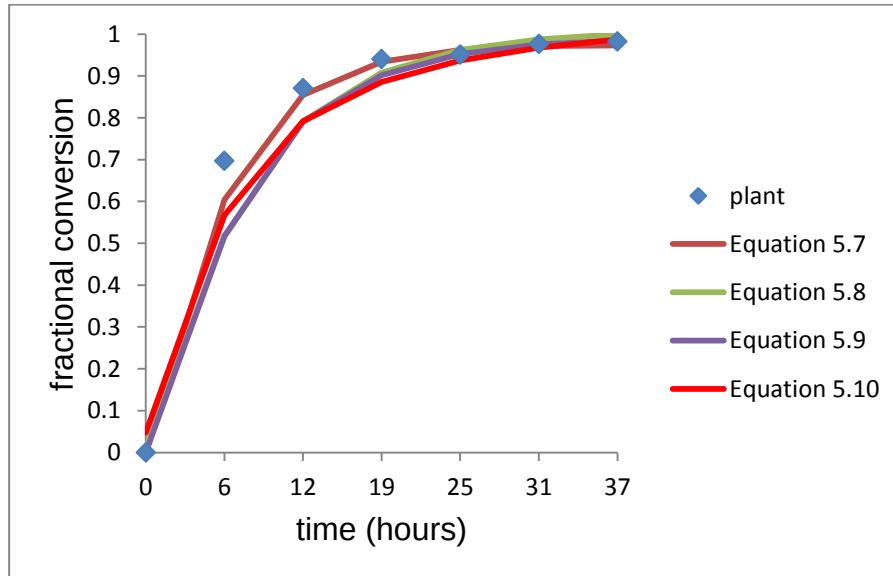


Figure 16: Empirical leaching model versus plant scale leach profile at 90°C

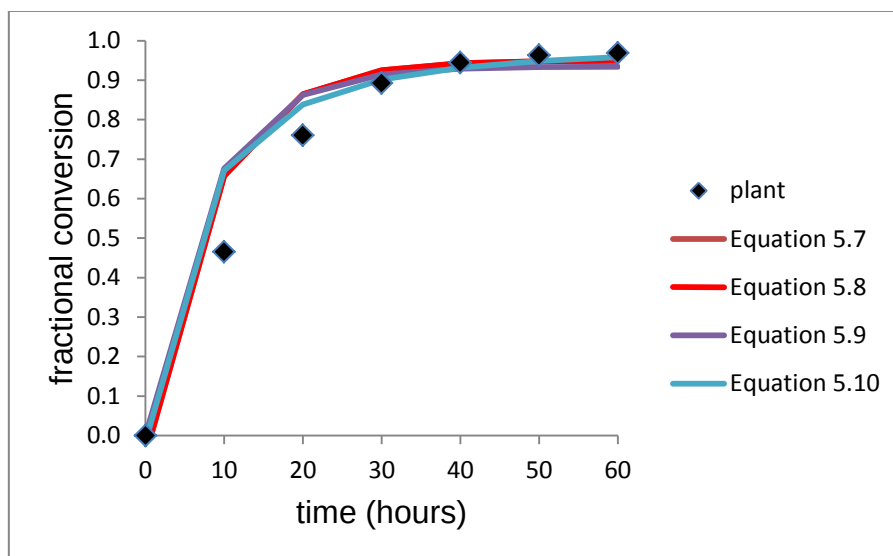


Figure 17: Empirical leaching model versus plant scale leach profile at 85°C

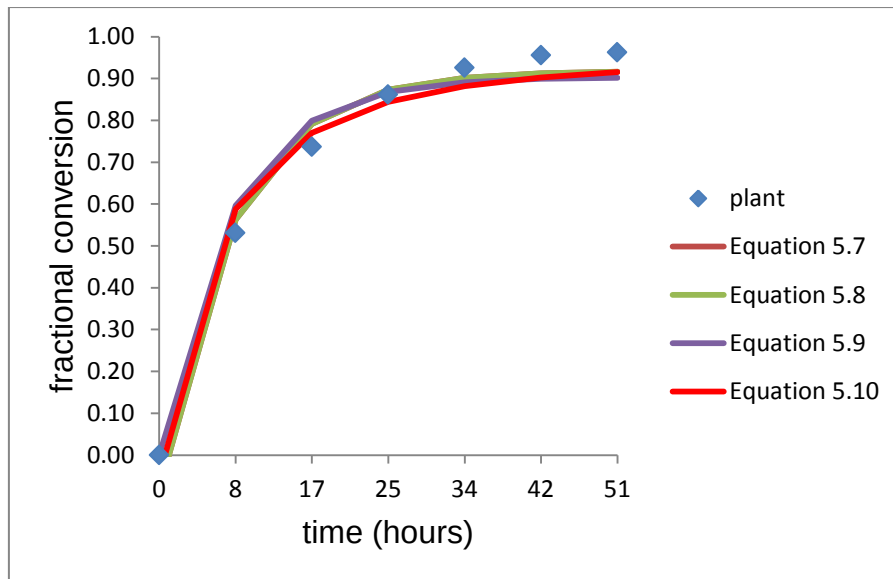


Figure 18: Empirical leaching model versus plant scale leach profile at 82°C

While empirical models developed in this work predicts the alkaline uranium leaching process with reasonable accuracy, the most preferred method of model development is the fundamental approach. The usefulness of fundamental models lies in the fact that they consist of quantitative formulation of a hypotheses (Christopoulos & Lew, 2000). Other than selecting function types, there is no basis of selecting the overall structure of the empirical function, such as the relative placement of temperature in the equation. Thus even if the chosen empirical relationship fits plant data, its reliability for future use is unpredictable. If the set-up of the leaching system or process conditions happens to change significantly, the initial empirical correlation will not apply to the new set-up. A new empirical function will then need to be developed or the existing one modified. However, empirical models are useful too. The Arrhenius equation for example is a highly accurate empirical formula of the temperature dependence of reaction rates (the Nobel prize, 2013), and is applied to all temperature driven chemical reactions.

5.5.2. MULTIVARIABLE LINEAR MODEL

In development of a multivariable model (giving the fractional leach extraction as a function of several leach parameters), parameters which have a noticeable effect on performance of the leaching plant were identified. The significance of process parameters' effects on leach efficiency and the exact relationship between each parameter and leach extraction was determined in section 5.5.2.8. The goal at this stage was to analyse general trends between leach efficiency and leach parameters without paying in-depth attention to data treatment or statistical screening of the data. When statistical screening was attempted in order to generate accurate graphical relationships between different parameters and leach efficiency, it was found that the exclusion of data points diminished model generation data. It was therefore difficult to validate generated models with absolute certainty and confidence. Statistical screening involved selection of leach extraction data points corresponding to a feed uranium grade within a defined narrow range for use in model generation.

Though temperature is the main driver of leaching rate at this industrial leaching plant, other parameters were found to have minor to significant impact on the efficiency of the leach process. With exception of temperature, the solution pH is the most sensitive parameter that impacts uranium extraction, in a sense that a marginal change results in a significant change in the amount of uranium extracted. Other parameters which affect performance of the leach plant are Na_2CO_3 concentration, NaHCO_3 concentration, the uranium grade of feed particles, vanadium content of the ore and residence time. A carnotite uranium ore is made up of a potassium-vanadium-uranium complex and vanadium is co-extracted with uranium during leaching. Thus vanadium competes with uranium during leaching.

5.5.2.1. Effect of feed grade on uranium extraction

Figure 19 shows the concentration of uranium (ppm) in solid particles exiting leach tanks as a function of uranium concentration in particles fed to a tank. It is evident from Figure 19 that the higher the concentration of uranium in the feed, the higher is the exit uranium concentration of the tank. The physical interpretation of Figure 19 is that; a high concentration of uranium in the feed does not necessarily increase the rate of leaching. This is corroborated by Figure 20 (fractional conversion versus feed uranium concentration) where the fractional conversion of uranium decreases with increase in feed uranium concentration. Fractional conversions shown in Figure 20 are fractional uranium extracted after leach tank 2 relative to uranium in the leach feed i.e. $(U_{\text{Feed}} - U_{\text{Tank2}})/U_{\text{Feed}}$.

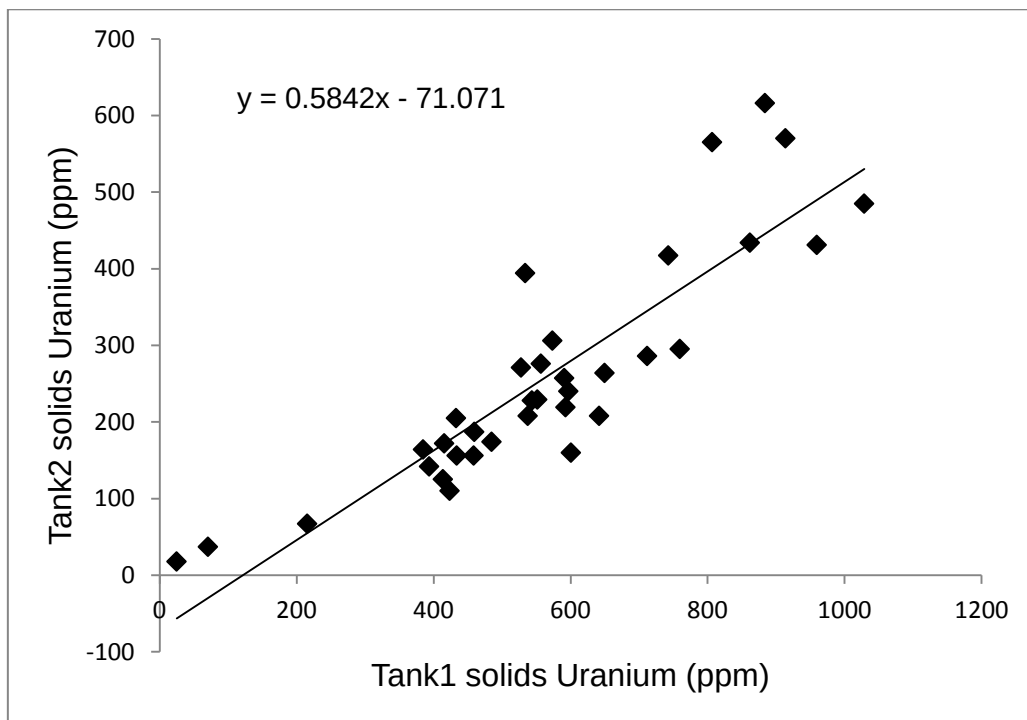


Figure 19: Effect of tank's feed uranium concentration

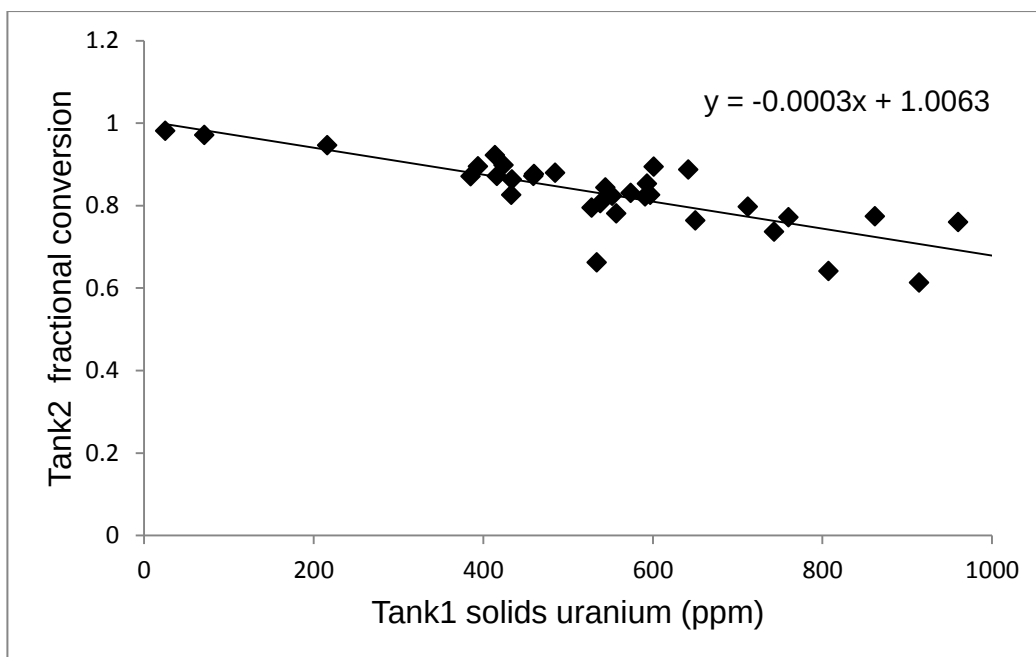


Figure 20: Fractional uranium conversion versus tank's feed uranium concentration

