


SIMULATION STUDIES OF MINERAL PROCESSING

(KAJIAN PENYELAKUAN PEMROSESAN MINERAL)



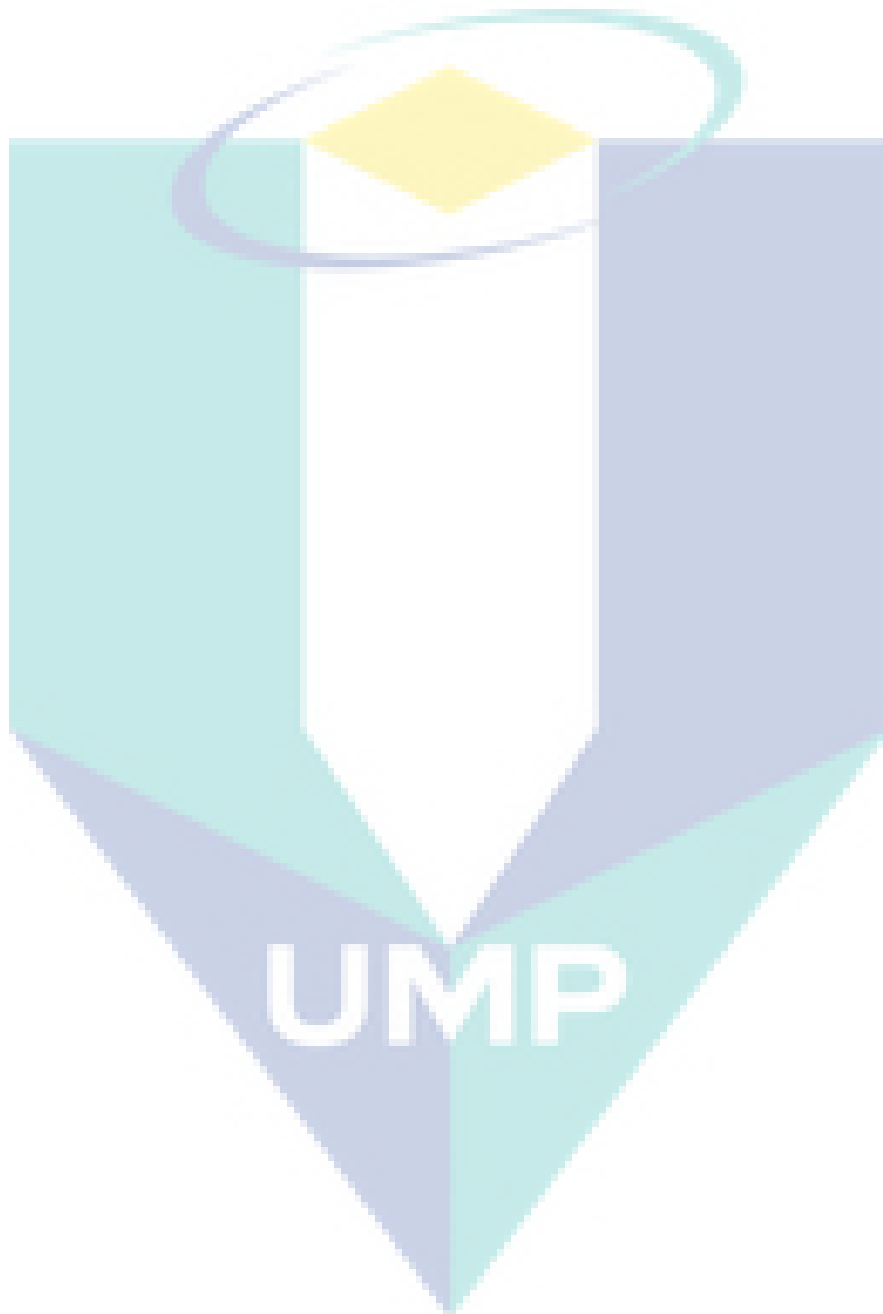
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ABSTRAK

Pemrosesan mineral mempamerkan sifat operasi yang kompleks dan memerlukan kerja pembangunan kuantitatif yang sukar. Dalam sesetengah kes, prinsip asas bagi sesetengah operasi juga tidak difahami dengan jelas. Dalam kebanyakan kes pula, kerumitan operasi menghalang analisis proses fizikal dan kimia dapat dijalankan dengan sempurna. Kajian ini bertujuan untuk mebangunkan simulasi hidrometalurgi bagi logam kritikal seperti nadir bumi dan emas. Perisian Aspen Plus dan HSC Chemistry telah digunakan sebagai platform dalam mebangunkan simulasi berdasarkan pelbagai kajian kes daripada penyelidikan yang lepas. Simulator yang dibangunkan adalah a) proses larut lesap nadir bumi dan b) proses pengekstrakan emas. Model tersebut mampu meramalkan hasil bagi sistem larut lesap dan pengekstrakan dari pelbagai jenis bijih. Dalam bidang pemrosesan mineral, simulator ini dapat membantu penyelidik menghasilkan kondisi optimum bagi sesuatu proses dengan lebih cepat dan murah.



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ABSTRACT

All mineral processing exhibits complex operating behaviour and building quantitative models for these operations is not a straightforward task. In some cases, the basic fundamental principles of a particular type of process are ill understood. In most cases the complexity of the operation precludes any complete analysis of the physical and chemical processes. This work focuses on the development of hydrometallurgical simulator for critical metals such as rare earth and gold. Using Aspen Plus and HSC Chemistry software as the platform, simulation models were established based on various case studies from the literature. The simulators on; a) leaching of rare earth and b) extraction of gold were successfully presented. These models are able to predict the output of the leaching/extraction system from assorted ores. In mineral processing field, this models able to aid mineralogist to optimized the process in a cheaper and less time-consuming way.



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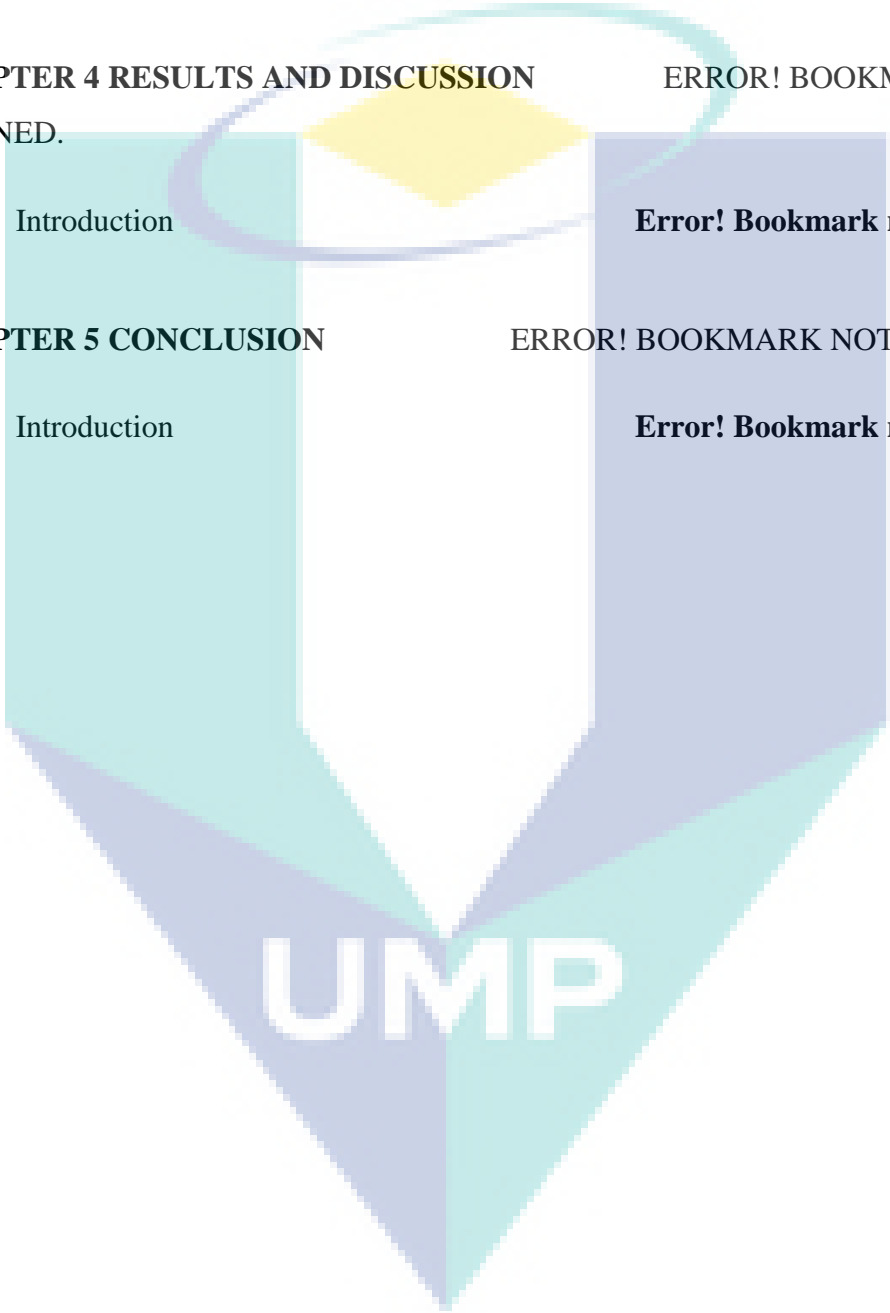
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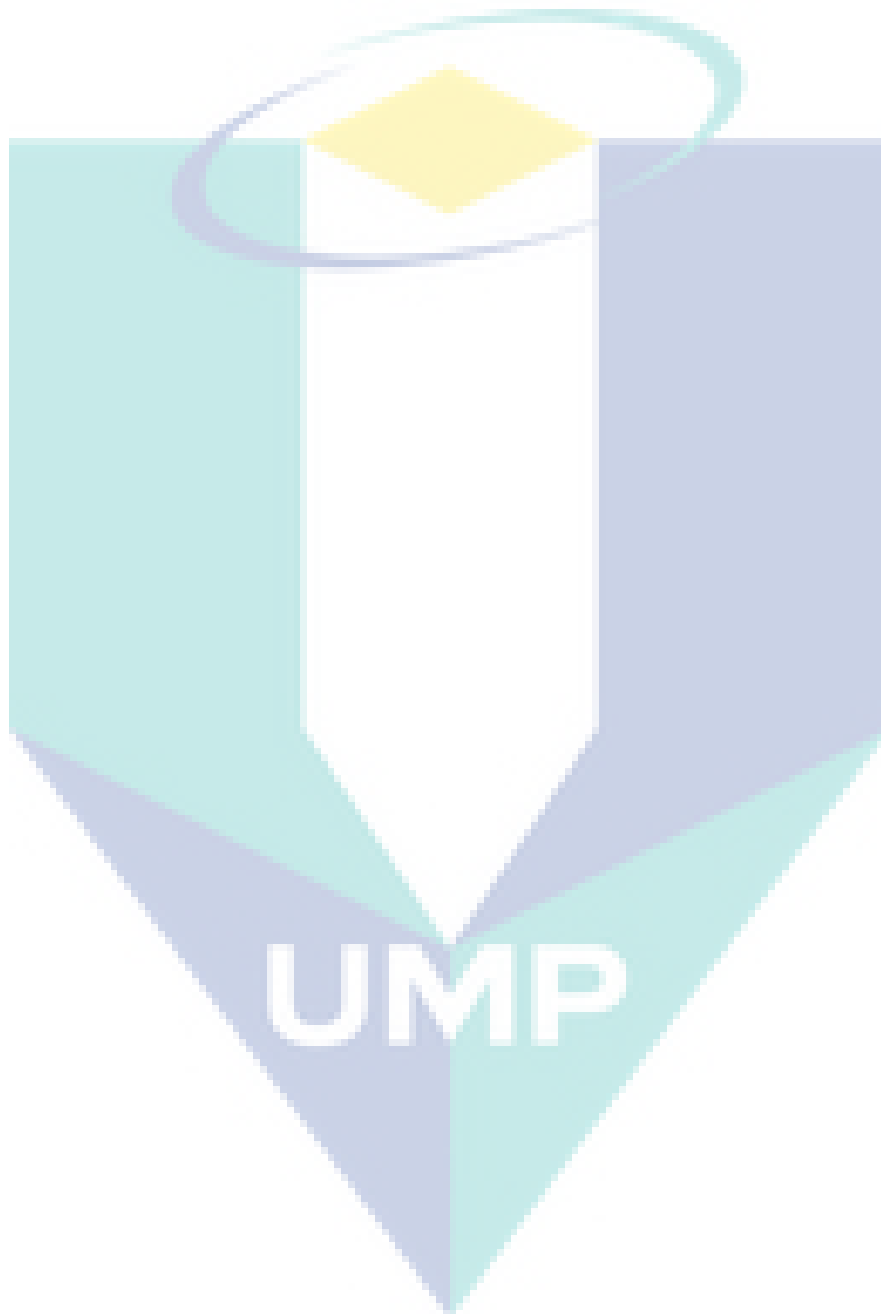
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Figure 34: Cyanidation of entropy

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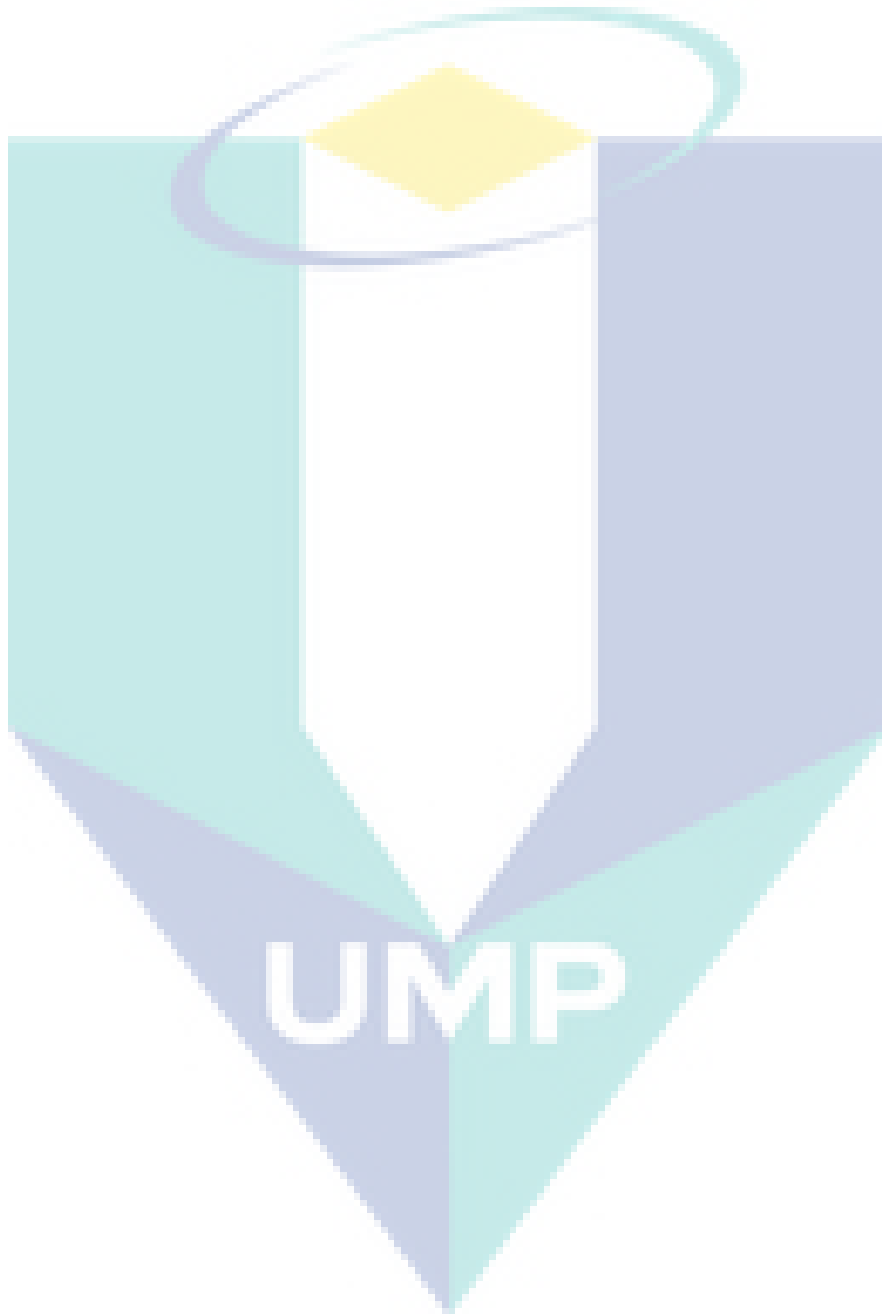
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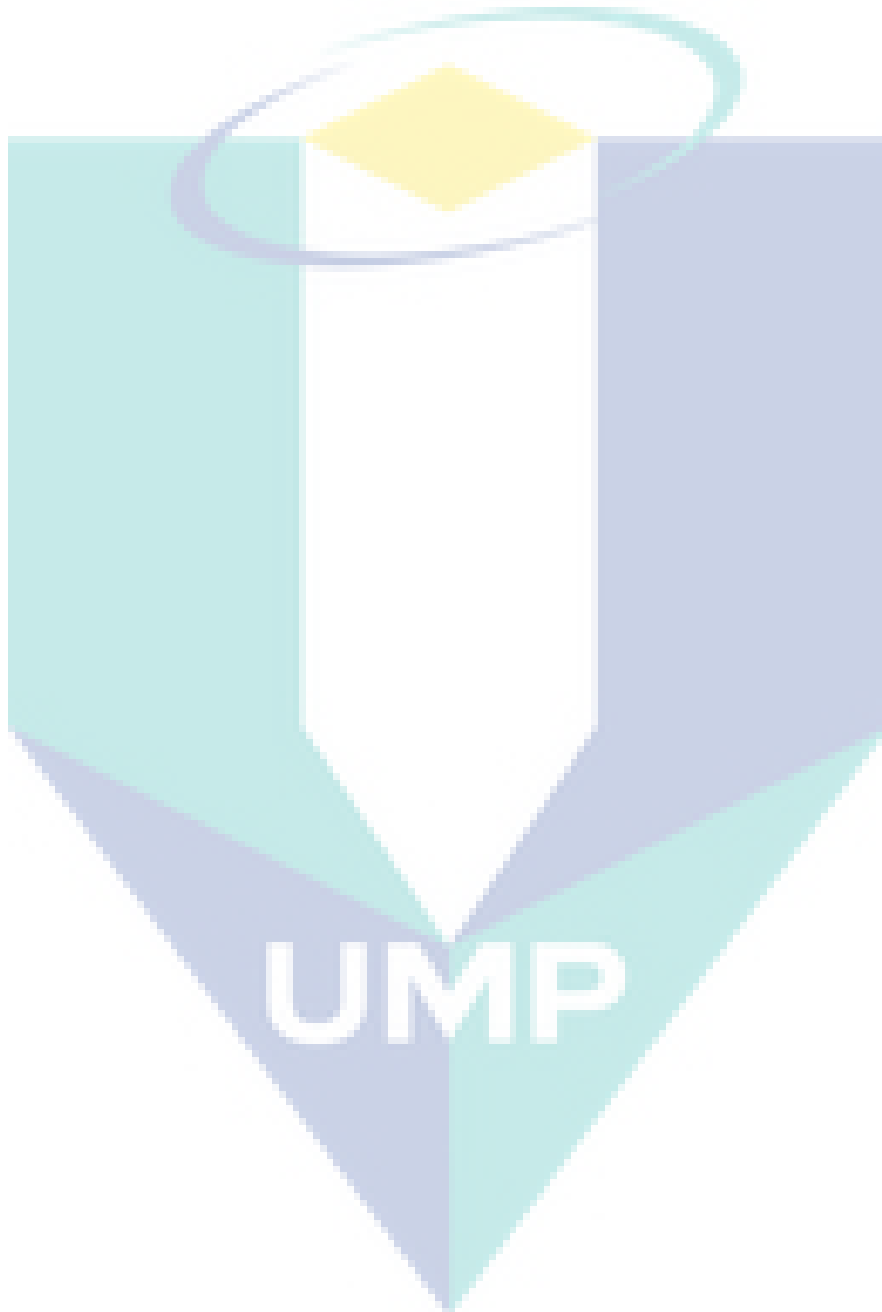
LIST OF SYMBOLS

SBPWM	Simple Boost Pulse Width Modulation
ZSI	Z source inverter



LIST OF ABBREVIATIONS

SBPWM	Simple Boost Pulse Width Modulation
ZSI	Z source inverter



CHAPTER 1

INTRODUCTION

1.1 Background of the research

Mineral processing has been defined as the mechanical processes which prepare ore for transportation or metallurgical processing, the refinement of mined resources without changing their chemical composition and preparation of ores by physical methods. The essential purpose of mineral processing is to separate impurities from the ore and so produce a concentrate. In the modern times, virtually no mineral is suitable for conversion to a final product without preparation. Concentration results in cheaper transportation, improved metallurgical efficiency and a smaller capacity requirement for subsequent metallurgical processing.

System simulations are combinations of several unit process models, which can be used to simulate entire mineral processing systems. If the models share a common particle description framework, they can communicate with each other. In this communication, the output variables of a model are utilized as the input variables of another. Nowadays, process simulation is widely applied in the mineral processing industry. The performance of entire mineral processing plants can be simulated on the basis of process models. Such simulations can be applied in, for example, viability studies, plant design, process optimization, process control, and operator training.

Process simulation of mineral processing consist of characteristics. Firstly, the principal purpose of such simulations is typically the determination of material, and elemental, flows. Secondly, the materials of interest are typically solids.

Finally, the solid materials are typically present as numerous individual entities of mass, which are referred to as particles.

1.2 Problem Statement

In spite of an extensive literature available on mineral processing, majority of the research strictly focus on experimental work whilst obliterate the use of simulation study. Consequently, plenty of mineralogist appear to follow similar route in separation measure. In general, the mineral processing especially in rare earth is governed by equilibrium considerations which are difficult to quantify and predict. These processes include process development, analysis, optimization and control of abounding parameters. Such operations are arduous and tedious given the usual laboratory technique is used for trial and error stages. Computer simulation expectantly could overcome the obstacles.

1.3 Objectives

The objectives of this research are:

- a. To study on chemical and physical properties of minerals containing rare earths and gold
- b. To developed a continuous mineral processing simulation for critical metals such as rare earth and gold using HSC Chemistry simulator

1.4 Organization of this Report

Chapter 2 discussed on the development of the leaching process of rare earth from monazite.

Chapter 3 discuss provides a description on the mineral processing of gold, phenomena in gold leaching, simulation of the gold processing using HSC Chemistry 8 software.

CHAPTER 2

SIMULATION OF RARE EARTH LEACHING PROCESS

2.1 Introduction

Rare Earth Elements (REE) are a group of 17 elements, 15 that belong to the chemical group lanthanides and yttrium and scandium. Nowadays, the uses of REE are more in new technologies such as electronics devices and military application. Besides, REE are important components of many modern technological products (Knutson, 2014). The world demand with high purity of these elements is increasing year by year (Antón, December 2012).

The global demand for rare earths has increased as more uses for these elements are found. Ranging from high tech (lasers, camera lenses, computer memory modules, x-ray machines), energy (batteries, lamps, superconductors) and industrial (aerospace, caustic cleaning agents, specialized glass) applications, there are a lots of uses from rare earth elements. The rare earth elements play an important role in many fields of advanced materials science due to their particular spectroscopic and magnetic properties and the industrial demand for them has increased (Abreu et al., 2010).

The increasing number of demand in industry has led to a growing interest in the exploration and exploitation of new sources and techniques for extraction. In order to meet demands, their separation and purification have gained considerable importance in the last decades (Abreu et al., 2014). However, because they have very similar chemical structures and properties REE are difficult to separate from each other. On the basis of their separability, they are divided into the “light rare earth element group” and the “heavy rare earth element group”. The differences of the REE influence the solubilities of salts, the hydrolysis of ions, and the

formation of complex species. The basis form of separation procedures of REE are by fractional precipitation, ion exchange, and solvent extraction (Kidela C. G., 2011).