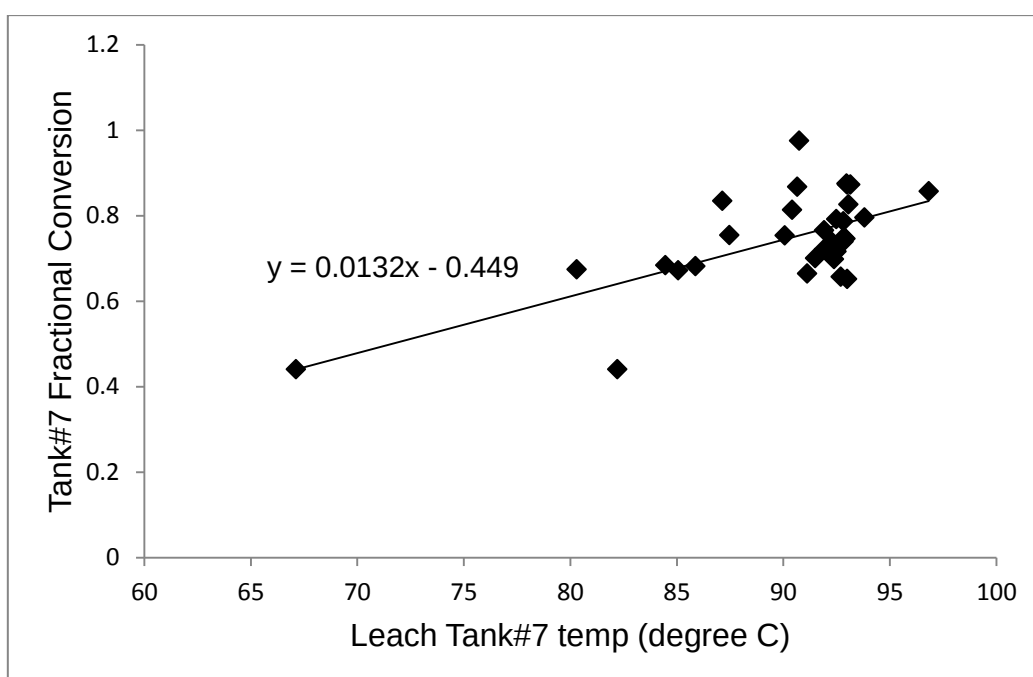


Figure 21: Effect of leach temperature

5.5.2.2. Effect of leach temperature on uranium extraction

High temperatures increase reaction rates and thus favour the rate of uranium dissolution during leaching. Figure 21 shows the effect of temperature on fractional uranium conversion of leach tanks. Temperature is the main driver of alkaline leaching of carnotite uranium ores but scattered data in Figure 21 imply that other parameters also have an influence on leaching.

5.5.2.3. Effect of Sodium Carbonate concentration

The effect of sodium carbonate concentration on fractional uranium extraction in leach tanks is shown in Figure 22. Sodium carbonate is the leaching agent (for dissolution of uranium) as it forms a soluble complex with uranium in a carnotite ore. According to Figure 22, the concentration of sodium carbonate has a marginal impact on uranium extraction. This is because the variation in uranium conversion attained does not correspond to the variation in sodium carbonate concentrations.

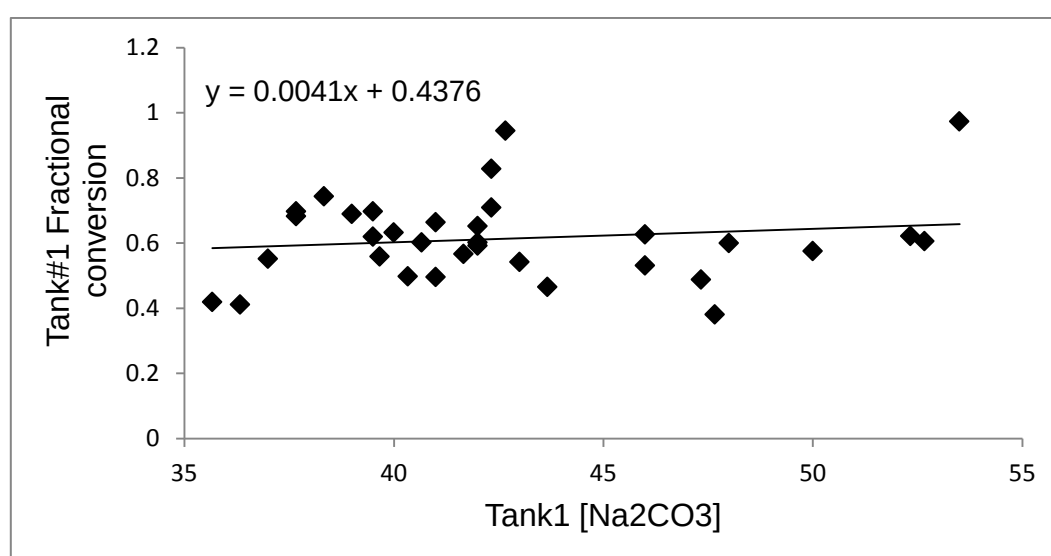


Figure 22: Effect of sodium carbonate concentration

5.5.2.4. Effect of sodium bicarbonate concentration

The effect of sodium bicarbonate concentration on uranium extraction of leach tanks is shown in Figure 23. Sodium bicarbonate is used in alkaline uranium leaching of carnotite ores to consume hydroxyl ions produced by the reaction between sodium carbonate and carnotite. In that way, it buffers the solution pH to prevent uranium from precipitating out of solution as sodium diuranate (NaU_2O_7). According to Figure 23, there is no noticeable effect on uranium leaching caused by varying concentrations of sodium bicarbonate in the concentration range studied.

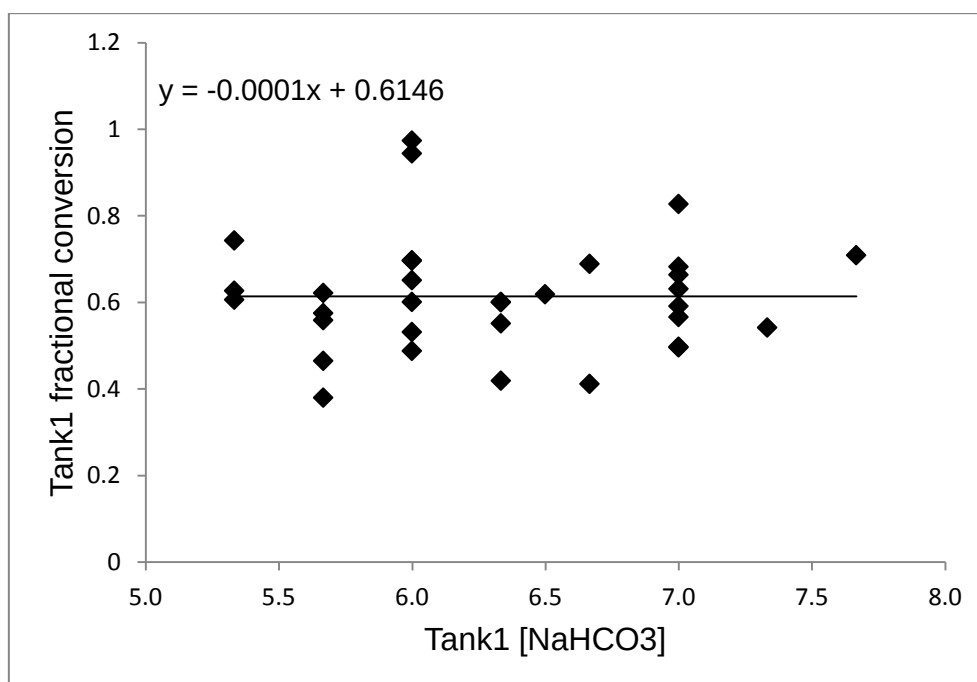


Figure 23: Effect of sodium bicarbonate concentration

5.5.2.5. Effect of solution pH

The effect of solution pH on uranium extraction is shown in Figure 24. According to Figure 24, there is no strong correlation between the leach solution pH and uranium extraction in the

pH range studied. The pH at the industrial uranium leaching plant studied is maintained within a narrow range and thus no effect on uranium extraction will be noticeable from a trend line.

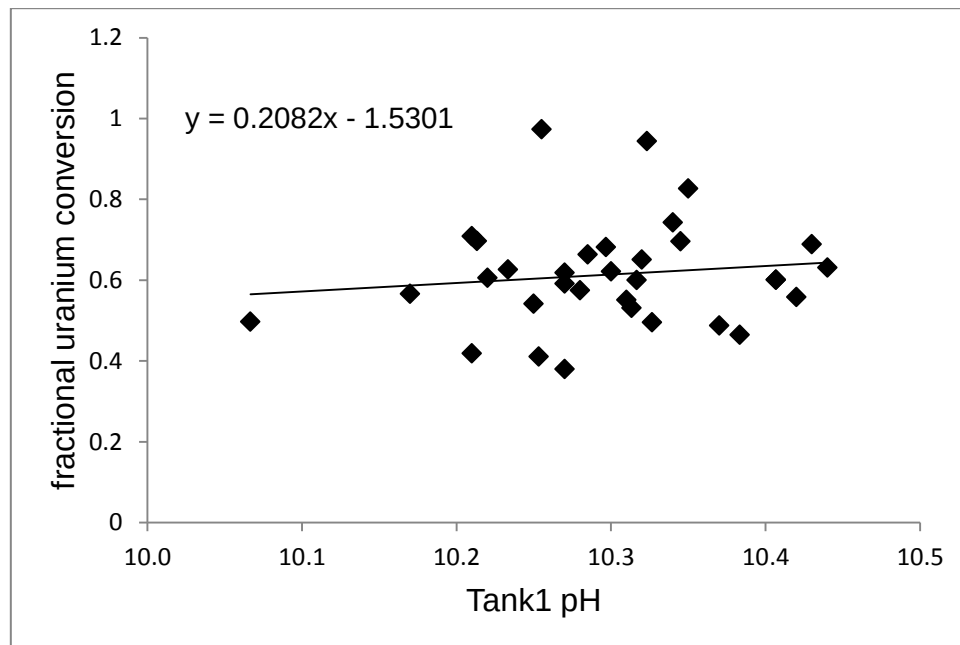


Figure 24: Effect of solution pH

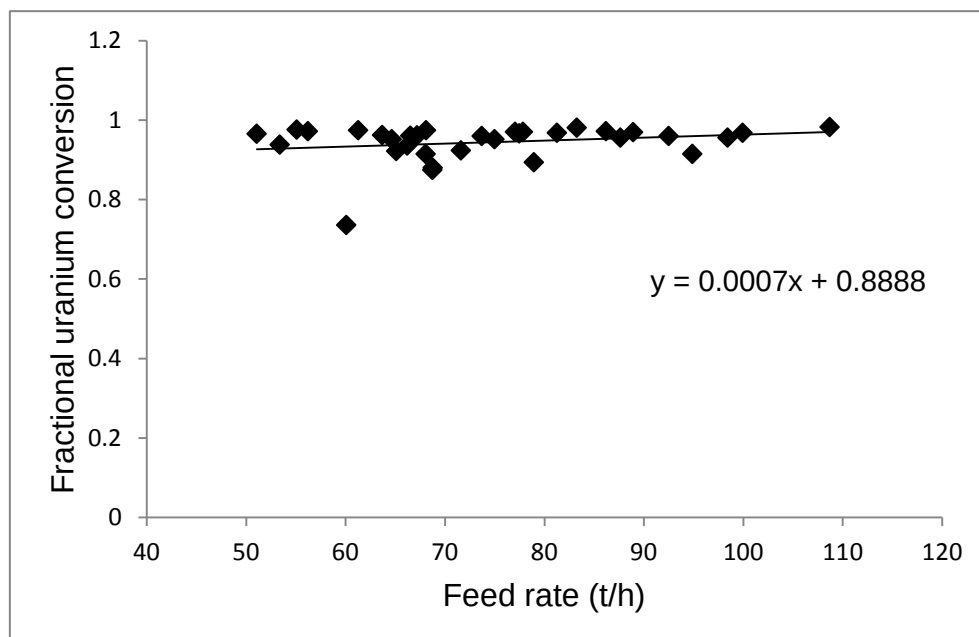


Figure 25: Effect of leach feed rate

5.5.2.6. Effect of feed rate

The effect of the leach feed rate (dry tons/hour) on single pass uranium extraction is given in Figure 25. The leach feed rate does not have a noticeable impact on uranium extraction in individual tanks. This is despite the large range of recorded leach feed rates, between 50 and 150 tonnes per hour. Because the feed grade does not noticeably affect the amount uranium extracted, it can be concluded that the leach plant is operated under conditions that ensure maximum uranium extraction. The main driver of the carbonate uranium leaching process is temperature. High leaching temperatures are employed at the industrial carbonate uranium leaching plant studied, which facilitate the extraction of almost all uranium in the feed. If the leaching process was operated at lower temperature, the effect of feed uranium grade would be noticeable. This is because the temperature would not be high enough to extract large amounts of uranium from the feed.

5.5.2.7. Effect of particle size

The effect of the leach feed particle size on uranium extraction is shown in Figure 26. Based on Figure 26, the leach feed particle size does not have a major impact on uranium extraction. This can be attributed to the fact that particles fed to the leaching plant are made up of fine particles (95% less than 500 microns).

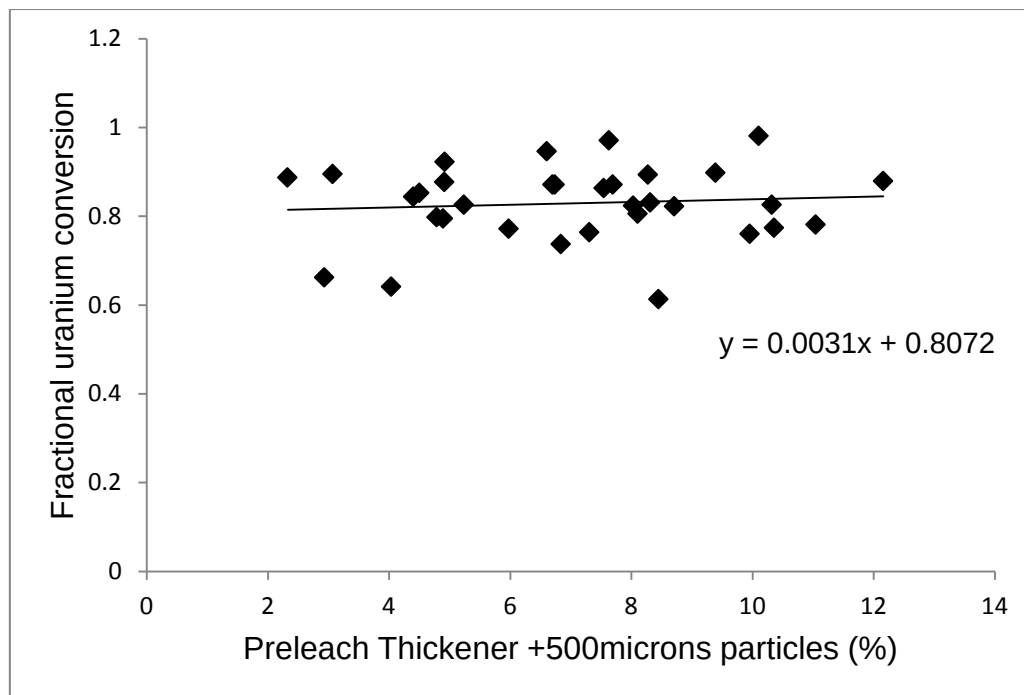


Figure 26: Effect of leach particle size

5.5.2.8. Linear Model Coefficients

Relying on data trends (such as those shown in Figure 19 to Figure 26) to determine the effect of process parameters on the performance of leaching operations has serious shortcomings. In multi-variable problems, data trends are only capable of determining a qualitative relationship between parameters and plant performance but cannot give a quantitative description of that relationship. Trend lines are also considerably affected by outlier observations and a certain data series may display a trend which is not representative of the real situation. Furthermore, two dimensional plots of data trends cannot highlight or identify scenarios where two or more parameters changed at the same time.

Multi-variable linear models giving a quantitative determination of process response with respect to all process parameters are a useful solution to problems of data trends. Coefficients

of a linear multi-variable leaching model were determined using linear regression in excel.

The linear leaching model giving the fractional conversion of uranium in tank i (X_i) for 6 leach tanks in series is given by equation 5.11.

$$\begin{aligned}
 \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \\ X_6 \end{bmatrix} = & - \begin{bmatrix} 0.00016 \\ 0.00013 \\ 0.00008 \\ 0.00006 \\ 0.00009 \\ 0.00006 \end{bmatrix} G_{U_3O_8} + \begin{bmatrix} 0.0001 \\ 0.00002 \\ 0.00002 \\ 0.00003 \\ 0.00008 \\ 0.00006 \end{bmatrix} G_{V_2O_5} - \begin{bmatrix} 0.029 \\ 0.019 \\ 0.011 \\ 0.007 \\ 0.006 \\ 0.004 \end{bmatrix} wt\% + \begin{bmatrix} 0.0092 \\ 0.0097 \\ 0.0066 \\ 0.0036 \\ 0.0035 \\ 0.0027 \end{bmatrix} C_{Na_2CO_3} \\
 & - \begin{bmatrix} 0.0289 \\ 0.0202 \\ 0.0214 \\ 0.0158 \\ 0.0068 \\ 0.0076 \end{bmatrix} C_{Na_2HCO_3} + \begin{bmatrix} -0.0267 \\ -0.0482 \\ -0.0062 \\ 0.01739 \\ 0.04437 \\ 0.04672 \end{bmatrix} pH + \begin{bmatrix} 0.01787 \\ 0.01992 \\ 0.01458 \\ 0.01105 \\ 0.00738 \\ 0.00647 \end{bmatrix} T + \begin{bmatrix} 0.00173 \\ 0.00049 \\ -0.00029 \\ -0.00002 \\ -0.00035 \\ -0.00014 \end{bmatrix} t
 \end{aligned}
 \tag{5.11}$$

Where: X_i = Fractional uranium conversion at tank i

T = Leach temperature, °C

$wt\%$ = Percentage solids (%)

G = Feed uranium grade, ppm

t = Residence time, hours

C = Concentration, g/l

Figure 27 shows the difference between leaching profiles predicted by the linear multi-variable leaching model and plant data. Percentage residuals, which are differences between

values predicted by the linear multi-variable leaching model and actual plant data, are given in Table 7.

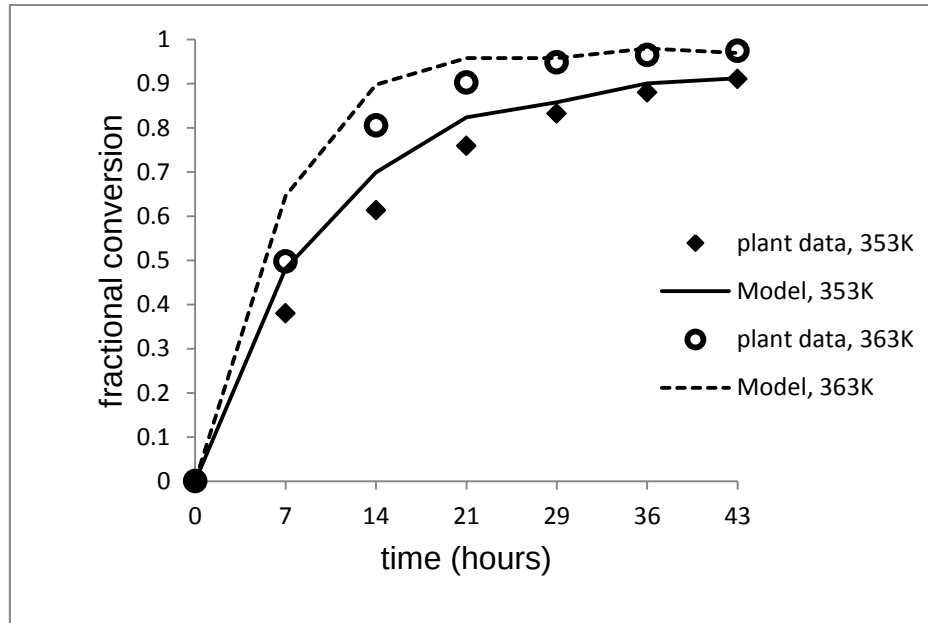


Figure 27: Linear multi-variable leaching model versus plant scale leach profile at 80°C and 90°C

Table 7: Residuals between model and observed percent uranium conversion values

Observation #	1	2	3	4	5	6	7	8
X1	2.8	16.0	4.84	14.88	5.8	4.22	7.4	10.4
X2	6.1	8.5	3.08	9.21	7.71	0.26	4.26	0.1
X3	4.44	5.70	0.68	5.52	3.57	0.10	1.93	0.13
X4	2.89	3.68	1.95	0.95	0.30	1.51	2.17	0.35
X5	0.67	1.55	1.78	1.43	0.09	0.98	1.47	0.90
X6	0.63	0.98	2.08	0.53	0.34	1.19	0.96	1.11

Table 7 continued

Observation #	9	10	11	12	13	14	Average
X1	15.29	11.01	7.6	10.61	0.2	2.3	4.75
X2	1.32	8.38	3.80	1.67	0.74	2.68	
X3	0.52	4.48	0.04	0.66	0.02	0.70	
X4	1.75	1.68	3.52	3.56	2.26	0.01	1.68
X5	2.02	0.65	3.62	3.74	0.39	2.42	
X6	3.10	0.06	3.14	3.11	2.85	2.09	

Analysis of coefficients of the vector equation (equation 5.11) reveals that a high uranium concentration in the feed to leach tanks results in a slight decrease in uranium extraction. An increase in vanadium content of the ore results in a negligible increase in uranium extraction but this also suggests that the presence of vanadium in the ore does not inhibit uranium dissolution. An increase in the solids content of the leach feed results in a decrease in uranium extraction. This implies that an increased solution density at constant agitator speed lowers the degree of contact between the liquid reactant and the solid particles, resulting in lower uranium extractions. An increase in sodium carbonate concentration results in a small increase in uranium extraction. It is expected that the amount of uranium extracted increase with an increase in the concentration of sodium carbonate. This is because sodium carbonate forms the soluble complex with uranium which results in uranium extraction from the ore. Increasing sodium bicarbonate concentration results in lower uranium extractions. Sodium bicarbonate reacts with sodium carbonate to buffer the solution pH and thus creates competition between the uranium dissolution reaction and the pH buffer reaction. The

leaching temperature increases uranium extraction because temperature increases rates of all endothermic reactions.

The solution pH and residence time are the only parameters with a combination of positive and negative signs. In the first tanks, uranium extraction decreases with increase in pH and increases with increase in residence time and vice versa for the last tanks. This suggests that there is a possibility of leached uranium precipitating out of solution in the first tanks. The concentration of uranium in solid particles in the first tanks is higher and a large residence time is required to extract a maximum amount of uranium. In the last tanks however, the solution is loaded with a higher amount of uranium, which makes it easier for uranium to precipitate out of solution. Hence the longer the slurry stays in the last leach tanks, the more uranium will precipitate out of solution. That is why the residence time does not favour uranium extraction in the last tanks.

The significance of the multi-variable leaching equation (equation 5.11) is that it can be used for multiple purposes. One; it can be used to accurately predict the efficiency of the leaching process from varying combinations of leach variables. Two; the equation can be used to predict the financial gains achievable from the process and its associated operational costs. Three; it can be used to determine consumption of consumables required to achieve a pre-determined leach process efficiency. Four; it can be used as an optimisation tool for the leaching process.

Figure 28 was constructed from the multi-variable model by varying the solution pH at various temperatures and predicts the fractional percent of uranium extracted from the ore. It can be seen from the figure that increasing pH at a constant temperature increases the amount

of uranium extracted and thus revenue. The fractional uranium conversion can be fixed but moving to a high pH region affords an opportunity to reduce operating temperature. This reduces the operating cost of the process because a reduction in leach temperature means reduced steam requirements and thus reduced diesel consumption in boilers. The boilers are used to generate steam which is in turn used to increase leach temperature. This is a typical process optimisation scenario.

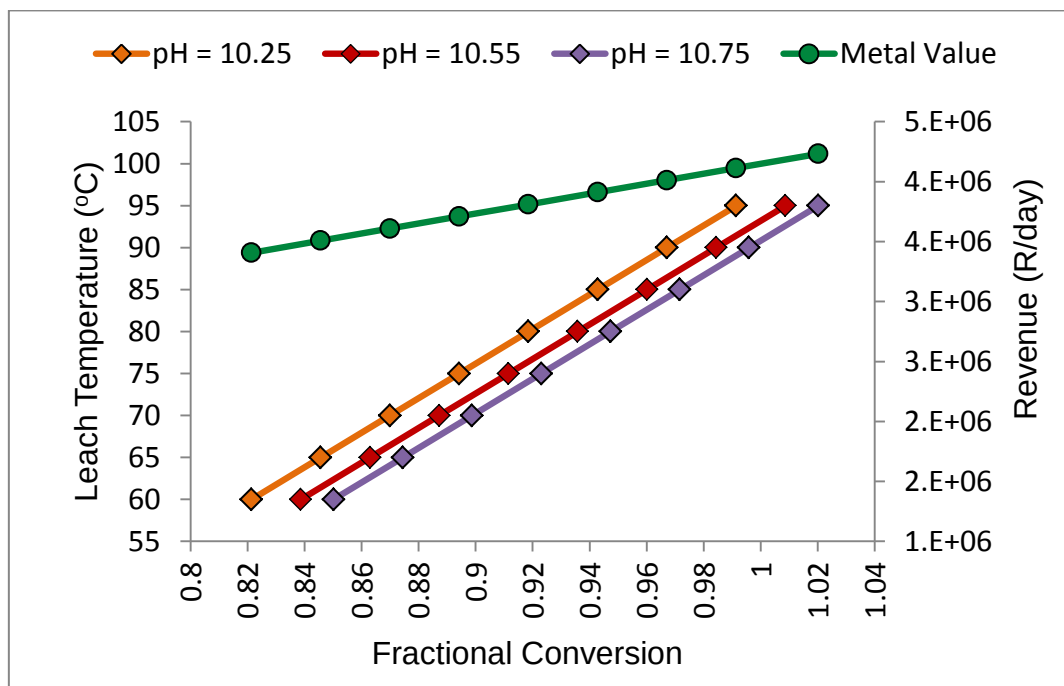


Figure 28: Possible optimisation routes

A comparison between two sets of leaching variables is shown in Table 8. An important finding from the comparison of parameters is that; it is possible to operate the leach process at lower temperatures and still attain high efficiencies and produce more uranium. Operating in accordance with the first set of parameters given in Table 8 instead of the second set of parameters has a potential of increasing uranium production by 20% and reduce steam consumption by half. Reduction in slurry density which favours uranium extraction reduces

the quantity of uranium in the slurry but this can be offset by lowering residence time (increasing throughput) and thus increasing uranium production. Economic evaluations of operating in accordance with the two sets of leach parameters are shown in Table 8.