Solvent extraction is one of the important separation and recovery methods for rare earth metal (Nakamura T. N., 2007). Due to the need to be able to handle larger volumes of dilute pregnant liquors, solvent extraction is generally accepted as the most appropriate commercial technology for separating rare earths (Xie F. Z., 2013). Besides, since REE have very similar chemical and physical properties chemical separation methods require multiple stages to complete the extraction process (Kidela C. G., 2011).

Simulation process analysis, control and optimization of rare earth solvent extraction are difficult and process requires a reliable model for the extraction equilibrium. In addition, very few models for describing the relevant equilibrium between rare earth elements and different extraction systems in the open literature, and these are usually only applicable to a limited and specific range of conditions. Therefore, little progress has been made with regard to the development of a general approach for modeling rare earth solvent extraction systems (Xie F. Z., 2013). It is usually considered counter-current circuits, due to their ubiquity. Stage-wise calculations offer efficiency and flexibility are based on the McCabe–Thiele method (Xie et al., 2013 ; McCabe et al., 2005)

In this research, simulation study is the first step before the experiment involving pure REE with their own chemical and physical properties can be conducted. The challenge is to be able accurately, simulate the rare earth separation process as similar physical and chemical properties individual rare earths itself are difficult to separate from each other.

2.1.1 Rare Earth Elements

The rare earth elements (REE) are a group of 17 chemical (metallic) elements which appear in the periodic table. The group consists of the 15 lanthanide elements along with Yttrium and Scandium. They share many similar properties, which is why they occur together in geological deposits. The 17 REEs are found in all REE deposits but their distribution and concentrations vary. They are

referred to as 'rare' because it is not common to find them in commercially viable concentrations. REEs generally fall into one of two categories – light rare earths (LREE) and heavy rare earths (HREE), with varying levels of uses and demand. REE mineral deposits are usually rich in either LREE or HREE, but rarely contain both in significant quantities. In general, they are vital to some of the world's fastest growing markets: clean energy and high technology. Silvery-white or gray in colour, these metals have a high lustre and tarnish readily when exposed to air. REEs are found in most everyday applications because of their unique chemical and physical properties. New applications have arisen consistently over the past 50 years CIBC, including important environmental innovations such as catalytic converters and the development of permanent magnets which have enabled greater efficiency, miniaturization, durability and speed in electric and electronic components.

Rare earth metals are basic materials for the production of high technology goods and systems, and their demand at high purity has therefore been increasing in recent years. The rare earth metals are also widely used as fluorescent materials for lamp, CRT and plasma displays, and for the permanent magnet motors for hybrid cars. In Japan, most rare earth metals are now imported from China, and the value of these metals is rising with increasing demand. As the development of effective recovery processes for rare earth metals is a quite attractive issue from the view point of resources sustainability, the recovery of these metals from increasing amounts of fluorescent wastes is worthy of study. (Solvent Extraction Research and Development, Japan, 2007, Vol. 14, 105 – 113).

2.1.2 Solvent Extraction Process

Solvent extraction of processes for separation and purification of rare earth have been reviewed during 1990's (Reddy M. L., 1995). Solvent extraction starts with separating different groups of rare earths from the leachate. Depending on the process, some primary rare earths may choose to sell intermediate, mixed products, or perform different downstream separations to produce individual rare earth salts or oxides (Xie F. Z., 2013). The process of solvent extraction uses

chemical agents to break down the components within a substance. Those materials which more soluble or react more readily to a particular acid or base get separated from the rest.

Because of the similarity in REE in terms of atomic weight, chemical separation methods require multiple stages to complete the extraction process. One stream in this process often takes hundreds of steps, involving a cascade of dozens of different tanks and machines for mixing, settling, filtering and evaporating all the various solutions (Kidela C. G., 2011).

In the 1940's the need for the separation and recovery of radioactive materials saw the introduction of solvent extraction to large-scale operations, and from this the technique has been applied to metallurgical processing. The large amount of continuing work on both reagents (different extractants) and systems (mixer-settler or column) has resulted in the adoption of solvent extraction as a unit process in hydrometallurgical operations for the recovery of a number of non-ferrous metals. The process of solvent extraction, which also may be called liquid-liquid extraction, as applied in metallurgical processes, can be described quite simply by equation (1) :



Where M, metal and E is extractant.

2.1.3 Mixer Settler

Each mixer-settler unit provides a single stage of extraction. The two phases enter the mixing section where they are mixed using an impeller. The two-phase solution flows into the settling section where they are allowed to separate by gravity due to their density differences. Typical mixer settlers have mixing times on the order of a few minutes and settling times of several minutes. The separate phases exit the settling section by flowing over a weir (organic solution) or through an underflow then over a weir (aqueous phase). The separation interface is controlled by the height of the weirs on the outlets of the settler section.

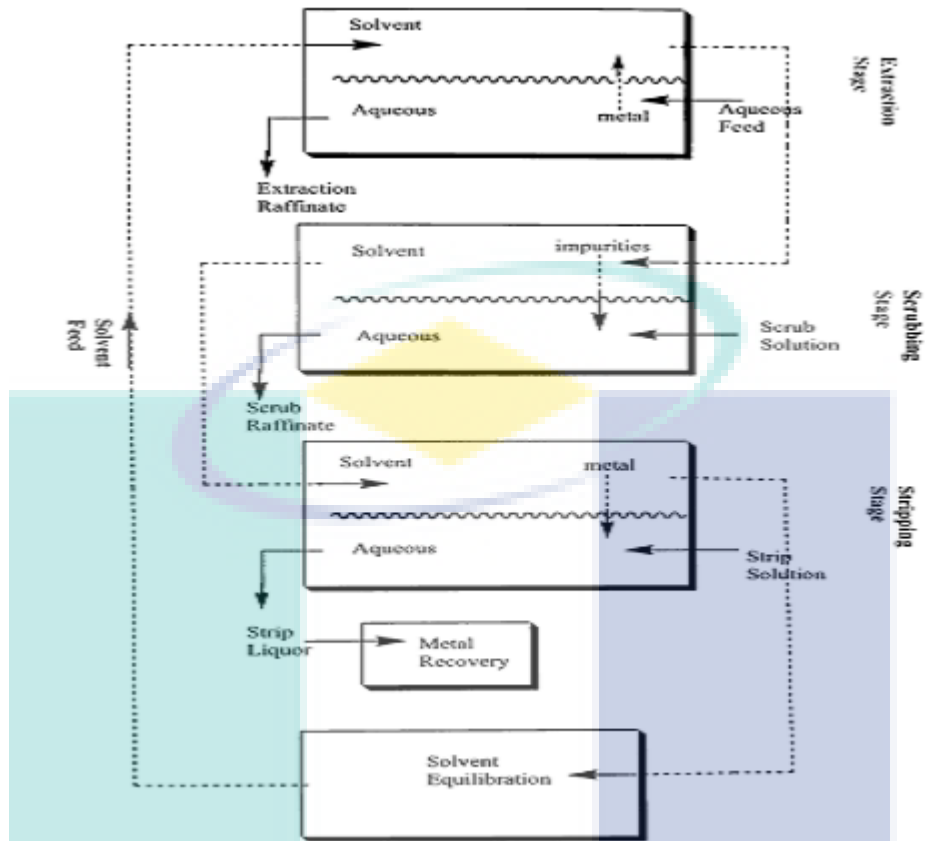


Figure 1: The general process of Solvent Extraction (Desouky, 2006)

Only minimal instrumentation is required and mechanical maintenance is limited to occasional mixing motor replacement. In a countercurrent process, multiple mixer settlers are installed with mixing and settling chambers located at alternating ends for each stage (since the outlet of the settling sections feed the inlets of the adjacent stage's mixing sections). Mixer-settlers are used when a process requires longer residence times and when the solutions are easily separated by gravity. They require a large facility footprint, but do not require much headspace, and need limited remote maintenance capability for occasional replacement of mixing motors (Colven, 1956; Davidson, 1957).

2.1.4 Previous Study on Rare Earth Extraction

Solvent extraction is one of the important separation and recovery methods for valuable metals, such as vanadium, molybdenum, indium and rare earth metal.

Although solvent extraction has been recently avoided due to the usage of organic solvent, it is still attractive because of their simplicity, speediness and easiness of scale up view (Nakamura, et al 2007). Kubota et al. investigated the recovery of rare earth metals from CRT wastes from TVs by solvent extraction with calixarene derivatives as extractants. Takahashi et al. Also reported the separation and recovery of rare earth metal from fluorescence lamp waste. High purity of rare earth metal recovery has been demonstrated mainly Y, Eu and La can be achieved by using ion exchange or solvent extraction methods. However, there is no practical rare earth separation process using solvent extraction has been commercialized due to the issue of cost performance.

Process simulation is well known to be effective for determining the appropriate conditions as well as predicting the operational conditions. A few study have been made using computer simulation of counter current solvent extraction processes for metal separation. Tanaka et al. Investigated on the role of the extraction with chelate type reagents in both counter current and cross current extraction system. Nishihima et al. Have developed a process simulation method for a counter current mixer settler cascade, based on extraction equilibrium and stoichiometric relationships. An effective separation and recovery process for rare earth metals could be developed by using process simulation since it not costing.

2.2 Objectives

These are the objectives for this study:

- a. To conduct a simulation study on rare earth separation processes in order to develop model based on rare earth elements physical and chemistry phenomena.
- b. To find the most suitable and economically separation process to separate the rare earth elements which is by using solvent extraction in mixer settler.

2.2.2 Scope of this research

The major objectives of this research is to develop the separation process in Aspen Plus. We need to design a model based on our case study which is rare earth

separation process and whether Aspen Plus is compatible for the modelling of the rare earth separation process. There are few scope has been determine to accomplish the goal of research which is:-

- a. Modelling and simulate the separation process based on experimental process by using new version of Aspen Plus.
- b. Pertain the simulation and analysis the effect on the parameters that has been determined.
- c. Validate the result of the simulation with the actual data in the experiment if it is possible.

2.2.3 Main contribution of this work

In separation process, we develop a model by using Aspen Plus, its make differs when we able to predict raw material also with its product physical and chemical properties (purity %, recovery %, mass fraction, acid pH, temperature, extraction % and others). The system will control the model automatically and if there is mistake happen for the input data, we just only change the data and it is not harmful because we just planned visual model not the real one. This study will overcome the limitation of model that had been proposed by other research by presenting a simultaneous target and design of new rare earth separation process. By simulate the system in the latest software of modelling and designing, this paper will generate a worthy result and can be used as a future references.

2.3 Methodology

2.3.1 Materials and Methods

This paper presents simulating model of solvent extraction of rare earth separation process using Aspen Simulation. Aspen is a process simulation software package widely used in industry today. Aspen uses mathematical models to predict the performance of the process and it can be used in an iterative fashion to optimize the design. This accurate modeling of thermodynamic properties is particularly important in the separation of non-ideal mixtures, and Aspen has a large data

bases of regressed parameters. Besides, it can handle very complex processes, including multiple-column separation systems, chemical reactors, distillation of chemically reactive compounds, and even electrolyte solutions like mineral acids and sodium hydroxide solutions (Aspen Technology I. , 2004). Aspen function is not to design the process but it use design that user supplies and simulates the performance of the process according to the design specifically. Therefore, a solid understanding of the underlying chemical engineering principles is required to supply reasonable values of input parameters and to evaluate the suitability of the results obtained.

2.3.2 Simulation Program

The software that have been used in this case to develop the separation process is by using mixer settler in Aspen Plus. Aspen Plus is Aspen Simulation Workbook that is the sub-programme from the Aspen Tech. For plant operations, Aspen Simulation Workbook accelerates the adoption of process models for operations decision support, bringing the power of simulation to non-simulation experts (Aspen Technology I. , 2004).The actual plant behaviour can be represented, simulated and designed if the simulation process has be given reliable thermodynamic data, realistic operating conditions and rigorous equipment models (Incharean & Srinophakun).

Simulation process is well known to be effective for determining the appropriate conditions as well as operational condition. According to Nakamura et al., Several studies about solvent extraction process using computer simulation had been made such as Radhika et al., reported Solvent extraction and separation of rare-earths from phosphoric acid solutions and Cheng et al., study about Adjacent stage impurity ratio in rare earth counter current extraction process. In this study, simulation study on rare earth separation by solvent extraction was investigated.