Table 8: Variation of leach parameters and corresponding uranium production and steam

	Solids U₃O₈	Solids V₂O₅	% Solids	Solution Na₂CO₃	Solution NaHCO₃	Solution pH	Leach temperature	Residence time
	<i>ppm</i>	<i>ppm</i>	<i>Wt.%</i>	<i>g/L</i>	<i>g/L</i>	<i>None</i>	<i>°C</i>	<i>hours</i>
Set 1	1000	800	27.00	45.00	5.00	11.35	75	50
Set 2	1000	800	30.00	40.00	6.00	10.25	85	60
Difference	0.00	0.00	-3.00	5.00	-1.00	1.10	-10.00	-10.00

		Uranium prod.		Metal Value	Energy Cost	
T	X_{final}	Ore (t/day)	(t/day)	(R)	(R)	Net Val
75	0.987	6400	5.49	4,240,000	23,000	4,220,000
85	0.967	5480	4.55	3,520,000	57,000	3,450,000

The use of a multi-variable leaching model solves a number of operational problems. From time to time, inefficiencies arise in the leaching process due to deviations from normal in one or more of the leaching parameters. Because variations in operating parameters often occur at random intervals and simultaneously, it can be difficult to quantify the overall impact of multiple changes in process parameters. A multi-variable leaching model solves this problem.

5.5.2.9. Model User Interface

In order to enable easy visualisation of the multi-variable leaching model, a user interface has been designed with customised entry and action buttons. The user interface can be either desktop based or portable (integrated onto smart mobile phones). The user interface enables an interactive calculation of consumable costs and revenue from the process based on user entries of parameters values. The user interface consists of several pages (cards), where a user can navigate to and from. The steam card contains steam properties (temperature and pressure) which determine the heat value of steam.

It is necessary to determine the enthalpy of steam from a given pressure and temperature because enthalpy is a function of temperature and pressure. The specific enthalpy of steam at various temperatures and pressures affects the amount of steam required to raise the leach temperature to a desired value. A two variable equation has been developed (using regression) from steam tables by Rogers and Mayhew (1995); that give the enthalpy of steam at any temperature and pressure. An equation is required because the program built onto the user interface cannot read values from steam tables or thermodynamic charts. The enthalpy of steam in kJ/kg at any temperature and pressure was found to be given by equation 5.12.

$$\hat{H}(T, P) = 2443.86 - 3.034P + 2.12T \quad (5.12)$$

The main card is for the model itself and contains text fields where a user enters values of leach parameters (feed grade, pH, concentrations etc.). There are display fields on this card where predicted values of the most probable leach efficiency are displayed. The program then calculates the revenue that is obtainable from a certain feed rate and the predicted leach

efficiency, and displays this information in a display field. The program further iteratively calculates the required amount of steam from a given leach feed temperature and the required leach temperature. The program then calculates the cost of steam and displays it in a display field. Screen shots of the user interface showing the card for steam properties and the main model were taken from a Samsung smartphone (GT S5300) and are shown in Figure 29.

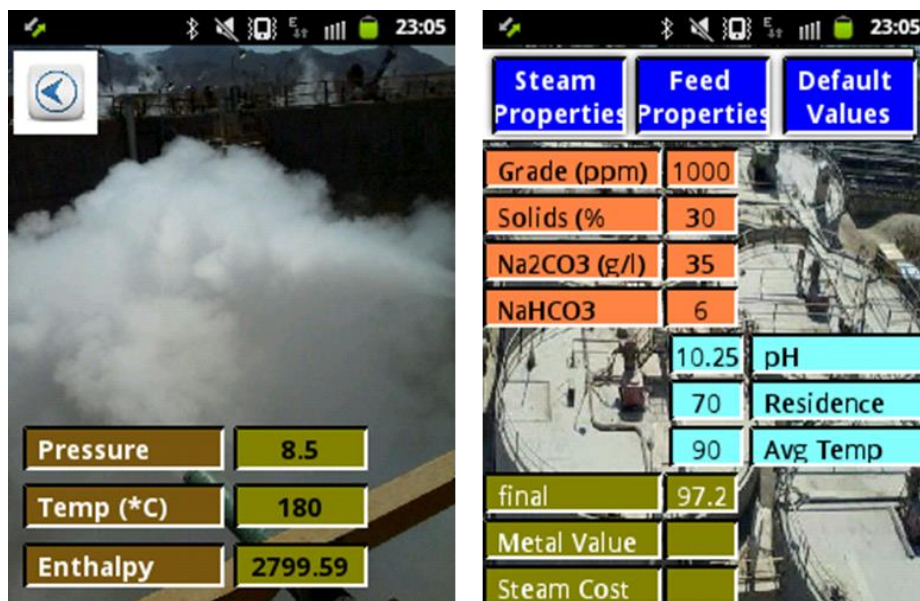


Figure 29: User interface for a multi-variable leaching model

Despite its usefulness, the problem of a linear multi-variable model is that it does not recognise physical boundaries. Also, the predictions of the model are limited only to the ranges within which it was developed and thus the user has to be aware of such boundaries. If for example a user wishes to predict leaching efficiency at 100°C (above the maximum temperature for which the model was developed), an efficiency of more than 100% will be obtained which is physically impossible. Also, entering a residence time of zero in the multi-variable model predicts a uranium conversion of more than 90% (depending on values of other parameters) which is at all impossible. But this is because the model was developed for

residence times of not less than 50 hours. It is inconvenient for the model user to keep note of ranges of the many variables of the model during use. To solve this, the user interface is customised to signal the user if a value of a parameter entered is out of the range within which the model was developed by opening up dialog boxes.

5.6. SENSITIVITY ANALYSIS

There are 8 different parameters which affect leach efficiency at the industrial carbonate leaching plant studied as shown in the vector equation of a multi-variable leaching model. In terms of operation of the leach circuit, there is no direct control over the uranium and vanadium contents of the ore which are controlled by preceding unit operations (pit grade control and ore beneficiation). Thus there are 6 parameters which are in direct control of the leach circuit operator namely; pulp density, sodium carbonate and sodium bicarbonate concentrations, solution pH, leach temperature and residence time. Thus the leach circuit operator can manipulate these parameters to obtain the most economical operating philosophy of the leach unit. A sensitivity analysis of the leach circuit relative to changes in the 6 controllable parameters is discussed below.

5.6.1. SENSITIVITY TO TEMPERATURE

Figure 30 depicts the effect of varying temperature on uranium leaching. Profiles for uranium conversion versus leaching time reach a maximum value that depends on leaching temperature. The point at which uranium conversion stops occurs at roughly the same leaching time for all temperatures. Temperatures of 90°C and above are capable of achieving

complete conversion of uranium depending on leaching time. Complete conversion can be reached after 40 hours of leaching at 90°C and less than 17 hours of leaching at 100°C.

5.6.2. SENSITIVITY TO SODIUM CARBONATE CONCENTRATION

Figure 31 shows the effect of varying the concentration of sodium carbonate on uranium leaching. The leaching rate is faster at high sodium carbonate concentrations although the final uranium conversion does not differ significantly between differing concentrations of sodium carbonate. Sodium carbonate concentrations of 40 g/l are capable of achieving complete uranium conversion at 28 hours of leaching while a concentration of 45 g/l is capable of achieving complete conversion at less than 18 hours of leaching.

5.6.3. SENSITIVITY TO SOLUTION pH

Figure 32 shows the effect of varying the leach solution pH on uranium extraction. pH has a marginal effect on uranium extraction in the ranges studied. However, low solution pH favours uranium extraction in the first 20 hours of leaching at a residence time of 50 hours. After 20 hours of leaching however, the pH effect is reversed and a high solution pH favours uranium conversion. A pH of 10.55 is capable of achieving complete conversion of uranium after 34 hours of leaching at a residence time of 50 hours. On the other hand, a pH of 11.15 is capable of achieving complete conversion of uranium after 28 hours of leaching.

5.6.4. SENSITIVITY TO SOLIDS CONTENT

Figure 33 shows the effect of varying the solids content of the leach slurry. It can be seen from Figure 33 that the lower the solids percent in the leaching slurry is; the faster is the rate

of leaching. Solids percent of 27 in the slurry is capable of achieving complete uranium conversion within 32 hours of leaching. 25% solids content in leach slurry is capable of achieving complete dissolution of uranium within 26 hours of leaching. A high solids content in the leach slurry result in a high slurry density. While a low slurry density favours uranium extraction, it will result in low metal production.

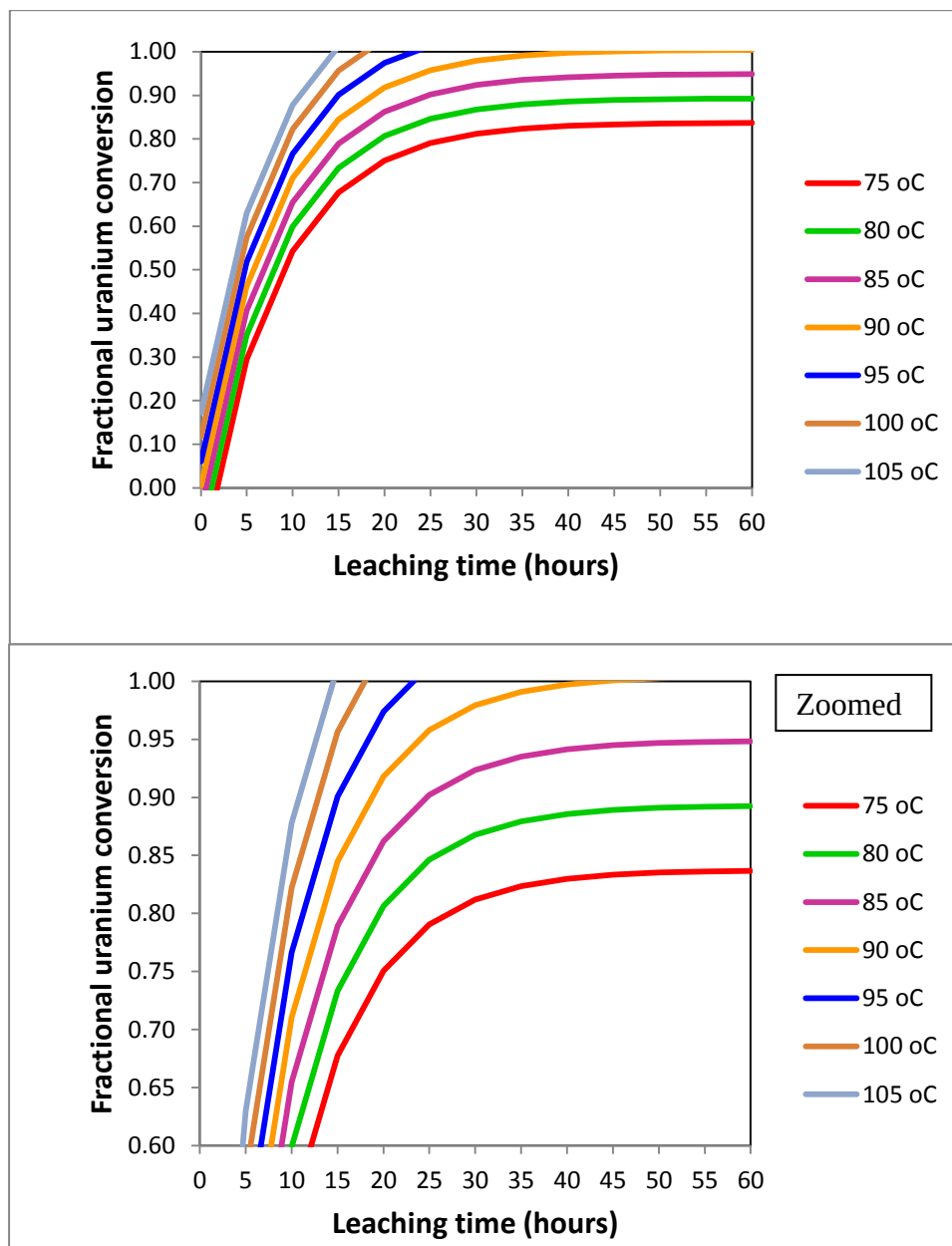


Figure 30: Sensitivity of uranium leaching to temperature

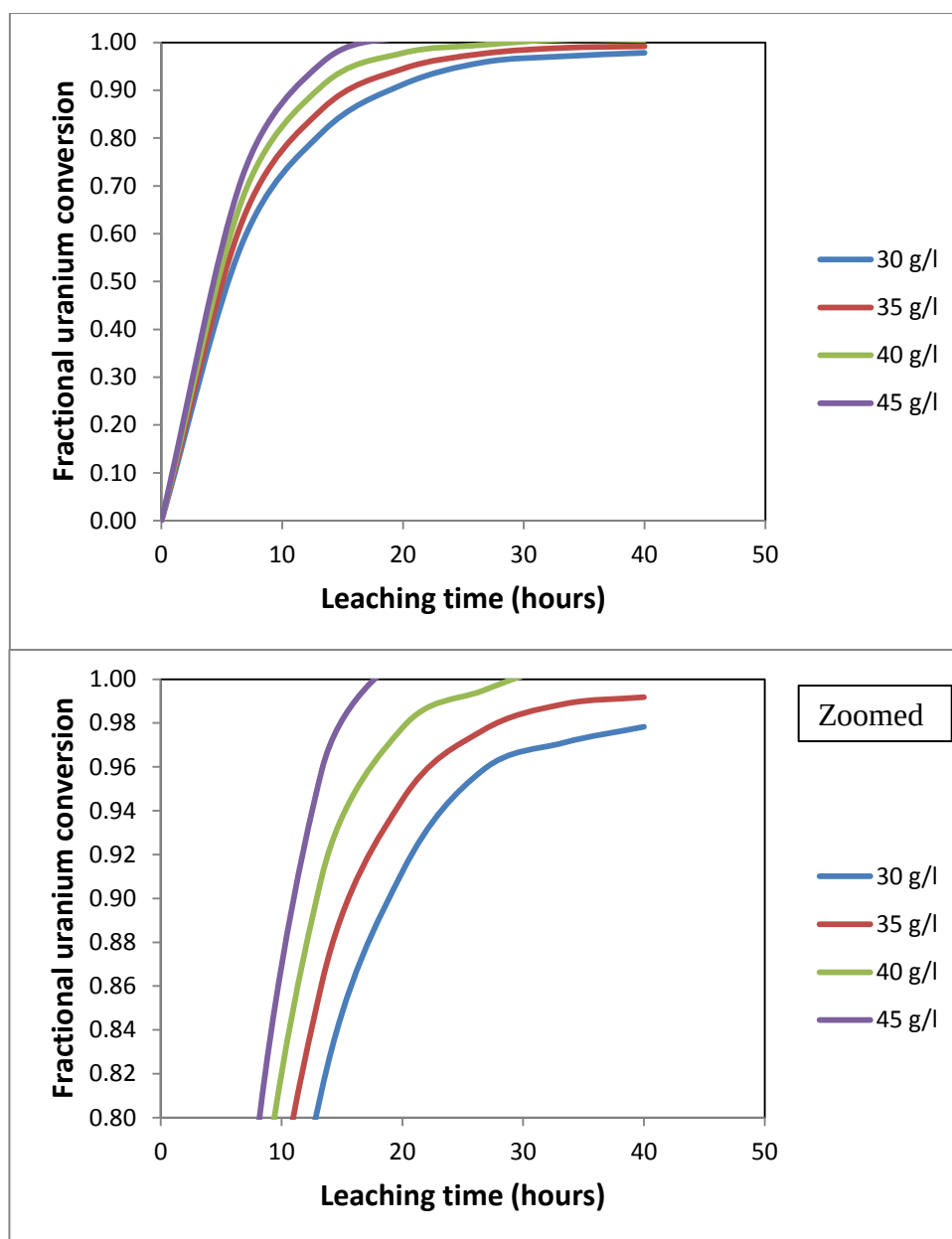


Figure 31: Sensitivity of uranium leaching to sodium carbonate concentration

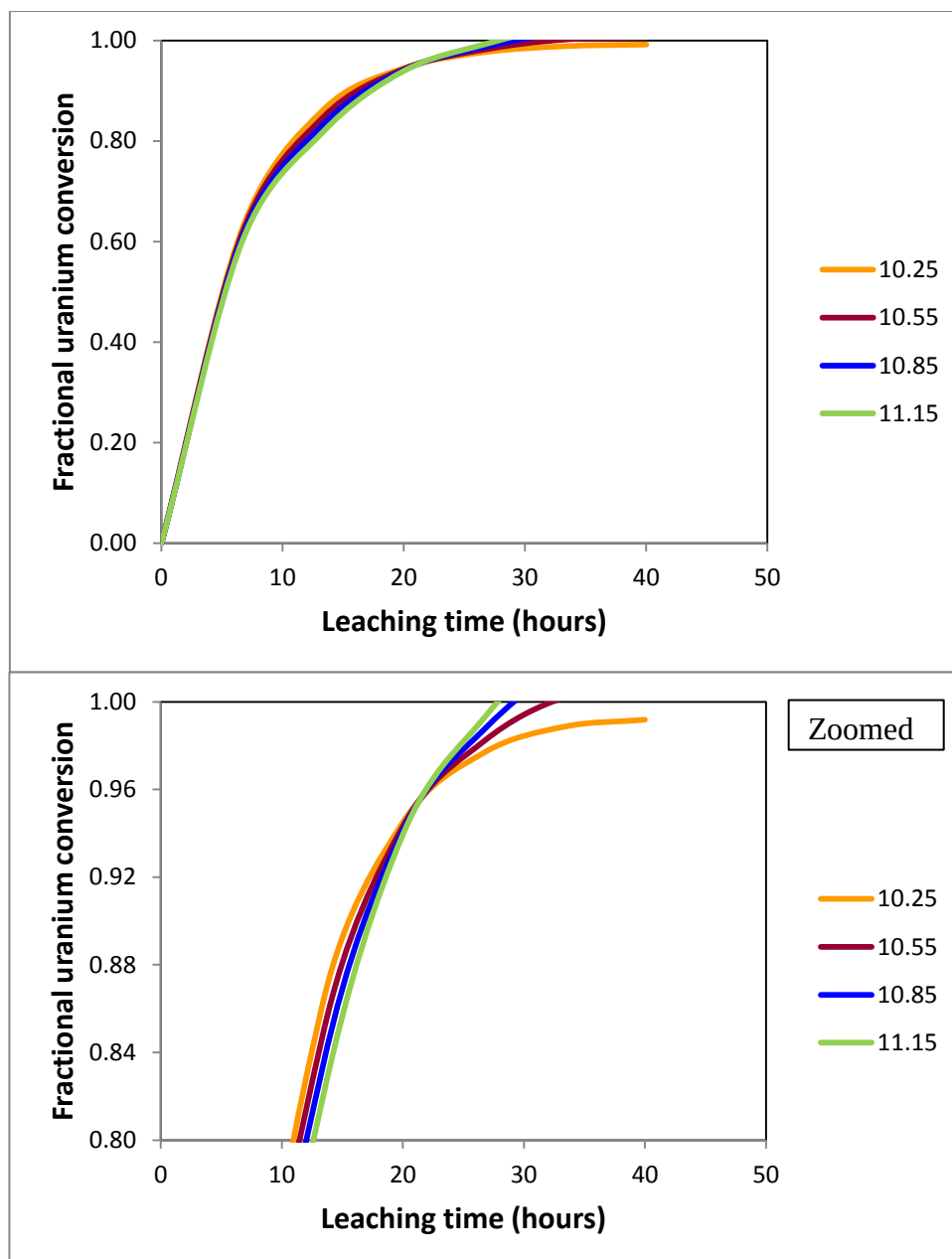


Figure 32: Sensitivity of uranium leaching to the solution pH

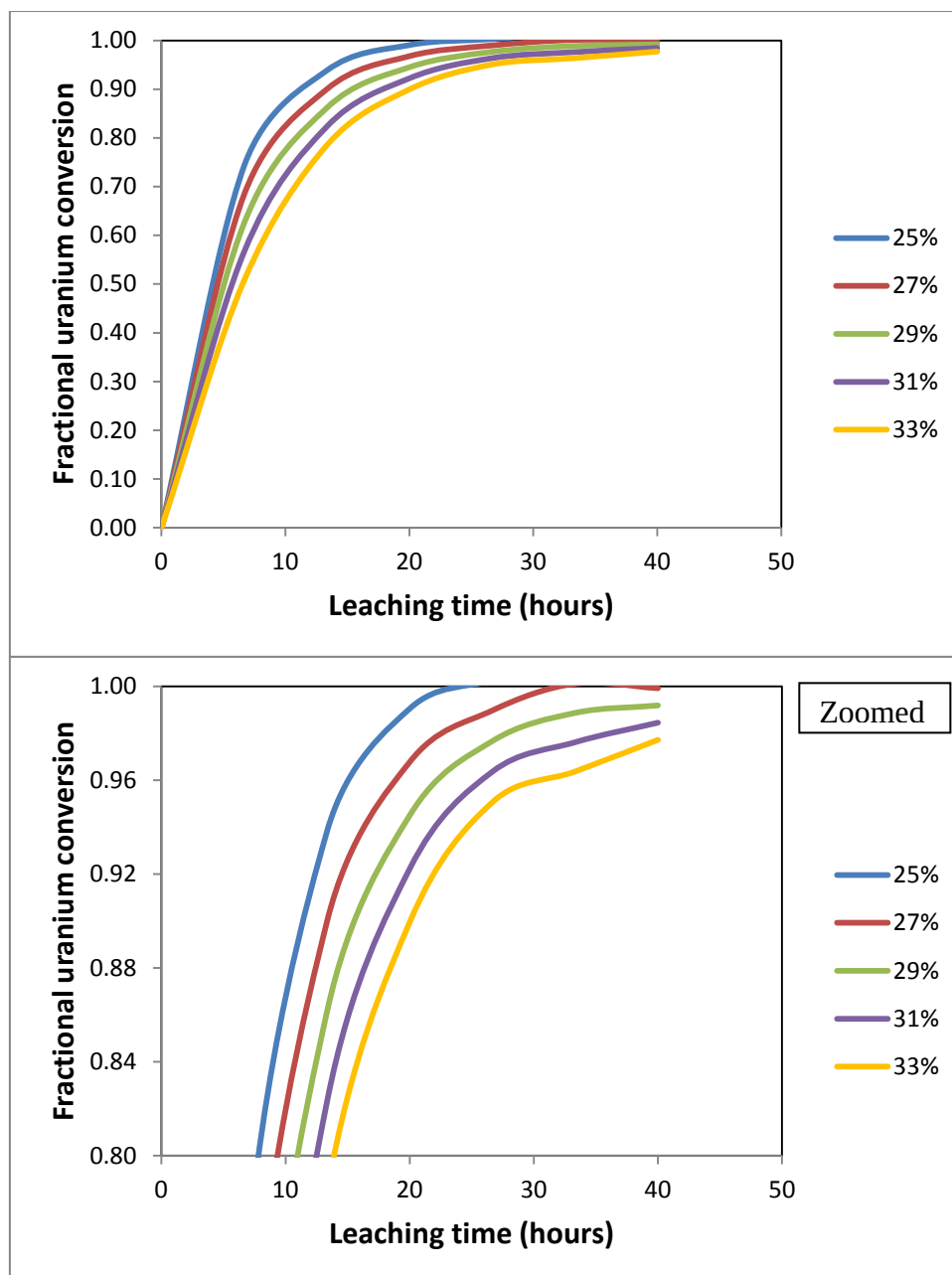


Figure 33: Sensitivity of uranium leaching to the slurry solids content

CHAPTER 6

6. CONCLUSION AND RECOMMENDATIONS

6.1. CONCLUSIONS

The aim of this research was to develop empirical and fundamental models describing the rate of carnotite leaching. The study was then to utilise developed empirical and theoretical models to predict the performance of a carbonate uranium leaching process and develop predictive tools for leaching processes based on empirical and theoretical models.

Mathematical models developed in this work (fundamental, empirical and linear multi-variable) all predict the performance of a leaching process well. Four different types of exponential empirical models were correlated to plant and data, and it was found that they all predicted the leaching process with reasonable accuracy. The percent error between models' uranium conversion prediction and actual values from plant data is relatively small and acceptable. This error however should be viewed not only in terms of the models' inability to perfectly match the physical leaching system but the underlying simplifications in model development and system orientation. Models were developed assuming a uniform particle size distribution of the leach feed and uniform uranium grade distribution in particles of different sizes. At the industrial carbonate leaching plant studied, the leach feed is relatively fine with more than 90% percent of particles less than 0.6mm. Thus an assumption of a uniform size distribution should not affect the accuracy of the model significantly. Assuming a uniform grade distribution however will greatly affect the accuracy of the model. This is because there is a considerable variation in uranium content between particles of different sizes. Assumptions of uniform size and grade distributions can be overcome by applying equation

2.5 to each size class and equation 2.6 (section 2.1) to obtain the overall rate of leaching. Though this can be done, it will result in a complex mathematical model. Furthermore, the fundamental model was developed under an assumption of negligible particles segregation in leach tanks. This implies that all particles spend more or less the same time in one leach tank. In reality, particles of different sizes spend different times in a continuous leach process due to differing hydrodynamics, which is a function of particle diameter.