A process consists of components being mixed, separated, heated, cooled, and converted by unit operations. These components are transferred from unit to unit through process streams. Process simulation allows the prediction of process behaviour by using basic engineering relationships, such as mass and energy

balances, and phase and chemical equilibrium. Given reliable thermodynamic data, realistic operating conditions and rigorous equipment models, the actual plant behaviour can be represented, simulated and designed. Process design can be considered as one of the synthesis activities and can be viewed as a sequence of decision and evaluation steps which involve a wide variety of activities ranging from the initial synthesis of the process structure to detailed equipment sizing. The early design decisions generally have significant impact on the final process performance.

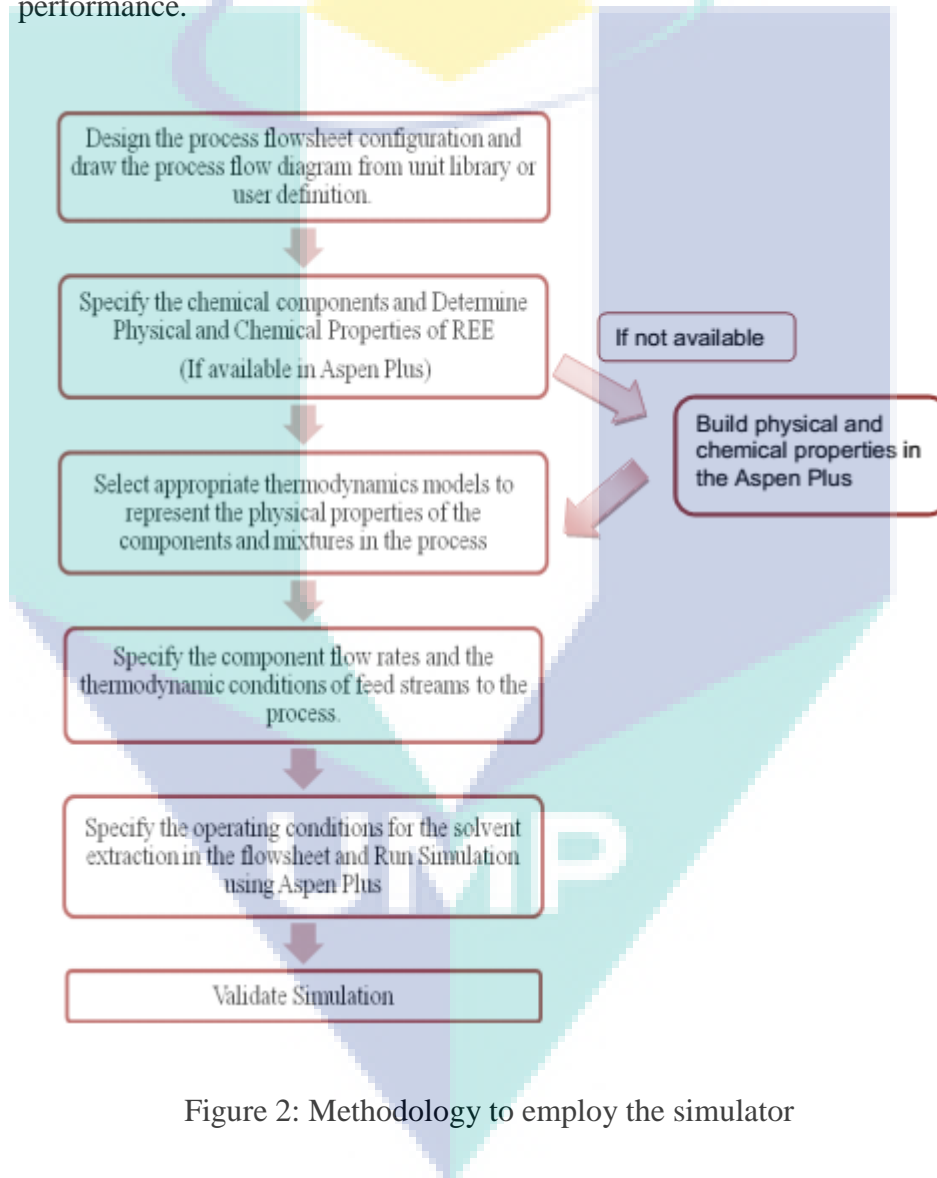


Figure 2: Methodology to employ the simulator

2.3.3 Case Study (Base on Literature Survey, Experiments On Re Separation) (Radhika, et al, 2011)

TOPS 99, an equivalent to di-2-ethylhexyl phosphoric acid has been employed for the solvent extraction and separation of a mixture of rare-earths (four light rare-earths (LREs) La, Ce, Pr, Nd, and seven heavy rare earths (HREs) like Tb, Dy, Y, Ho, Er, Yb and Lu) into some fractions from phosphoric acid solutions.

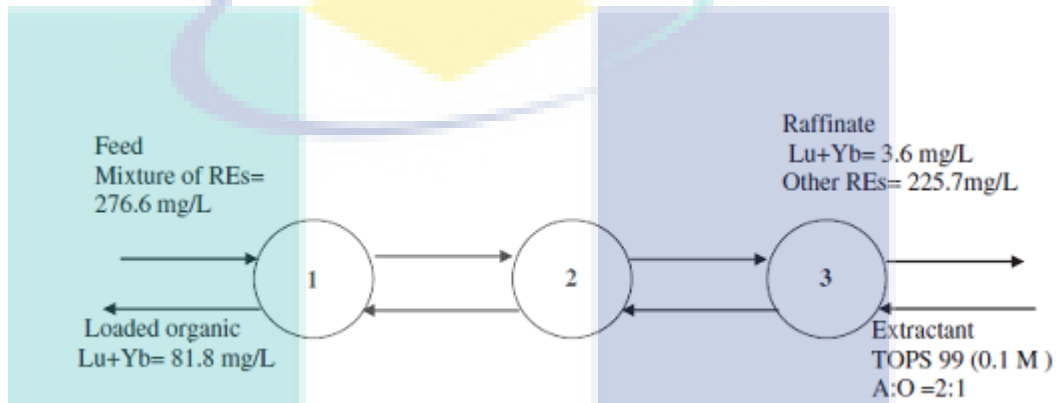


Figure 3: Three stage counter-current extraction simulation for Lu+Yb.

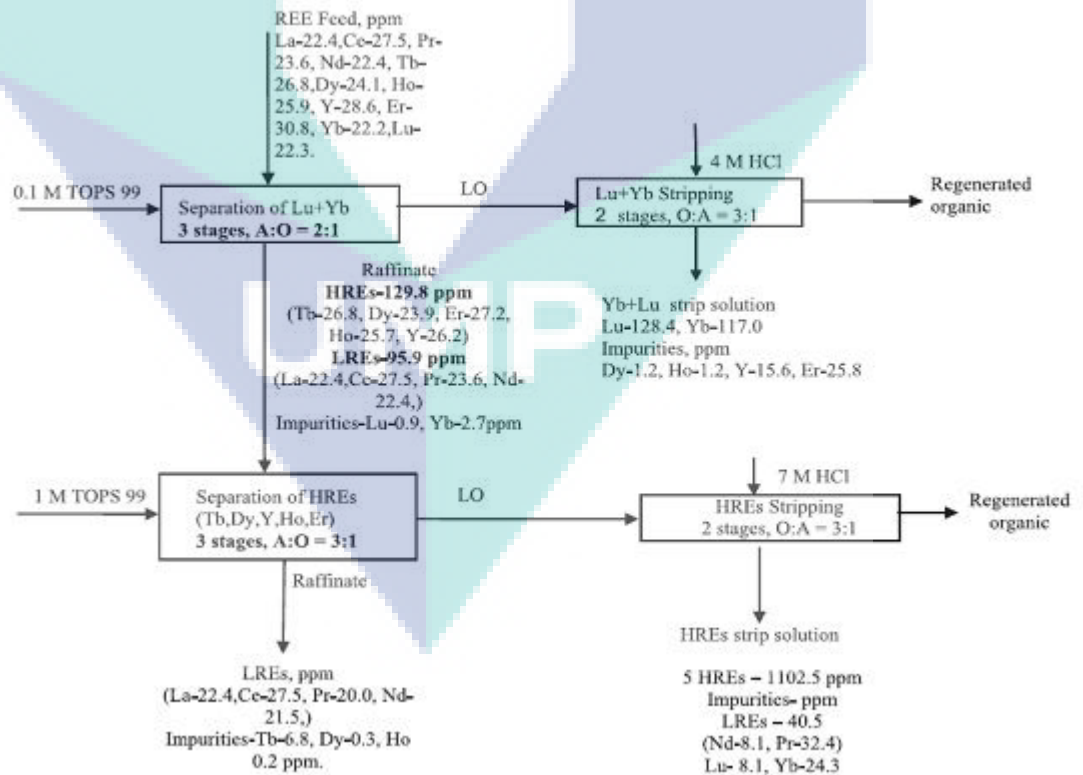
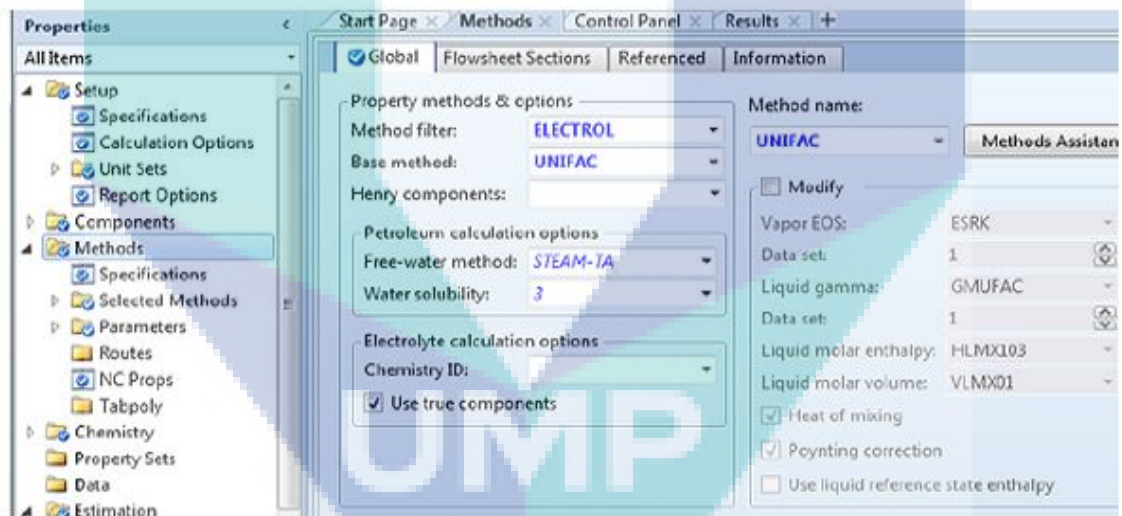


Figure 4: Flow sheet for the separation and recovery of REs from phosphoric acid

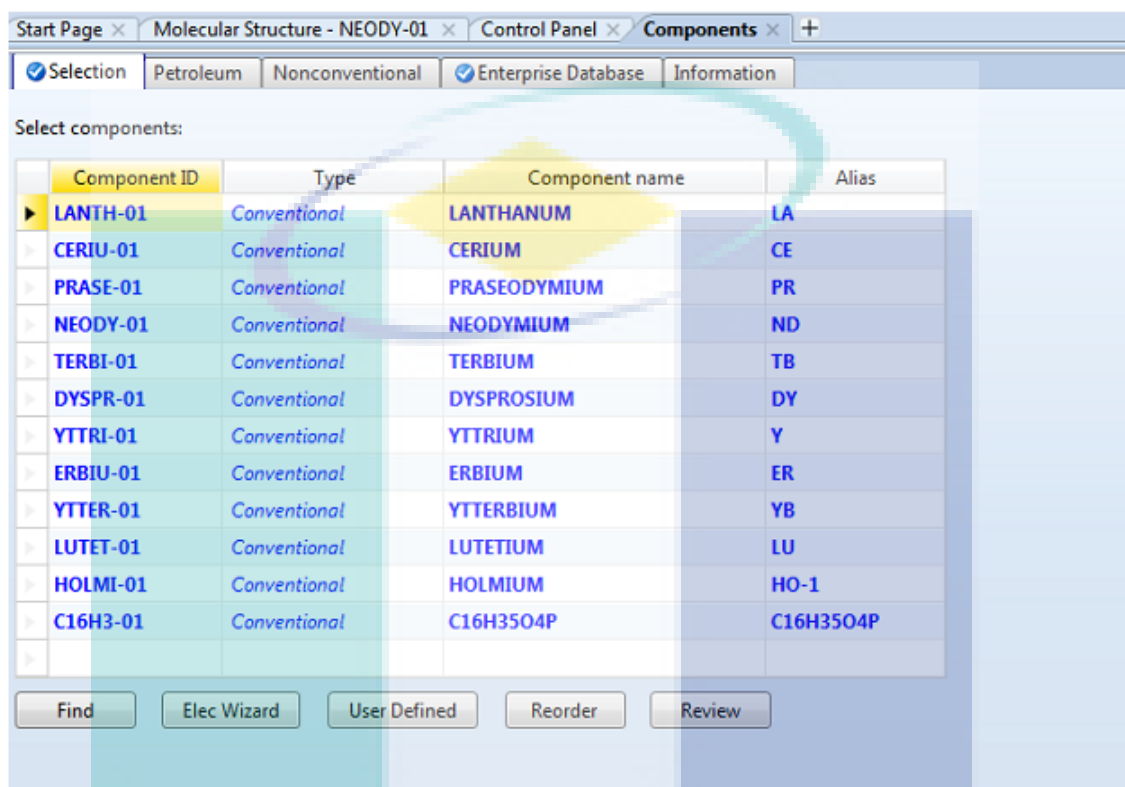
Solvent extraction of a mixture of REs from phosphoric acid medium has been investigated using TOPS 99 with different concentrations. From the acid and extractant effect on the extraction of a mixture of REs, 0.1M and 1 M TOPS 99 concentrations were selected for the fractionation of a mixture of REs into three concentrates: one is Lu+Yb fraction and the other two fractions are five HREs (Dy+Tb+Y+Ho+Er) and LREs. By using 0.1 M TOPS 99, an overall extraction of 91.9% of Lu+Yb is achieved at an A/O ratio of 2 within three stages of CCES. From loaded organic, Lu+Yb stripped with 4 M HCl. 94.4% extraction is found for HREs with 1 M TOPS 99 at an A/O ratio of 3 in three stages of CCES, whereas stripping of HREs is achieved with 7 M HCl. A flowsheet for the separation of a mixture of REs was developed.

2.3.4 Determine Physical and Chemical Properties of REE

I. CHOOSE METHOD



- II. 30 I. INSERT THE COMPONENTS BY INSERTING EITHER COMPONENT ID OR COMPONENT NAME AND ALSO FORMULA OF THE COMPONENT



2.3.5 Summary

This paper presents the procedure to achieve our objective. There are several steps to complete the task which are design the process flowsheet, specify the chemical components by either selecting from provided databanks or user definition, select appropriate thermodynamics models to represent the physical properties of the components and mixtures in the process, specify the component flow rates and the thermodynamic conditions of feed streams to the process, specify the operating conditions for the solvent extraction in the flowsheet and Simulate and analysis with options of sensitivity analysis, control configuration, and optimization aspects.

2.4 RESULT & DISCUSSION

The developing of process simulation technology gets together real world manufacturing and operating into computerize era and provides most effective procedure and time for designers and operators. This paper will apply and bring the capability of simulation into the solid process. In Aspen Plus simulator, there are still limitations where there are uncompleted and unavailable data for some molecules and components especially solid components either solid or aqueous solid. For this research, estimation of properties of reactants and products from the reactions and all along the extraction process is estimated by aspen. However, the molecules or the components need to be drafted in “molecular structure” in “Component Section” in Aspen. There are periodic table of elements with their own property such as molecular weight, charges, etc in aspen plus as shown in Fig 4.

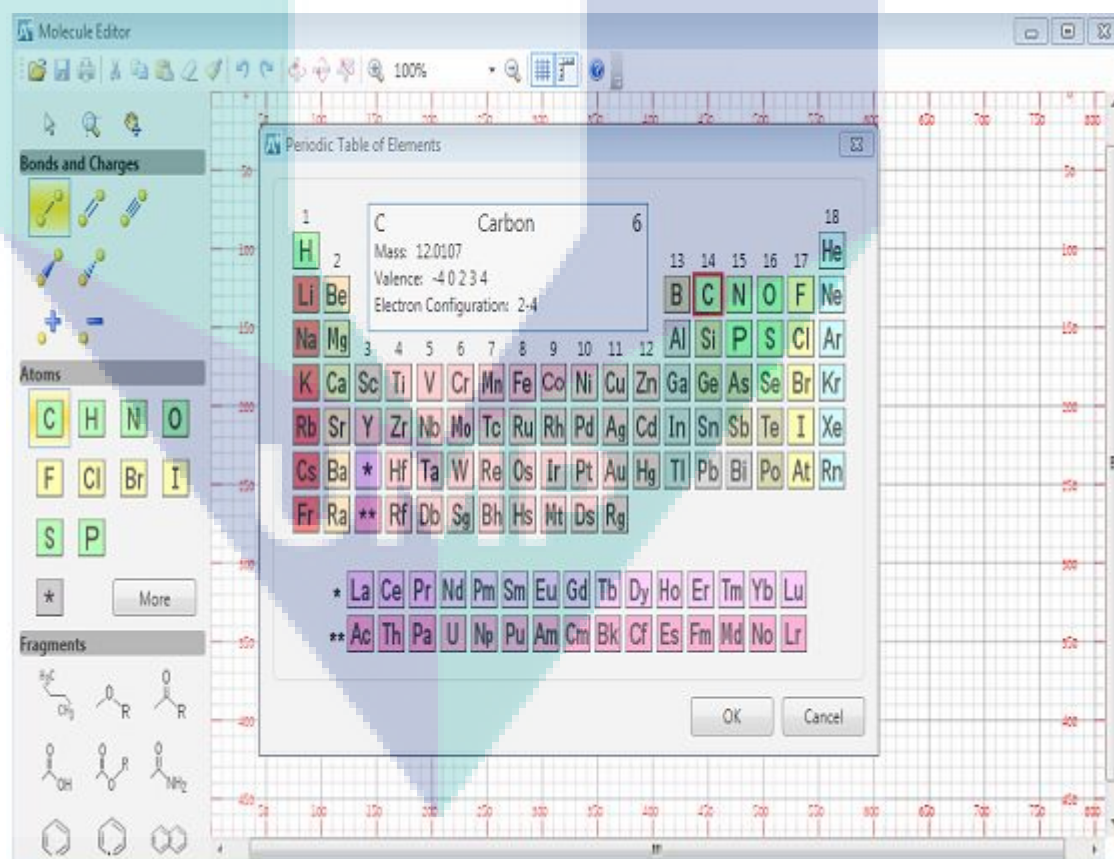


Figure 5: Molecular Editor in Aspen

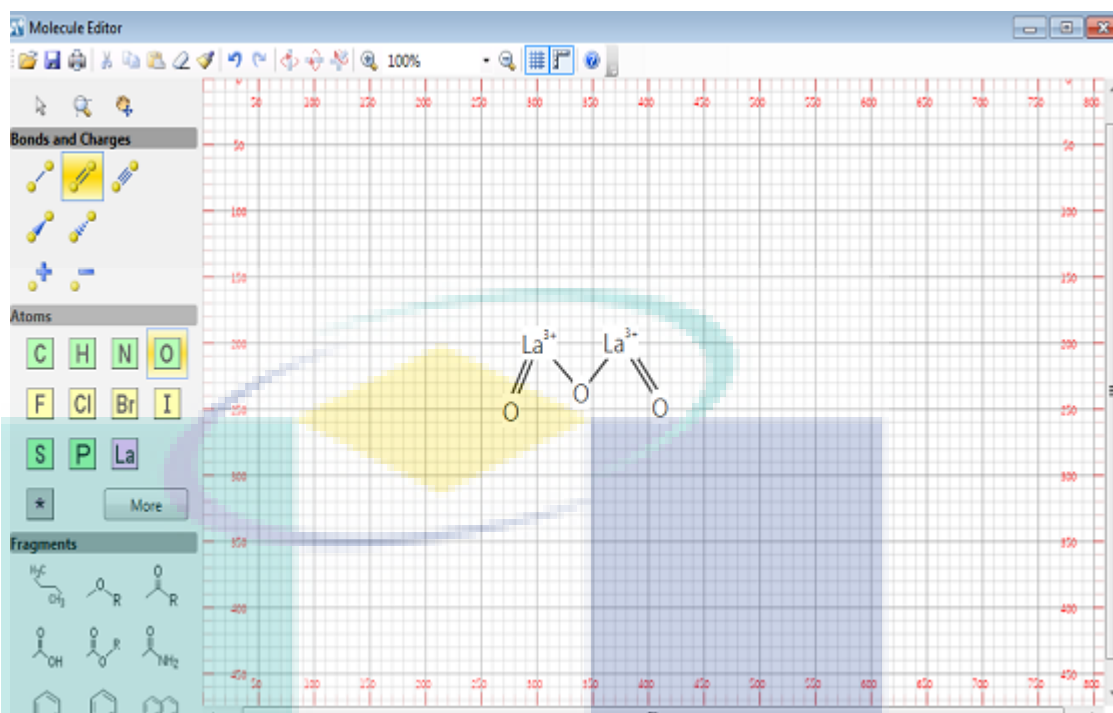


Figure 6: Example of molecular structure draw (La_2O_3)

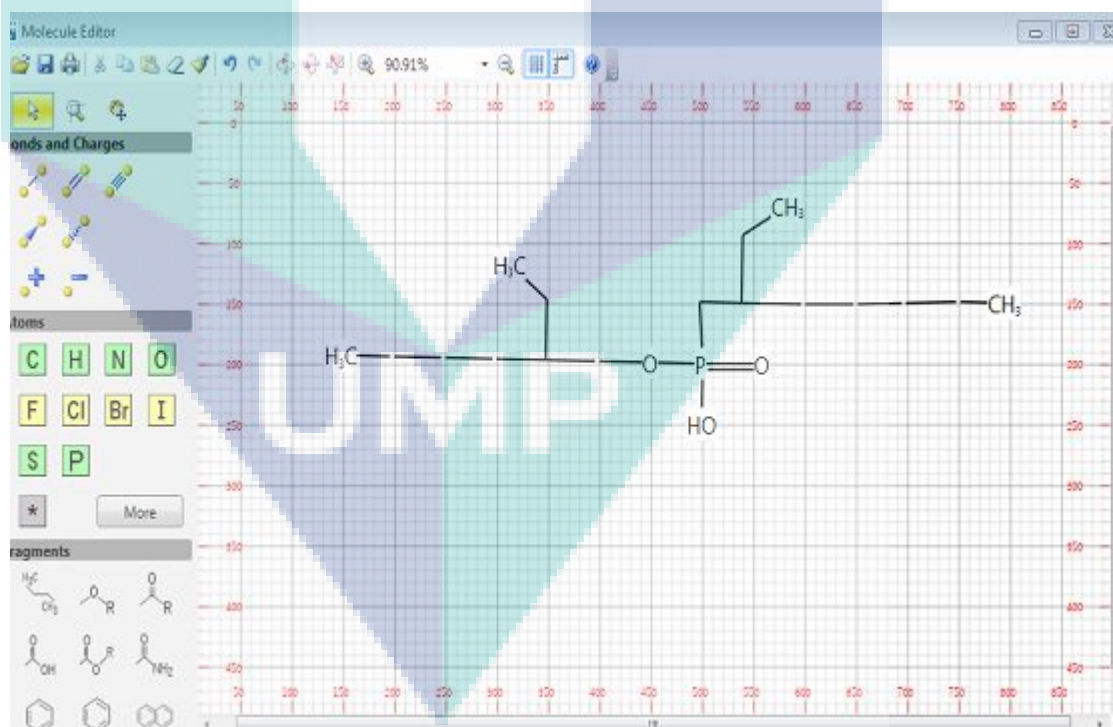


Figure 7: Example of molecular structure draw solvent (D2EHPA)

2.4.1 Discussion

In this study of Aspen simulator the change of any specifications such as flowsheet configuration, operating conditions and feed compositions performs in interactive style. Aspen also has features of estimating and regressing physical properties which strongly recommends in solid process, generating custom graphical and tabular output results. Solid process requires specific physical property model for mass and heat balance which may not be relevant from liquid characteristics. For the special operation such as electrolyte process the need of solution chemistry data bank is critical stage. Solution chemistry has a major impact on the simulation of electrolyte system especially phase equilibrium calculations. The presence of ions in liquid phase causes highly non-ideal thermodynamic behaviour.