Another significant factor that could have impacted the accuracy of leaching models is the configuration of the leach tanks and the practical method of sampling. Because of long residence times, the slurry enters the first leach tank at time t_0 but enters subsequent tanks at later times of t_1, t_2, t_3 and so on. The times ($t_0, t_1, t_2, \dots, t_n$) vary between 0 and 40 hours or more. Samples of leach profiles (giving uranium conversion at tank n) that are taken daily are not taken in accordance with time t_1, t_2, t_3 etc. This introduces a significant error in model development because leach profiles analysed in a single day correspond to temperatures of different days. Another significant source of error is the presence of outliers in the data sets from which the model was developed, and outliers in data sets on which the model was tested. As stated in Section 3.3, an outlier is interpreted as an observation whose dependent variable is unusual (Bhar, n.d.), or “when an observation has a large value where such a value would indicate that the observation is a large number of standard deviation from the mean” (Gray & MacDonell, 1997). The source of outliers in data can be attributed to operational mistakes (Bhar, n.d.), or error in measurements and can have considerable impacts on the efficacy of estimation models. Outlier observations arise from the fact that it is almost impossible to run a plant scale leaching circuit smoothly without disturbances for consecutive days. Disturbances results in measurements with large deviations from the mean.

Furthermore, the inability of the model to perfectly match plant data could be caused by an exclusion from the model of parameters which have an impact on the performance of the leaching circuit which are not directly accounted for by the solution conditions factor. Reliability of measuring instruments (flow meters, densitometers, temperature probes etc.) also has a significant impact on the accuracy of leach models developed here. If instruments were faulty, then incorrect values of parameters were used in constructing models. For data collected over long periods as the case in this research, even if instruments were occasionally faulty the effect of in-correct measurements will be offset by other reliable data because instruments are regularly calibrated. Changes in mineralogy of the leach feed will also affect the accuracy of leach models. Ore mineralogy is not evaluated on a daily bases and thus leach models developed in this research do not account for the mineralogy of the ore.

The linear multi-variable leaching model was found to be the most useful compared to fundamental and exponential empirical models. Unlike the linear multi-variable model, the effects of process parameters are hidden in constants and the solution condition factor of exponential empirical and fundamental models. Thus, it cannot be deduced from exponential empirical and fundamental models how a change in leach parameters (other than temperature and residence time) will affect the performance of the plant. The linear multi-variable model on the other hand consists of an expression that gives a quantitative description of the leach process inclusive of all leach parameters. Though the linear multi-variable was found to be the most useful in terms of process optimisation, the fact that it is limited to the ranges within which it was developed is problematic. It cannot be used with confidence to predict process response to a completely new set of operating conditions. It is thus simply a tool to help process operators obtain the best operating philosophy from the process currently at hand.

The linear multi-variable leaching model can be used to optimise the leach process either to reduce operating cost (steam consumption) or to increase revenue (metal production). Implementing changes in process parameters to increase the production and cost efficiency of the industrial carbonate leach plant studied here is not complex. This involve reducing the slurry density by 2%, increasing the sodium carbonate concentration by 5g/l, reducing temperature by 10°C, reducing residence time by 10 hours amongst other changes. These changes can however impact negatively on downstream processes and on auxiliary equipment such as heat exchangers. Before implementation on plant scale, findings of the linear multi-variable model should be backed up with properly executed leaching experiments.

A cross platform (mobile phone and desktop) application has been developed for the multi-variable leaching model as a process optimisation tool. The mobile based application is made up of a customised and user friendly interface where a plant operator can experiment with different values of leach parameters. The operator can then compare the leach efficiency predicted by the model with a particular combination of parameters to efficiencies attained by reference leach parameters. The graphical user interface can be used for example in cases where for a given reason there is a restriction in one parameter. To counter the effects of that restriction, the operator can use the graphical user interface to seek parameters that can be modified to increase the leach process efficiency to target values.

6.2. RECOMMENDATIONS

It is recommended that implementation of findings of this research onto any leaching operation be backed up by properly executed leach experiments. It is also recommended that further research be undertaken to verify the findings of this research from laboratory

experiments. Controlled experiments will eliminate any statistical errors brought about by the presence of outliers in data sets or by the presence of false measurements caused by faulty measuring instruments.

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8. APPENDICES

8.1. PARTICLE SIZE AND GRADE DISTRIBUTION

The particle size distribution of the leach feed of the uranium carbonate leaching industrial facility is given in Table 9 while the grade distribution of the leach feed is shown in Table 10.

Table 9: Leach feed particle size distribution

size	mass%	Cumulative % Retained	Cumulative % Passing
0	31.78	100	0
38	9.22	68.22	31.78
75	8.85	59	41
106	6.41	50.15	49.85
150	7.35	43.74	56.26
212	8.09	36.39	63.61
300	10.53	28.3	71.7
400	4.29	17.77	82.23
500	3.27	13.48	86.52
600	7.71	10.21	89.79
850	1.2	2.5	97.5
1000	1.23	1.3	98.7
2000	0.05	0.07	99.93
4000	0	0	100

Table 10: Leach feed grade distribution

Grade	Mass percent	Cumulative % Retained	Cumulative % Passing
8721	0.7	99.28	0.72
6222	1.13	97.45	2.55
5029	1.83	95.62	4.38
2579	2.74	92.88	7.12
1035	5.56	87.32	12.68
589	8.77	78.55	21.45
451	7.2	71.35	28.65
366	9.73	61.62	38.38
252	19.46	42.16	57.84
147	9.19	32.97	67.03
82	31.34	1.63	98.37
41	1.63	0	100

8.2. RATE LIMITING MECHANISMS

The activation energy of carbonate leaching of carnotite uranium ore was determined from the rate constants associated with mechanisms which were found to be rate limiting.

8.2.1. CONSTANT SIZE PARTICLES

The rate constants associated with film diffusion, ash layer diffusion, and chemical reaction resistances for particles of constant size are given in Table 11 to

Table 13. These values were calculated from fractional uranium conversion data from the plant using equations derived in section 2.2 which govern particular rate limiting mechanisms.

Table 11: Rate constants of film diffusion resistance at various leaching times

Observation #	1	2	3	4	5	6	7	8
t1	0.411	0.419	0.697	0.743	0.558	0.619	0.497	0.632
t2	0.771	0.764	0.871	0.922	0.781	0.863	0.806	0.826
t3	0.892	0.872	0.940	0.963	0.903	0.926	0.903	0.916
t4	0.954	0.932	0.951	0.973	0.934	0.961	0.949	0.965
t5	0.972	0.936	0.976	0.981	0.962	0.975	0.965	0.970
t6	0.984	0.964	0.983	0.983	0.964	0.982	0.975	0.974

Table 11 Continued

Observation #	9	10	11	12	13	14	15	16
t1	0.601	0.606	0.621	0.575	0.380	0.531	0.488	0.465
t2	0.853	0.898	0.871	0.824	0.613	0.737	0.641	0.760
t3	0.931	0.932	0.942	0.925	0.759	0.861	0.777	0.892
t4	0.958	0.949	0.957	0.943	0.832	0.926	0.823	0.944
t5	0.961	0.968	0.960	0.960	0.880	0.956	0.874	0.963
t6	0.968	0.980	0.971	0.978	0.910	0.962	0.909	0.969

Table 12: Rate constants of ash diffusion resistance at various leaching times

Observation #	1	2	3	4	5	6	7	8
t1	0.070	0.073	0.253	0.301	0.144	0.185	0.109	0.195
t2	0.336	0.326	0.492	0.609	0.348	0.477	0.382	0.412
t3	0.535	0.494	0.661	0.740	0.561	0.620	0.560	0.592
t4	0.705	0.636	0.697	0.782	0.643	0.734	0.688	0.749
t5	0.780	0.647	0.800	0.823	0.737	0.791	0.751	0.771
t6	0.840	0.746	0.834	0.833	0.746	0.828	0.792	0.791

Table 12 Continued

Observation #	9	10	11	12	13	14	15	16
t1	0.187	0.154	0.059	0.127	0.104	0.093	0.139	0.238
t2	0.493	0.409	0.181	0.294	0.203	0.321	0.339	0.420
t3	0.667	0.615	0.320	0.473	0.342	0.535	0.504	0.551
t4	0.718	0.670	0.423	0.618	0.408	0.672	0.648	0.642
t5	0.731	0.729	0.510	0.713	0.499	0.740	0.591	0.713
t6	0.775	0.811	0.579	0.737	0.574	0.765	0.747	0.752

Table 13: Rate constants of chemical reaction resistance at various leaching times

Observation #	1	2	3	4	5	6	7	8
t1	0.162	0.165	0.328	0.364	0.238	0.275	0.205	0.283
t2	0.389	0.382	0.495	0.573	0.397	0.485	0.421	0.441
t3	0.523	0.496	0.609	0.666	0.541	0.581	0.540	0.562
t4	0.640	0.592	0.635	0.699	0.596	0.662	0.628	0.673
t5	0.697	0.599	0.713	0.732	0.664	0.706	0.674	0.690
t6	0.747	0.670	0.741	0.741	0.671	0.736	0.707	0.706

Table 13 Continued

Observation #	9	10	11	12	13	14	15	16
t1	0.277	0.248	0.147	0.223	0.200	0.188	0.235	0.318
t2	0.495	0.439	0.272	0.359	0.289	0.378	0.391	0.447
t3	0.613	0.577	0.378	0.482	0.393	0.524	0.503	0.534
t4	0.650	0.615	0.449	0.579	0.438	0.617	0.600	0.596
t5	0.659	0.658	0.507	0.647	0.499	0.666	0.561	0.646
t6	0.693	0.722	0.553	0.664	0.550	0.685	0.672	0.675

8.2.2. NON-CONSTANT SIZE PARTICLES

The rate constants associated with film diffusion and chemical reaction resistances for particles of changing size are given in Table 14 to

Table 15. These values were calculated from fractional uranium conversion data from the plant using equations derived in section 2.2 which govern particular rate limiting mechanisms.

Table 14: Rate constants of film diffusion resistance at various leaching times

Observation #	1	2	3	4	5	6	7	8
t1	0.298	0.303	0.549	0.596	0.420	0.474	0.368	0.486
t2	0.626	0.618	0.745	0.818	0.637	0.734	0.664	0.688
t3	0.773	0.746	0.847	0.888	0.789	0.824	0.789	0.808
t4	0.871	0.833	0.866	0.909	0.837	0.886	0.862	0.893
t5	0.908	0.839	0.918	0.928	0.887	0.913	0.894	0.904
t6	0.936	0.891	0.933	0.933	0.892	0.930	0.914	0.913

Table 14 Continued

Observation #	9	10	11	12	13	14	15	16
t1	0.477	0.435	0.273	0.397	0.360	0.341	0.414	0.534
t2	0.745	0.686	0.469	0.589	0.495	0.614	0.629	0.694
t3	0.851	0.821	0.613	0.732	0.632	0.773	0.753	0.783
t4	0.877	0.852	0.696	0.823	0.685	0.853	0.840	0.837
t5	0.884	0.883	0.757	0.875	0.749	0.888	0.807	0.875
t6	0.906	0.923	0.800	0.887	0.797	0.901	0.892	0.894

Table 15: Rate constants of ash diffusion resistance at various leaching times

Observation #	1	2	3	4	5	6	7	8
t1	0.162	0.165	0.328	0.364	0.238	0.275	0.205	0.283
t2	0.389	0.382	0.495	0.573	0.397	0.485	0.421	0.441
t3	0.523	0.496	0.609	0.666	0.541	0.581	0.540	0.562
t4	0.640	0.592	0.635	0.699	0.596	0.662	0.628	0.673
t5	0.697	0.599	0.713	0.732	0.664	0.706	0.674	0.690
t6	0.747	0.670	0.741	0.741	0.671	0.736	0.707	0.706

Table 15 Continued

Observation #	9	10	11	12	13	14	15	16
t1	0.187	0.154	0.059	0.127	0.104	0.093	0.139	0.238
t2	0.493	0.409	0.181	0.294	0.203	0.321	0.339	0.420
t3	0.667	0.615	0.320	0.473	0.342	0.535	0.504	0.551
t4	0.718	0.670	0.423	0.618	0.408	0.672	0.648	0.642
t5	0.731	0.729	0.510	0.713	0.499	0.740	0.591	0.713
t6	0.775	0.811	0.579	0.737	0.574	0.765	0.747	0.752

8.3. FUNDAMENTAL LEACHING MODEL

8.3.1. ACTIVATION ENERGY

The activation energy was calculated from the Arrhenius plot where the natural logarithm of rate constants are plotted versus the inverse of absolute temperature. The overall rate constants of the carbonate leaching of carnotite uranium are given in Table 16.