Process development, analysis, control and optimization of rare earth solvent extraction are complex tasks in simulation. Computer simulation program for monitoring or optimizing the rare earth solvent extraction process requires a reliable model for the extraction equilibrium. However, very few models for describing the relevant equilibrium between rare earth elements and different extraction systems have appeared in the open literature, and these are usually only applicable to a limited and specific range of conditions. This probably reflects the similarities of the lanthanides, their propensity for interactions make it difficult to predict their behaviors in various extraction systems. Therefore, this research is a little progress that has been made with regard to the development of a general approach for modeling rare earth solvent extraction systems.

Since the solid-based components, still in build in Aspen simulator, many data such as ΔG , ΔH , ΔS , T_b , T_m , T_c , P_c of the components that required in order to run the simulation is unavailable that cause the simulation design difficult to build. Therefore, the simulation result is not converge. Thus, the data analysis is focusing on developing physical and chemical properties of rare earth elements itself in the Aspen plus. From the main reference, the data given only equation but in order to build the physical and chemical properties in Aspen Plus the structure of the components, formula or functional group is needed. Since former studies is not concluded the structure and most of data needed. The molecular

structure of cerium, REE before react and after react is drawn so Aspen simulator can estimate all the missing parameter.

2.5 Conclusion

Process development, analysis, control and optimization of rare earth solvent extraction are complex tasks. Computer simulation program for monitoring or optimizing the rare earth solvent extraction process requires a reliable model for the extraction equilibrium. However, very few models for describing the relevant equilibrium between rare earth elements and different extraction systems have appeared in the open literature, and these are usually only applicable to a limited and specific range of conditions. This probably reflects the similarities of the lanthanides, their propensity for interactions make it difficult to predict their behaviors in various extraction systems. Therefore, little progress has been made with regard to the development of a general approach for modeling rare earth solvent extraction systems.

In order to acquire all the missing parameter, data for each components and molecules can be required from molecular modelling which can determined all the data for solid liquid-gas based components. The separation process of rare earth using mixer settler in Aspen Plus can be successfully simulated and the results obtained from the simulation which is extraction of mixed RE Chloride to industrial RE Oxide will demonstrated that 'mixer-settler' in Aspen Plus is a potential solution for simulating rare earth separation process.

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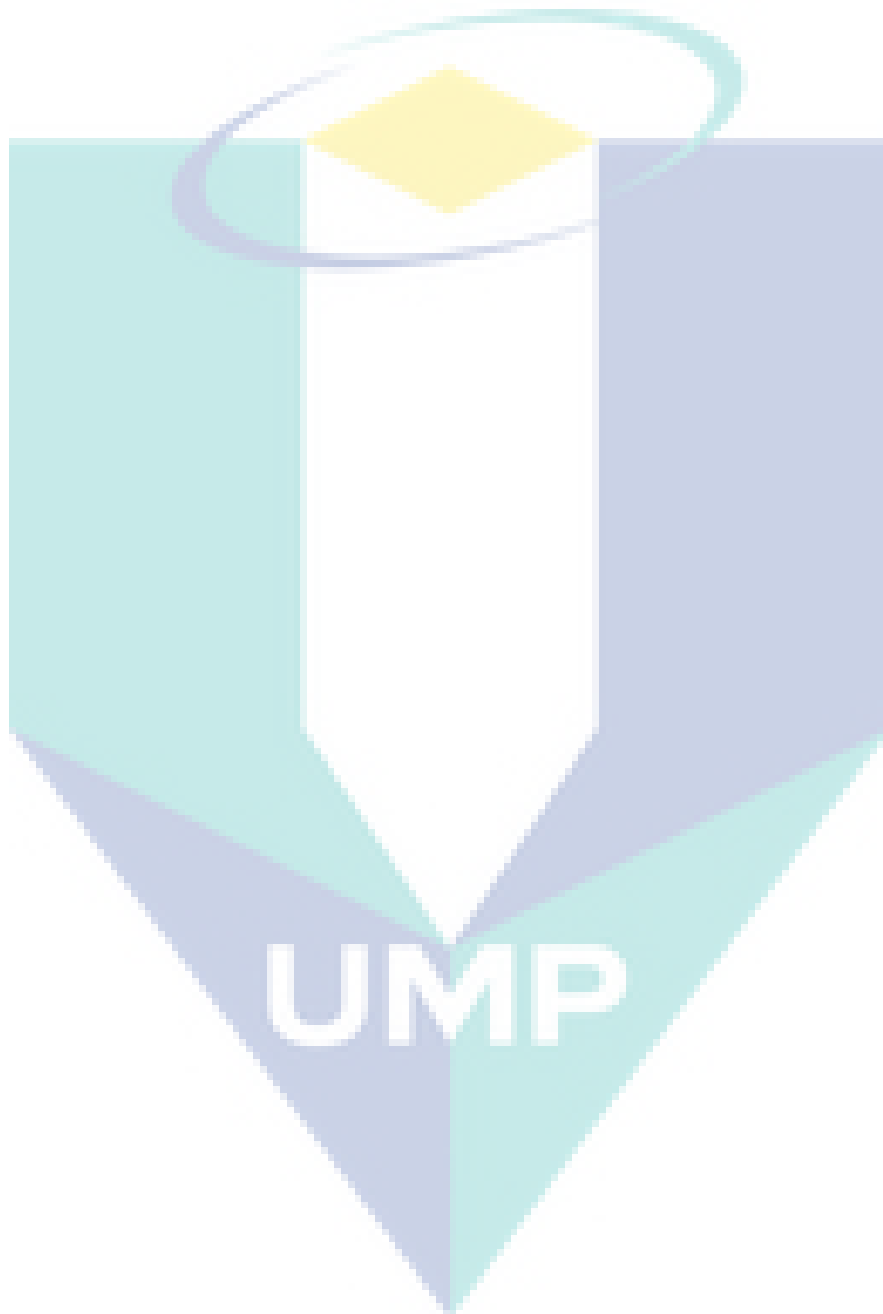
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CHAPTER 3

SIMULATION STUDY ON ALTERNATIVE TO CYANIDATION IN GOLD EXTRACTION PROCESSING

3.1 Introduction

3.1.1 Motivation and statement of problem

Gold was first discovered as shining yellow nuggets and soft metallic element. Gold became a part of every human culture because gold is dispersed widely throughout the geologic world, its discovery occurred to many different groups in many different localities. World's largest gold producing countries are China, Australia, Russia and United States.

How gold can be separated from mineral resources? Separation process is the transfer of any mass that converts the substance mixture into distinctive product mixtures. Types of separation process that is appropriate for gold processing is leaching process. Leaching is a process of extracting a soluble constituent from a solid by means of solvent. (Christie John Geankoplis, 2011). Leaching processes also are used extensively in the metals processing industries and is a main stage of reactant in gold production. (L.R.P de Andrade Lima, 2006)

Based on the title of this research, simulators are used to show how process of gold can occurs. HSC Chemistry is one of simulators that will be used. HSC Chemistry is a versatile tool for thermodynamically and process calculation. The program calculates the steady state of the process. Its many automated functions speed up process calculation. (Pori/Petri Kohylin, 2014)

Typically, gold is leached from its ore using an aqueous sodium cyanide solution. Cyanide has featured prominently as a leach reagent at gold mines because of its

high efficiency, robustness and relatively low cost. But, cyanide gave the environmental damages resulting from its mismanagement, thus, have initiated widespread research aimed at identifying and developing less toxic leaching agent. (Gavin Hilson, 2006). In cyanidation process for gold, suitable leaching methods are; heap or dump leaching; percolation or vat leaching; or agitation or pulp leaching. The selection of the method is dependent on particle size and the gold's mode of occurrence in the concentrate.

The use of cyanide in mining is becoming more and more controversial. Mining such low-grade ores creates vast open pits, unearthing and releasing a host of potentially dangerous toxins. A teaspoon of a 2% cyanide solution can kill a person. (Toolkit, 2000) We can be exposed to cyanides by breathing air and drinking water, touching soil or water containing cyanide, or eating foods that contain cyanide. So, cyanide is extremely toxic. However, there are currently being developed the potential to change the way the industry processes gold. There are some alternatives to extract gold without used a cyanide and replaced it's with Halides, Thiosulphate and Thiourea. (A.Rubo, 2000; Gavin Hilson, 2006; L.R.P de Andrade Lima, 2006; McMullen.J, 2008). This is because to prevent environmental impacts from cyanide.

1.1 Objectives

Based on the research background and problem statements described in the previous section, there are the following objectives of this research:

- a. To study on case study of the cyanidation and the other alternative solvent which are currently used in gold extraction process.
- b. To demonstrate the effectiveness of the new process by using HSC Chemistry simulator.

1.2 Scope of this research

The following are the scope of this research:

- a. Identify suitable solvent as alternative to extract gold. Theoretically, study on the physical and chemical properties of the alternative.

- b. Modelling and simulation of gold extraction by using HSC Chemistry 8.0 software.
- c. Validation of the simulation of gold with results from experimental work in literature and comparison between experimental work and simulation.

3.2 LITERATURE REVIEW

3.2.1 Overview

This research present the simulation studies process of gold extraction by using simulator and the other alternative solvents besides cyanide in extraction gold. Gold cyanidation is one of the principle gold extraction technique. The chemistry and phenomena in gold cyanidation is highlighted as it is an important factor in the production of gold. The design features of a multistage mixer settler extractor are described. The introduction as well as of Chemical Reaction & Equilibrium Software (HSC Chemistry).

3.2.2 Process of Gold

3.2.3 Properties of Gold

Table 1: Physical Properties of Gold

What are the Physical Properties of Gold?	
Color	Bright Yellow
Luster	It has a shine or glow
Ductility	It can be beaten into extremely thin sheets of gold leaf
Malleability	Capable of being shaped or bent
Conductivity	Good electrical conductor
Solubility	Solubility (ability to be dissolved)
Hardness	A relatively soft metal, gold is usually hardened by alloying with copper, silver, or other metals.
Density	It is a dense metal
Melting point	It melts at 1065°C

Table 2: Chemical Properties of Gold

What are the Chemical Properties of Gold?	
Chemical Formula	Au

Activity	Gold is chemically inactive, it's extremely resistant to chemical action
Compounds	Ready reducibility from compounds to metal. Auric chloride and chloro-auric acid are its most common compounds.
Reactivity with acids	Aqua regia, a mixture of nitric and hydrochloric acids, has the ability to dissolve gold
Isotopes	It has one stable isotope, ¹⁹⁷ Au
Reactivity with Non-metals	Gold does not react with the Non-metals, except for halogens, with which it forms halides
Alloys	Silver and platinum

3.2.3.1 Process Description of leaching section

The ore is first reduced in size (typically 80% passing 75µm) in crushing. After grinding, the small size of ore or pulp is dilute and thickening might be performed to increase the pulp density about 50% solid by mass. Leaching reagents in the form of cyanide and an oxidant such as air or oxygen are added after thickening. The creation of a large number of small oxygen bubbles and dispersing them in the slurry long and deep enough provides adequate oxygen concentration for gold dissolution.

In a leaching process, the ore is leached in a series of agitated vessels, typically about 6 vessels, each having a retention time of about 4 hours. The agitated vessels preferably have a cover for the solution to minimize the transfer of oxygen from the slurry to air. The cover can be either a stationary cover or a floating cover. In the agitated leaching reactor the gold is dissolved from the pulp. Pure oxygen or natural air which can be bubbled into the vessels is injected at the lower part of the leach tank.

3.2.4 Chemistry of Gold Cyanidation

Cyanide has been used in the gold mining industry since its value as a leach reagent for gold ores was recognized by John Stewart Arthur in the 1880s. Cyanide is universally used because of its relatively low cost and great effectiveness for gold dissolution. Also, despite some concerns over the toxicity of cyanide, it can be applied with little risk to health and the environment.

According to (Barriga-Ordenez, 2006), during the application of cyanide to treat precious metals, waste has to be disposed of or treated properly to achieve the environmental requirements. In spite of procedures to decrease the hazardous effects of using cyanide, sometimes the concentration of cyanide in waste processes reaches up 2000mg/L total cyanide.