Table 16: Overall leaching rate constants at various temperatures

T	k	T_{avg}	k_{avg}	T_{avg} (K)	1/T_{avg} (K⁻¹)	ln (k)
82.2	0.0163	82.8	0.02185	355.9	0.00281	-3.824
83.3	0.0274					
85.1	0.0275	86.2	0.02775	359.4	0.00278	-3.585
87.3	0.0280					
88.3	0.0322	88.4	0.03050	361.5	0.00277	-3.446
88.5	0.0288					
90.4	0.0528	90.5	0.035475	363.6	0.00275	-3.339
90.8	0.0374					

8.3.2. FUNDAMENTAL MODEL PREDICTIONS

Fractional uranium conversions predicted by the fundamental leaching model are given in

Table 17 while the actual uranium conversion data from the leach plant are given in Table 18. Absolute errors between percentage uranium conversion predicted by the fundamental model and actual uranium conversions are given in Table 19.

Table 17: Fractional uranium conversions predicted by the fundamental leaching model

Observation #	1	2	3	4	5	6	7	8
X_0	0	0	0	0	0	0	0	0
X_1	0.604	0.690	0.459	0.724	0.679	0.667	0.674	0.710
X_2	0.854	0.890	0.696	0.913	0.885	0.878	0.875	0.899
X_3	0.934	0.949	0.819	0.962	0.949	0.945	0.937	0.951
X_4	0.962	0.965	0.883	0.975	0.968	0.967	0.955	0.963
X_5	0.972	0.967	0.917	0.974	0.972	0.972	0.955	0.960
X_6	0.973	0.959	0.935	0.965	0.968	0.969	0.946	0.947

Table 17 Continued

Observation #	9	10	11	12	13	14	15	16
X_0	0	0	0	0	0	0	0	0
X_1	0.764	0.452	0.420	0.462	0.520	0.613	0.581	0.633
X_2	0.919	0.681	0.646	0.690	0.743	0.823	0.814	0.853
X_3	0.951	0.799	0.769	0.805	0.842	0.898	0.908	0.930
X_4	0.948	0.861	0.837	0.863	0.885	0.923	0.947	0.958
X_5	0.927	0.893	0.875	0.892	0.902	0.926	0.962	0.966
X_6	0.889	0.908	0.895	0.905	0.905	0.917	0.967	0.965

Table 18: Actual fractional uranium conversions from plant data

Observation #	1	2	3	4	5	6	7	8
X_0	0	0	0	0	0	0	0	0
X_1	0.697	0.743	0.558	0.619	0.497	0.632	0.601	0.689
X_2	0.871	0.922	0.781	0.863	0.806	0.826	0.853	0.871
X_3	0.940	0.963	0.903	0.926	0.903	0.916	0.931	0.927
X_4	0.951	0.973	0.934	0.961	0.949	0.965	0.958	0.957
X_5	0.976	0.981	0.962	0.975	0.965	0.970	0.961	0.966
X_6	0.983	0.983	0.964	0.982	0.975	0.974	0.968	0.968

Table 18 Continued

Observation #	9	10	11	12	13	14	15	16
X_0	0	0	0	0	0	0	0	0
X_1	0.621	0.575	0.380	0.531	0.488	0.465	0.552	0.682
X_2	0.871	0.824	0.613	0.737	0.641	0.760	0.774	0.831
X_3	0.942	0.925	0.759	0.861	0.777	0.892	0.877	0.899
X_4	0.957	0.943	0.832	0.926	0.823	0.944	0.936	0.934
X_5	0.960	0.960	0.880	0.956	0.874	0.963	0.915	0.956
X_6	0.971	0.978	0.910	0.962	0.909	0.969	0.965	0.966

Table 19: Absolute errors between the fundamental model predictions and actual plant conversions

Observation #	1	2	3	4	5	6	7	8
X_0	0	0	0	0	0	0	0	0
X_1	9.3	5.3	10.50	18.17	3.5	7.30	2.1	25.7
X_2	1.7	3.3	4.96	7.97	5.22	2.25	2.75	8.9
X_3	0.66	1.40	3.62	4.61	2.94	0.55	2.31	3.90
X_4	1.09	0.72	1.35	1.98	0.17	0.35	0.56	2.87
X_5	0.47	1.40	0.04	0.68	0.17	0.56	0.62	3.07
X_6	1.02	2.37	1.62	0.69	0.56	2.27	2.09	4.76

Table 19 Continued

Observation #	9	10	11	12	13	14
X_0	0	0	0	0	0	0
X_1	1.52	14.23	6.9	14.77	3.0	4.9
X_2	9.81	4.78	4.68	6.32	3.99	2.24
X_3	5.62	0.83	5.66	0.57	3.08	3.16
X_4	4.72	0.89	6.27	2.10	1.05	2.36
X_5	6.44	3.30	6.37	3.65	4.68	1.05
X_6	8.74	8.18	5.68	5.20	0.22	0.02

8.3.3. EXPONENTIAL EMPIRICAL MODEL

Fractional uranium conversions predicted by the exponential empirical leaching model are given in Table 20 while the absolute errors between percentage uranium conversion predicted by the exponential empirical leaching model and actual uranium conversions are given in Table 21.

Table 20: Fractional uranium conversions predicted by the exponential empirical leaching model

Observation #	1	2	3	4	5	6	7	8
X_0	0	0	0	0	0	0	0	0
X_1	0.516	0.620	0.440	0.628	0.593	0.581	0.636	0.654
X_2	0.791	0.856	0.689	0.865	0.836	0.826	0.864	0.879
X_3	0.908	0.946	0.822	0.957	0.937	0.931	0.944	0.956
X_4	0.962	0.981	0.893	0.992	0.979	0.975	0.973	0.983
X_5	0.988	0.994	0.931	1.005	0.996	0.994	0.983	0.992
X_6	0.999	0.999	0.952	1.011	1.004	1.002	0.986	0.995

Table 20 Continued

Observation #	9	10	11	12	13	14	15	16
X_0	0	0	0	0	0	0	0	0
X_1	0.746	0.525	0.571	0.563	0.658	0.658	0.510	0.563
X_2	0.927	0.766	0.789	0.792	0.843	0.865	0.760	0.809
X_3	0.969	0.864	0.858	0.873	0.888	0.925	0.883	0.917
X_4	0.979	0.903	0.880	0.902	0.899	0.943	0.943	0.964
X_5	0.982	0.919	0.887	0.912	0.902	0.948	0.973	0.985
X_6	0.982	0.925	0.890	0.916	0.903	0.949	0.988	0.994

Table 21: Absolute errors between the exponential empirical leaching model and actual plant conversion

Observation #	1	2	3	4	5	6	7	8
X_0	0	0	0	0	0	0	0	0
X_1	18.1	12.3	0.94	9.53	5.0	3.45	3.5	29.0
X_2	8.0	6.6	0.22	3.00	0.04	1.12	0.77	9.5
X_3	3.24	1.64	3.03	3.40	1.48	1.30	2.89	2.86
X_4	1.09	0.82	3.04	3.03	1.01	1.44	2.55	0.90
X_5	1.12	1.33	3.09	3.10	2.40	2.17	2.57	0.09
X_6	1.68	1.65	2.91	2.89	2.79	1.78	2.73	0.22

Table 21 Continued

Observation #	9	10	11	12	13	14
X_0	0	0	0	0	0	0
X_1	12.84	12.46	3.1	19.29	4.1	11.9
X_2	2.62	5.53	5.48	10.48	1.39	2.13
X_3	3.80	2.71	1.19	3.30	0.59	1.85
X_4	5.10	2.23	2.36	0.12	0.74	3.03
X_5	6.99	2.14	4.36	1.50	5.78	2.94
X_6	8.10	1.12	4.62	1.96	2.30	2.85

8.3.4. LINEAR MULTI-VARIABLE LEACHING MODEL

Fractional uranium conversions predicted by the linear multi-variable leaching model are given in

Table 22 while the absolute errors between percentage uranium conversion predicted by the linear multi-variable leaching model and actual uranium conversions are given in Table 23.

Table 22: Fractional uranium conversions predicted by the exponential empirical leaching model

Observation #	1	2	3	4	5	6	7	8
X_0	0	0	0	0	0	0	0	0
X_1	0.725	0.903	0.605	0.571	0.646	0.690	0.643	0.615
X_2	0.932	1.007	0.821	0.832	0.898	0.903	0.855	0.829
X_3	0.985	1.020	0.914	0.919	0.958	0.952	0.930	0.908
X_4	0.980	1.010	0.936	0.942	0.958	0.962	0.943	0.936
X_5	0.983	0.996	0.953	0.957	0.980	0.971	0.951	0.952
X_6	0.976	0.992	0.958	0.961	0.969	0.971	0.956	0.958

Table 22 Continued

Observation #	9	10	11	12	13	14	15	16
X_0	0	0	0	0	0	0	0	0
X_1	0.732	0.630	0.482	0.607	0.467	0.571	0.550	0.705
X_2	0.955	0.842	0.699	0.775	0.693	0.776	0.767	0.857
X_3	0.987	0.917	0.824	0.861	0.822	0.885	0.877	0.906
X_4	0.974	0.922	0.858	0.890	0.859	0.908	0.913	0.934
X_5	0.967	0.945	0.901	0.920	0.898	0.925	0.919	0.932
X_6	0.972	0.948	0.913	0.931	0.913	0.938	0.936	0.945

Table 23: Absolute errors between the exponential empirical leaching model and actual plant conversion

Observation #	1	2	3	4	5	6	7	8
X_0	0	0	0	0	0	0	0	0
X_1	2.82	16.0	4.84	14.88	5.83	4.22	7.42	10.4
X_2	6.10	8.48	3.08	9.21	7.71	0.256	4.26	0.072
X_3	4.44	5.70	0.68	5.52	3.57	0.096	1.93	0.131
X_4	2.89	3.68	1.95	0.951	0.299	1.51	2.17	0.35
X_5	0.672	1.55	1.78	1.43	0.092	0.977	1.47	0.898
X_6	0.625	0.977	2.08	0.534	0.343	1.19	0.961	1.11

Table 23 Continued

Observation #	9	10	11	12	13	14
X_0	0	0	0	0	0	0
X_1	15.29	11.01	7.59	10.61	0.154	2.33
X_2	1.32	8.38	3.80	1.67	0.737	2.68
X_3	0.522	4.48	0.038	0.660	0.022	0.703
X_4	1.75	1.68	3.52	3.56	2.26	0.008
X_5	2.02	0.655	3.62	3.74	0.386	2.42
X_6	3.10	0.062	3.14	3.11	2.85	2.09

8.4. LINEAR MULTI-VARIABLE MODEL USER INTERFACE

8.4.1. ENTHALPY FUNCTION

In order to allow calculations of steam required to raise leaching temperature to desired levels, a two variable (temperature and pressure) function of the steam specific enthalpy was determined. The steam enthalpy function was constructed using linear regression, utilising values of pressure, temperature and specific enthalpy from steam tables.

Table 24 depicts the statistical results and summary of the linear regression.

Table 24: Regression output and statistical summary of steam enthalpy linear function

Regression Statistics								
Multiple R	0.9998							
R Square	0.9996							
Adjusted R Square								
Standard Error	3.0129							
Observations	30							
		Significance						
	df	SS	MS	F	F			
Regression	2	674966	337483	37177	3.62E-47			
Residual	27	245	9.078					
Total	29	675211						
		Standard				Upper	Lower	Upper
	Coefficients	Error	t Stat	P-value	Lower 95%	95%	95.0%	95.0%
Intercept	2444	3.404	718	2.45E-59	2437	2451	2437	2451
Pressure (bar)	-3.03	0.322	-9.42	5.03E-10	-3.70	-2.37	-3.70	-2.37
Temperature (°C)	2.12	0.0078	272.5	5.60E-48	2.10	2.14	2.10	2.14

Table 23 Continued

RESIDUAL OUTPUT

Observation	Predicted Y	Residuals
1	2852.69	4.314
2	2958.69	3.314
3	3064.69	0.314
4	3170.69	-2.686
5	3276.69	-4.686
6	2849.65	1.349
7	2955.65	2.349
8	3061.65	0.349
9	3167.65	-1.651
10	3273.65	-3.651
11	2846.62	-0.617
12	2952.62	2.383
13	3058.62	1.383
14	3164.62	-0.617
15	3270.62	-1.617
16	2843.58	-3.583
17	2949.58	1.417
18	3055.58	1.417
19	3161.58	0.417
20	3267.58	-0.583
21	2840.55	-5.549
22	2946.55	1.451
23	3052.55	2.451
24	3158.55	1.451
25	3264.55	1.451
26	2837.51	-8.514
27	2943.51	0.486
28	3049.51	2.486
29	3155.51	2.486