3.2.4.1 Chemistry of Cyanide Solution

Simple cyanide salts such as sodium cyanide (NaCN), potassium cyanide (KCN) and calcium cyanide [Ca(CN)₂] dissolves and ionize in water to form their respective metal cation and free cyanide ions (CN⁻) as presented below:



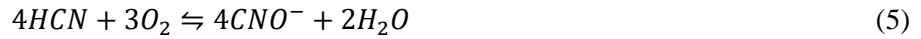
The solubility and the relative cyanide content of the different cyanide salts are shown in Table 2.0. Sodium and potassium cyanide are more soluble than calcium cyanide.

Table 3: Properties of simple cyanide salts

Compound	Available cyanide %	Solubility in water at 25°C
NaCN	53.1	48
KCN	40.0	50
Ca(CN) ₂	56.5	Decomposes
Compound	Available cyanide %	Solubility in water at 25°C
NaCN	53.1	48
KCN	40.0	50
Ca(CN) ₂	56.5	Decomposes

Cyanide ions hydrolyze in water to form hydrogen cyanide (HCN) and hydroxyl (OH⁻) ions which also increase pH. At higher pH, the total cyanide greatly exists as free cyanide ions. (Marsden J, 1992)



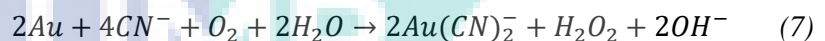


These reactions are undesirable during leaching because hydrogen cyanide (free cyanide) can be oxidized with oxygen to form cyanate (CNO^-) which reduce the free cyanide concentration, and the cyanate species formed does not dissolve gold.

Hydrogen cyanide is miscible with water, giving a weak acid. The CN triple bond is readily hydrolyzed by strong alkali or acid giving formic acid and ammonia, with higher temperature favoring these reactions.

3.2.4.2 Gold Dissolution

The dissolution of gold in cyanide solutions includes an anodic reaction (gold oxidation) and a cathodic reaction (oxygen reduction). Before that, although gold is inert to oxidation, it is widely accepted that, in the presence of a suitable complex agent such as cyanide, gold is oxidized and dissolved to form the stable complex ion $[Au(CN)_2]$. Oxygen is reduced and hydrogen peroxide is formed as an intermediate product in the first step and become oxidizing agent in the second step, leading to the following chemical reactions which proceed in parallel (Ling, 1996; Marsden J, 1992)



The summation of the two partial reactions is presented in equation (9) by Elsner's:



The equation, called Elsner's equation is stoichiometrically correct.

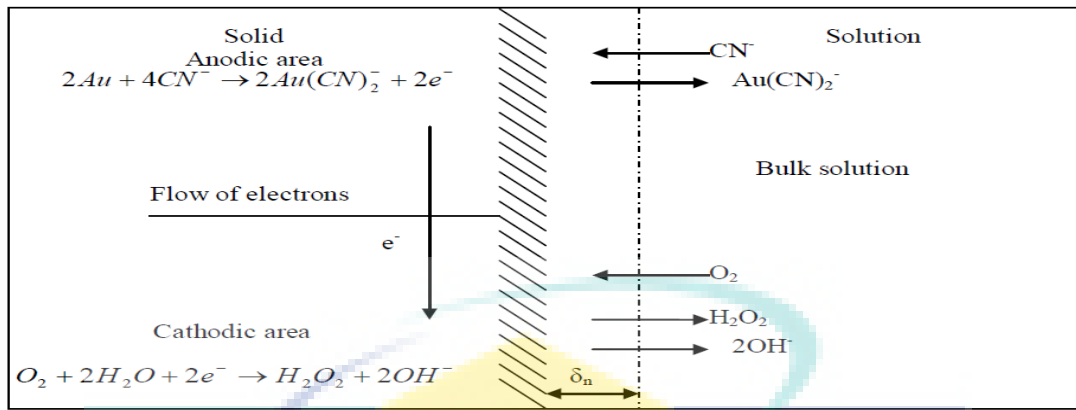


Figure 8: Schematic representation of the local corrosion cell at a gold surface in contact with an oxygen-containing cyanide solution. (Marsden J, 1992)

Figure 8 illustrates the major reactions of the two electron processes. The rate limiting conditions appear when the diffusion rates of cyanide and oxygen are equal. The slower diffusion rate of any species will provide the rate limiting factor. (Marsden J, 1992). The description of anodic and cathodic reaction:

Anodic reaction

Dissolution involves an electrochemical process in which the anodic reaction is gold oxidation. The important steps during the anodic reaction in the solution phase are:

- a) Adsorption of cyanide on gold surface



- b) Electrochemical extraction of an electron



- c) Combination of the adsorbed intermediate with another cyanide ion



Where (s) refers to surface adsorbed species and AuCN is a neutral intermediate species adsorbed on the surface.

- d) Overall anodic reaction



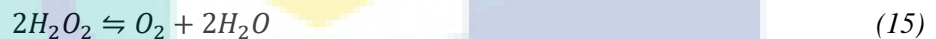
Cathodic reaction

The cathodic reduction of oxygen involving several parallel and series reactions:

- a) Oxygen reduction to H_2O_2



- b) Hydrogen peroxide decomposition



- c) Oxygen reduction to hydroxide ions



The hydrogen peroxide formed is a strong oxidizing agent which may be able to reduce to hydroxide ions (OH^-) as follows:



However, it has been shown that the reaction of this species is difficult to happen and the dissolution rate of gold in oxygen-free solutions containing hydrogen peroxide is very slow (Marsden J, 1992)

3.2.4.3 Competitive reaction in alkaline cyanide solution

Many other elements and minerals are able to dissolve in dilute alkaline cyanide solution as well. These competitive reactions may increase reagent consumption and consequently reduce the efficiency of gold leaching. As we know, the ability of cyanide to form strong complexes and stabilize gold allows it to be used in the cyanidation process. The other metals also can react with cyanide and form cyanide complexes. This leads to:

- Increase in the consumption of cyanide in gold extraction circuits
- Waste waters that may be difficult to treat
- Complications in the analysis of cyanide solution (Mudder, 2001)

The sulfides, for example are dissolved and produce metal cyanide complexes and various sulfur-containing species, such as sulfate, sulfide, thiocyanate and thiosulfate ions. (Deschenes, 1998). Other minerals, such as copper, one of common copper mineral is Chalcocite (Cu_2S) showing low solubility in cyanide solution. It is reported that concentration of this copper mineral 300 and 400 ppm in solution does not affect gold leaching.

3.2.5 Phenomena in Gold Leaching

Liquid-solid leaching or simply leaching is separation process which is the two phases are in intimate contact and the solute or solutes can diffuse from the solid to the liquid phase. Leaching process dividing by 2. Leaching processes for biological substances mostly for food processing and leaching process for inorganic and organic materials are used extensively in the metal processing industries. Case study of gold which is gold is leached from its ore using an aqueous sodium cyanide solution was under process of inorganic and organic materials.

3.2.5.1 Reaction Kinetics

Many researchers have attempted to model the kinetics of gold dissolution. The rate of pure gold dissolution relies on the rate of film diffusion of cyanide ions or dissolved oxygen towards the gold surface as shown below has being used rotating gold disc. (Ling, 1996)

$$-\frac{dN_{Au}}{Adt} = \frac{2D_{CN^-} - D_{O_2} C_{CN^-} - C_{O_2}}{\delta[(D_{CN^-} - C_{CN^-}) + (4D_{O_2} C_{O_2})]} \quad mol \ kg^{-1} h^{-1} \quad (18)$$

$dN_{Au}Adt = 2D_{CN^-} - D_{O_2} C_{CN^-} - C_{O_2} \delta D_{CN^-} - C_{CN^-} + 4D_{O_2} C_{O_2} \quad mol \ kg^{-1} h^{-1}$ (18), it can be seen easily that when $D_{CN^-} - C_{CN^-} < 4D_{O_2} C_{O_2}$ or low cyanide concentration, gold dissolution rate depends primarily on that cyanide concentration. Similarly, for high cyanide concentration, the gold dissolution rate becomes mainly dependent on the oxygen concentration. Consequently the majority of the mills operate at cyanide level dependent on the dissolved oxygen level.

De Andrade Lima and Hodouin (2005) also investigated the kinetic model for the cyanide consumption as function of cyanide concentration and particle size. The following pseudo-homogenous model describes the consumption process:

$$-r_{\text{CN}^-} = k_{\text{CN}^-} C_{\text{CN}^-}^{\eta} \quad \text{mgdm}^{-3}\text{h}^{-1} \quad (19)$$

$$k_{\text{CN}^-} = \frac{c_3}{d^{\theta} - c_4} \quad (20)$$

The rate expression which is derived from the anodic and cathodic half-reactions is one-half order in the concentration of cyanide and oxygen. The cyanide concentration determines the cathodic reduction of oxygen.

3.2.5.2 Method for Gold Leaching

There are several suitable leaching methods in cyanidation process such as heap or dump leaching, percolation or vat leaching or agitation or pulp leaching;

- a) For lump from ores the leaching can be carried out using heap or dump leaching methods. In these methods crushed ore is piled on a slightly inclined base, and the base is covered with asphalt or plastic sheet. After the ore is piled, the leaching agent is sprayed on the top of the heap and let to flow through the pile. The leaching agent reacts with the gold in the pile and removes it from the ore body. The leach solution can be collected from the bottom of the heap. Leaching time for this method is several months and it happens in ambient environmental temperature and pressure. (Neuvonen, 2013)
- b) Percolation or vat leaching is suitable for ores that include sandy and porous material. In these methods the material is placed in tank, which is equipped with false bottom. The false bottom is covered with filtering medium. The leach solution is added in the tank from the top of it and the solution is allowed to flow through the material. The leaching time varies between 2-4 days, the temperature and pressure conditions for leaching are at ambient conditions. (Neuvonen, 2013)
- c) Agitation or pulp leaching is used for finely ground ores. The leaching agent is added to the raw material so that they form a pulp inside the reactor or autoclave. The used vessel is equipped with mechanical agitation. This

method is used when the metal is in fine grain size and for cases when the metal is fine grain size. The leaching is carried out in the shortest possible time and high pressure and temperature can be used as booster for the reaction. Agitation for the process can be provided mechanically. The equipment used in agitation or pulp leaching can be ambient pressure leaching reactors in high pressure conditions. (Neuvonen, 2013)

3.2.5.3 Mass Transfer

Gas-liquid

Mass transfer from gas to liquid phase has a significant role in cyanidation using oxygen in the stirred tank reactor. Gas is introduced in the form of bubbles into the liquid by an appropriate distributor. The important characteristics affecting the gas-liquid mass transfer are the energy dissipation, the gas hold-up and the bubble size. (Garcia-Ochoa E, 2004)

Solid-liquid

Solid-liquid dispersion in stirred tank reactors has been widely studied. The main reason for applying the mechanical agitation is to ensure that all of the surface area available for mass transfer is utilized. In the case of fine particles ($d_p \leq 100 \mu\text{m}$), which are commonly found in processes such as crushed ores in leaching tank, the mass transfer coefficient increases greatly with decreasing particle size. (Pangarkar, 2002)

3.2.6 Environmental effect

The Environmental Protection Agency (EPA) identifies the most serious hazardous waste sites in the nation is cyanide. When a substance is released either from a large area such as it enters the environment. If you are exposed to high level of cyanide for a short time harms the brain and heart and can even cause coma and death. You can be exposed to a substance only when you come in contact with it and may be exposed by breathing, eating or drinking the substance or by skin contact. Cyanide is a chemical group consisting of one atom of carbon connected to one atom of nitrogen by three molecular bonds ($\text{C}\equiv\text{N}$). At the high

concentrations found in some landfill leachates (water that seeps through landfill soil), cyanide becomes toxic to soil microorganisms.