8.4.2. COMPUTER CODES

8.4.2.1. Application front page

on preopenstack

layoutCard

put "" into line 1 of field "code"

end preopenstack

on preopenCard

layoutCard

end preopenCard

on resizeStack

layoutCard

end resizeStack

on layoutCard

put the height of this stack into tStackHeight

put the width of this stack into tStackWidth

set the height of image "front.jpg" to tStackHeight

set the width of image "front.jpg" to tStackWidth

set the height of image "front2.jpg" to tStackHeight

set the width of image "front2.jpg" to tStackWidth

set the topleft of image "front.jpg" to (0,0)

set the topleft of image "front2.jpg" to (0,0)

if tStackHeight > tStackWidth **then**

set the visible of image "front.jpg" to false

set the visible of image "front2.jpg" to true

else

set the visible of image "front.jpg" to true

set the visible of image "front2.jpg" to false

end if

set the bottom of image "Go.jpg" to $0.98 * \text{tStackHeight}$

set the right of image "Go.jpg" to $0.98 * \text{tStackWidth}$

set the height of image "Go.jpg" to $0.08 * \text{tStackHeight}$

set the width of image "Go.jpg" to $0.08 * \text{tStackHeight}$

set the bottom of field "Code" to $0.98 * \text{tStackHeight}$

set the right of field "Code" to $0.98 * \text{the left of image "Go.jpg"}$

set the height of field "Code" to $0.08 * \text{tStackHeight}$

set the width of field "Code" to $0.45 * \text{tStackWidth}$

end layoutCard

8.4.2.2. steam properties page

on preopenCard

 layoutCard

end preopenCard

on resizeStack

 layoutCard

end resizeStack

on layoutCard

put the height of this stack into tStackHeight

put the width of this stack into tStackWidth

set the height of image "steam.jpg" to tStackHeight

set the width of image "steam.jpg" to tStackWidth

set the height of image "steam2.jpg" to tStackHeight

set the width of image "steam2.jpg" to tStackWidth

set the topleft of image "steam.jpg" to (0,0)

set the topleft of image "steam2.jpg" to (0,0)

set the height of image "backbutton2.jpg" to $0.15 * tStackHeight$

set the width of image "backbutton2.jpg" to $0.15 * tStackHeight$

set the topleft of image "backbutton2.jpg" to (3,3)

if tStackHeight > tStackWidth **then**

set the visible of image "steam2.jpg" to false

set the visible of image "steam.jpg" to true

else

set the visible of image "steam2.jpg" to true

set the visible of image "steam.jpg" to false

end if

set the bottom of field "enthalpyL" to $0.98 * tStackHeight$

set the left of field "enthalpyL" to $0.02 * tStackWidth$

set the height of field "enthalpyL" to $0.08 * \text{tStackHeight}$

set the width of field "enthalpyL" to $0.45 * \text{tStackWidth}$

set the bottom of field "tempL" to $0.98 * \text{the top of field "enthalpyL"}$

set the left of field "tempL" to $0.02 * \text{tStackWidth}$

set the height of field "tempL" to $0.08 * \text{tStackHeight}$

set the width of field "tempL" to $0.45 * \text{tStackWidth}$

set the bottom of field "pressureL" to $0.98 * \text{the top of field "tempL"}$

set the left of field "pressureL" to $0.02 * \text{tStackWidth}$

set the height of field "pressureL" to $0.08 * \text{tStackHeight}$

set the width of field "pressureL" to $0.45 * \text{tStackWidth}$

set the bottom of field "enthalpyOut" to $0.98 * \text{tStackHeight}$

set the left of field "enthalpyOut" to $1.02 * \text{the right of field "enthalpyL"}$

set the height of field "enthalpyOut" to $0.08 * \text{tStackHeight}$

set the width of field "enthalpyOut" to $0.3 * \text{tStackWidth}$

set the bottom of field "tempIn" to $0.98 * \text{the top of field "enthalpyOut"}$

set the left of field "tempIn" to $1.02 * \text{the right of field "tempL"}$

set the height of field "tempIn" to $0.08 * \text{tStackHeight}$

set the width of field "tempIn" to $0.3 * \text{tStackWidth}$

set the bottom of field "pressureIn" to $0.98 * \text{the top of field "tempIn"}$

set the left of field "pressureIn" to $1.02 * \text{the right of field "pressureL"}$

set the height of field "pressureIn" to $0.08 * \text{tStackHeight}$

set the width of field "pressureIn" to $0.3 * \text{tStackWidth}$

end layoutCard


```
on closedcard  
  
  go to card "steam props"  
  
  close card  
  
end closedcard
```

8.4.2.3. Application main model page

```
local tVariables  
  
on preopencard  
  
  layoutCard  
  
end preopencard  
  
  
  
on resizestack  
  
  layoutCard  
  
end resizestack  
  
  
  
on layoutCard  
  
  put the height of this stack into tStackHeight  
  
  put the width of this stack into tStackWidth  
  
  
  set the height of image "tanks.jpg" to tStackHeight  
  
  set the width of image "tanks.jpg" to tStackWidth  
  
  set the topleft of image "tanks.jpg" to (0,0)  
  
  
  set the left of graphic "tab" to 0.01*tStackWidth  
  
  set the top of graphic "tab" to 0.005*tStackHeight  
  
  set the width of graphic "tab" to 0.98*tStackWidth  
  
  set the height of graphic "tab" to 0.17*tStackHeight
```

set the left of field "steam" to $0.03 * tStackWidth$

set the top of field "steam" to $0.02 * tStackHeight$

set the width of field "steam" to $0.3 * tStackWidth$

set the height of field "steam" to $0.14 * tStackHeight$

set the right of field "default" to $0.97 * tStackWidth$

set the top of field "default" to $0.02 * tStackHeight$

set the width of field "default" to $0.3 * tStackWidth$

set the height of field "default" to $0.14 * tStackHeight$

set the left of field "feed" to $0.35 * tStackWidth$

set the top of field "feed" to $0.02 * tStackHeight$

set the width of field "feed" to $0.3 * tStackWidth$

set the height of field "feed" to $0.14 * tStackHeight$

set the top of field "grade" to the bottom of graphic "tab" + $0.01 * tStackHeight$

set the left of field "grade" to $0.01 * tStackWidth$

set the width of field "grade" to $0.4 * tStackWidth$

set the height of field "grade" to $0.075 * tStackHeight$

set the top of field "solids" to the bottom of field "grade" + $0.01 * tStackHeight$

set the left of field "solids" to $0.01 * tStackWidth$

set the width of field "solids" to $0.4 * tStackWidth$

set the height of field "solids" to $0.075 * tStackHeight$

set the top of field "carbonate" to the bottom of field "solids" + $0.01 * tStackHeight$

set the left of field "carbonate" to $0.01 * tStackWidth$

set the width of field "carbonate" to $0.4 * tStackWidth$

set the height of field "carbonate" to $0.075 * tStackHeight$

set the top of field "bicarbonate" to the bottom of field "carbonate" + $0.01 * tStackHeight$

set the left of field "bicarbonate" to $0.01 * tStackWidth$

set the width of field "bicarbonate" to $0.4 * tStackWidth$

set the height of field "bicarbonate" to $0.075 * tStackHeight$

set the top of field "pH" to the bottom of field "bicarbonate" + $0.01 * tStackHeight$

set the right of field "pH" to $0.99 * tStackWidth$

set the width of field "pH" to $0.4 * tStackWidth$

set the height of field "pH" to $0.075 * tStackHeight$

set the top of field "residence" to the bottom of field "pH" + $0.01 * tStackHeight$

set the right of field "residence" to $0.99 * tStackWidth$

set the width of field "residence" to $0.4 * tStackWidth$

set the height of field "residence" to $0.075 * tStackHeight$

set the top of field "temp" to the bottom of field "residence" + $0.01 * tStackHeight$

set the right of field "temp" to $0.99 * tStackWidth$

set the width of field "temp" to $0.4 * tStackWidth$

set the height of field "temp" to $0.075 * tStackHeight$

set the top of field "gradeIn" to the bottom of graphic "tab" + $0.01 * tStackHeight$

set the left of field "gradeIn" to the right of field "grade" + $0.01 * tStackWidth$

set the width of field "gradeIn" to $0.17 * tStackWidth$

set the height of field "gradeIn" to $0.075 * tStackHeight$

set the top of field "solidsIn" to the bottom of field "gradeIn" + $0.01 * tStackHeight$

set the left of field "solidsIn" to the right of field "grade" + $0.01 * tStackWidth$

set the width of field "solidsIn" to $0.17 * tStackWidth$

set the height of field "solidsIn" to $0.075 * tStackHeight$

set the top of field "carbonateIn" to the bottom of field "solidsIn" + $0.01 * tStackHeight$

set the left of field "carbonateIn" to the right of field "grade" + $0.01 * tStackWidth$

set the width of field "carbonateIn" to $0.17 * tStackWidth$

set the height of field "carbonateIn" to $0.075 * tStackHeight$

set the top of field "bicarbonateIn" to the bottom of field "carbonateIn" + $0.01 * tStackHeight$

set the left of field "bicarbonateIn" to the right of field "grade" + $0.01 * tStackWidth$

set the width of field "bicarbonateIn" to $0.17 * tStackWidth$

set the height of field "bicarbonateIn" to $0.075 * tStackHeight$

set the top of field "pHIn" to the bottom of field "bicarbonateIn" + $0.01 * tStackHeight$

set the right of field "pHIn" to the left of field "pH" - $0.01 * tStackWidth$

set the width of field "pHIn" to $0.17 * tStackWidth$

set the height of field "pHIn" to $0.075 * tStackHeight$

set the top of field "residenceIn" to the bottom of field "pH" + $0.01 * tStackHeight$

set the right of field "residenceIn" to the left of field "pH" - $0.01 * tStackWidth$

set the width of field "residenceIn" to $0.17 * tStackWidth$

set the height of field "residenceIn" to $0.075 * tStackHeight$

set the top of field "tempIn" to the bottom of field "residenceIn" + $0.01 * tStackHeight$

set the right of field "tempIn" to the left of field "pH" - $0.01 * tStackWidth$

set the width of field "tempIn" to $0.17 * tStackWidth$

set the height of field "tempIn" to $0.075 * tStackHeight$

set the top of field "extraction" to the bottom of field "temp" + $0.01 * tStackHeight$

set the left of field "extraction" to $0.01 * tStackWidth$

set the width of field "extraction" to $0.4 * tStackWidth$

set the height of field "extraction" to $0.075 * \text{tStackHeight}$

set the top of field "metalVal" to the bottom of field "extraction" + $0.01 * \text{tStackHeight}$

set the left of field "metalVal" to $0.01 * \text{tStackWidth}$

set the width of field "metalVal" to $0.4 * \text{tStackWidth}$

set the height of field "metalVal" to $0.075 * \text{tStackHeight}$

set the top of field "steamcons" to the bottom of field "metalVal" + $0.01 * \text{tStackHeight}$

set the left of field "steamcons" to $0.01 * \text{tStackWidth}$

set the width of field "steamcons" to $0.4 * \text{tStackWidth}$

set the height of field "steamcons" to $0.075 * \text{tStackHeight}$

set the top of field "extractionOut" to the bottom of field "temp" + $0.01 * \text{tStackHeight}$

set the left of field "extractionOut" to the right of field "extraction" + $0.01 * \text{tStackWidth}$

set the width of field "extractionOut" to $0.17 * \text{tStackWidth}$

set the height of field "extractionOut" to $0.075 * \text{tStackHeight}$

set the top of field "metalValOut" to the bottom of field "extraction" + $0.01 * \text{tStackHeight}$

set the left of field "metalValOut" to the right of field "extraction" + $0.01 * \text{tStackWidth}$

set the width of field "metalValOut" to $0.17 * \text{tStackWidth}$

set the height of field "metalValOut" to $0.075 * \text{tStackHeight}$

set the top of field "steamconsOut" to the bottom of field "metalVal" + $0.01 * \text{tStackHeight}$

set the left of field "steamconsOut" to the right of field "extraction" + $0.01 * \text{tStackWidth}$

set the width of field "steamconsOut" to $0.17 * \text{tStackWidth}$

set the height of field "steamconsOut" to $0.075 * \text{tStackHeight}$

set the width of image "Arrow.png" to 65

set the height of image "Arrow.png" to 65

set the width of image "Arrowdown.png" to 65

```

set the height of image "Arrowdown.png" to 65

set the left of image "Arrow.png" to 1.07*(the right of field "gradeIn")

set the left of image "Arrowdown.png" to 1.07*(the right of field "gradeIn")


set the top of image "Arrow.png" to the top of field "solidsIn"

set the bottom of image "Arrowdown.png" to (the bottom of field "steamconsOut")


end layoutCard


on calculate

    put line 1 of field "gradeIn" into tgrade

    put line 1 of field "solidsIn" into tsolids

    put line 1 of field "carbonateIn" into tcarbonate

    put line 1 of field "bicarbonateIn" into tbicarbonate

    put line 1 of field "pHIn" into tpH

    put line 1 of field "residenceIn" into tresidence

    put line 1 of field "tempIn" into temp

    put (-0.00246406215839605*tgrade + -0.11306629946966*tsolids + 0.107734328421188*tcarbonate + -
0.703127324139607*tbicarbonate + 5.76108067489663*tpH + 0.0102034855146647*tresidence +
0.485779198574693*temp) into textraction

    put round(textraction,1) into field extractionOut

end calculate


on closedcard

    go to card "steam props"

    close card

end closedcard

```