Cyanide produce toxic effects at level of 0.05 milligrams of cyanide per deciliter of blood (mg/dL) or higher, and deaths have occurred at level of 0.3 mg/dL and higher. (MPC. 2000). Effect reported in exposed children are like those seen in exposed adults. Children who ate large quantities of apricot pits, which naturally contain cyanide as part of complex sugars, had rapid breathing, low blood pressure, headaches, and coma. Smoking is probably one of the major sources of cyanide exposure. For example, if a pregnant mother is exposed to tobacco smoke, the fetus will be exposed to cyanide. The baby and children have been born with thyroid disease. (MPC. 2000)



Figure 9: The collapse of a tailings dam at an Eti Silver Corporation facility has led to serious concern among environmentalists and officials. (Sunday's Zaman. 2011. 09 May, Monday)

3.2.7 Alternative to cyanidation in gold processing

Many attempts have been made to find an efficient alternative to the cyanide that can extract gold with high recovery levels and less environmental impacts. Some of alternative including thiourea, halides, thiosulfate and ammonia. (A.Rubo, 2000)

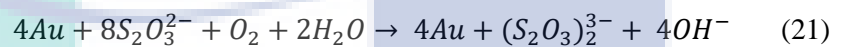
Table 4: Alternative lixiviates other than cyanide (% publication) (Aylmore M. G., 2005)

1	Thiosulfate	33%
2	Thiourea	26%
3	Halide	15%
4	Oxidative chloride processes	4%
5	Sulfide systems	5%
6	Ammonia/O ₂ or Cu(II)	2%

7	Bacteria/ natural acids	3%
8	Thiocyanate/Fe(III)	4%

3.2.7.1 Thiosulfate (S₂O₃²⁻) Leaching

Thiosulfate leaching has emerged as one of the more alternatives to cyanide because thiosulfate is considered a non-toxic reagent and can leach gold faster than cyanide. (Aylmore M. , 2001). Range pH of thiosulfate are between pH 8 to pH 10 (Fleming C.A, 1985). The overall chemical reaction is (Gavin Hilson, 2006)



The advantages of process is thiosulphate leaching yields similar gold recovery as cyanide in some cases. The thiosulphate leaching of gold ores has great potential to reduce the impact on the environment. The main chemical components of the leaching process (ammonium thiosulphate and ammonium sulphate) are common fertilizers, which opens up the additional possibility of using mine tailings solutions in agricultural application. (McMullen.J, 2008)

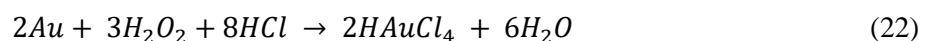
3.2.7.2 Halides

Another alternative may be used for the extraction gold is halide (fluorine, chlorine, bromine, iodine and astatine) systems for gold dissolution pre-dates cyanidation.

Table 5: Typical leaching conditions used in leaching gold with halides

Reagent	Ligand	Oxidant	Gold complex	Typical leaching condition	pH
Chlorine	Cl ⁻	Cl ₂	[AuCl ₄] ⁻	5-10 g/L Cl ₂ /NaCl	<3
Bromine	Br ⁻	Br ₂	[AuBr ₄] ⁻	2-5 g/L Br ₂ /NaBr	5-8
Iodine	I ⁻	I ₂	[AuI ₂] ⁻	1 g/L I ₂ , 9g/L NaI	5-9

- a) Chlorine: Gold dissolves in aqueous chloride solutions to form the formation of gold-chloride complex, AuCl₂⁻ : (Geoffroy & Cardarelli, 2005)



b) Bromine: In bromine/bromide medium, the gold is oxidized by bromine and stabilized by bromide as the gold bromide complex, in an electrochemical reaction represented by the half-cell reaction below: (Mariam Melaslinili, 2014)



Many factors affected the dissolution of gold by bromine leaching such as bromine and gold concentration, pH and electrochemical potential of anodic and cathodic processes. (Omer E. Kuzugudenli, 1999)

3.2.8 HSC Chemistry Software

3.2.8.1 Introduction

HSC Chemistry is a versatile tool for thermodynamically and process calculation. HSC has a wide range of application possibilities in industry, research, and education. The software is continuously being developed to meet the high expectations of our customers. This is a brief description of the calculation modules found in the program. HSC Sim includes four different modes (Particles, Reactions, Distributions and Experimental). The program calculates the steady state of the process. Each mode has its own area of application: Minerals Processing Models: Grinding, flotation à Particle based models, Particles mode. Hydrometallurgical Models: Leaching à Chemical reaction based models, Reactions mode. Pyrometallurgical Models: Smelting à Element distribution based models, Distributions mode. Experimental data analysis: Data measured from the process à Mass balancing models, Experimental mode. HSC Sim offers an easy to use interface for process modeling. Its many automated functions speed up process calculation. The drawing procedures of the flowsheet are similar in all calculation modes. (Kobylin, 2014)

3.3 Methodology

3.3.1 Overview

In this study, simulation will focus on the achievement of the conceptual study, simulation work, analyzing, and completion of the research. The detailed research procedure will be discussed in this chapter. The main work of this study is to develop the user added custom or proprietary models in HSC and be able to run the simulation and list down all the properties. The simulation works conducted focusing on performance of leaching process only; not the overall production of gold. In this part of study, it's consists of case study 1 and case study 2.

3.3.2 Study the physical and chemical properties of the alternative solvent.

Table 6: Physical and chemical properties of the alternative solvent

SOLVENT	Cyanide			Halides	
Chemical Formula	Hydrogen Cyanide	Sodium Cyanide	Potassium Cyanide	Hydrogen Bromide	Hydrogen Chloride
	HCN	NaCN	KCN	HBr	HCl
PHYSICAL PROPERTIES					
Molecular weight(g/mol)	27.03	49.01	65.12	79.904	36.46
Melting point (°C)	-13.4	563.7	634.5	265.9	-25.39
Boiling point (°C)	25.70	1496	No Data	331.9	108.33
Density(g/cm³)	0.6884	1.60	1.553	3.1023	1.05
Flammability limits	5.6-40%	Not combustible	Not combustible	Not combustible	Not combustible
CHEMICAL PROPERTIES					
Color	Colorless, white			Reddish brown	
Physical state	Gas or liquid			Solid and liquid	
Odor	Faint bitter almond odor			Stinky	
Solubility	Water(miscible),Organic solvent(soluble in ethanol,ether)			82.3 g/100 g at 32° F	

3.3.3 Case study

3.3.3.1 Case study 1

A feasibility study on the production of gold at a fictitious mine (Moapa mine) in Elko County, Nevada is to be performed. A sodium cyanide process is used to

extract gold from ore. The Block Flow Diagram of Leaching Process is shown in Figure 11.

In summarize, the PFD from unit 100 is designed the crusher to reduce size of gold. The small particles size of ore passing through output stream (stream 15). For my Undergraduate Research Project, focusing on leaching process starting at stream 15 which are mixed with a dilute aqueous solution of sodium cyanide. In my research, stream 20a was negligible. Next, stream 18 is fed into large mechanically stirred tanks where it is agitated with air at stream 17. Here, leaching occurs, and the gold is transferred from the ore and forms a gold-cyanide complex. The gold-cyanide complex is passing through output at stream 19.

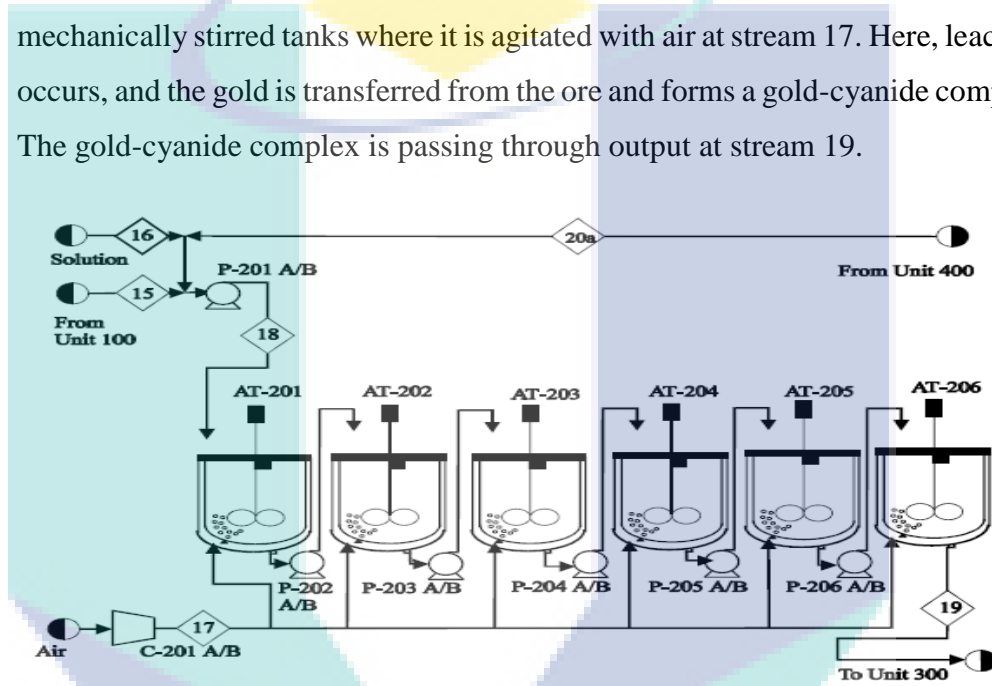


Figure 10: Block Flow Diagram of Leaching Process by Aspen Plus

3.3.3.2 Case Study 2

Case study 2 covers leaching process in an experimental setup. Gold ore sample were supplied from the Sukari Gold Mine, Eastern Desert, Egypt by Centamin Egypt Limited. In order to study the gold leaching rate of different ore size fractions, about 1 kg of ore sample was screened into different size fraction by using sieves of 38, 75, 106 and 125 μm . four size fractions, -38 , $-75+38$, $-106+75$ and $-125+106$ μm , were collected. Finally, each size fraction was mixed well and 100 g samples were packed for the leaching experiments.

Table 7: The elementary analysis (Wt.%) of the gold ore

Element	-38 μ m	-75+38 μ m	-106+75 μ m	-125+106 μ m
Au, ppm	4.12	4.23	5.39	3.22
Si, %	66	68	70.5	67.6
Al, %	15.1	14.6	13.6	14.6
Ca, %	2.08	1.6	1.28	1.6
Fe, %	4.5	4.19	3.68	4.22
K, %	2.14	2.15	1.95	2.17
Mg, %	0.44	0.47	0.4	0.48
Na, %	5.37	5.15	4.95	5.09
P, %	0.04	0.04	0.035	0.04
S, %	0.29	0.38	0.4	0.42
Ti, %	0.34	0.33	0.3	0.34
Mn,%	0.08	0.08	0.07	0.08

3.3.4 Condition of Leaching Production using HSC Software

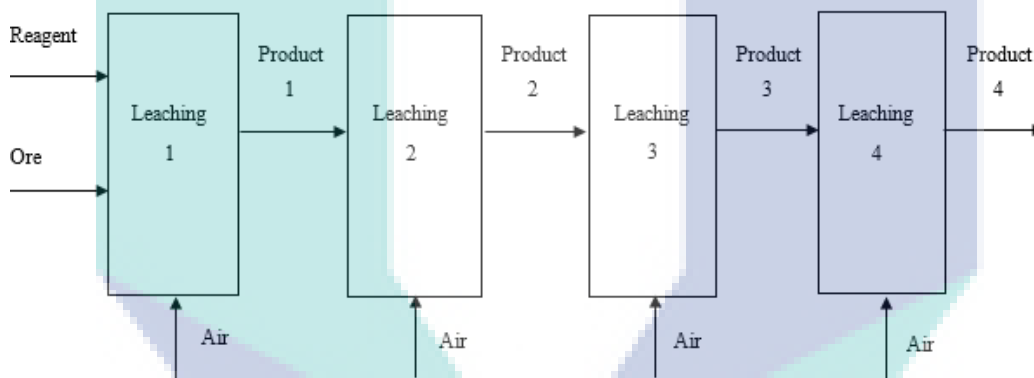
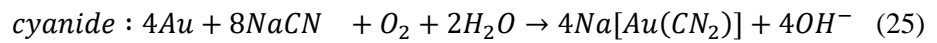


Figure 11: Block Flow Diagram for Leaching Process generally

3.3.4.1 Assumptions of the Model

In this model work, it was assumed that leaching process is in steady state condition. The system of gold cyanidation is assumed to be well mixed so that the solid-liquid mass transfer resistances can be neglected. In these studies, the most popular leaching equipment is multistage mixer-settler. It is widely used in industry because it gives a stable operation and high stage efficiency. The reactor configuration was described as a series of ideal CSTR, the reaction were described by kinetic model with experimental data. The difference condition between case study 1 and 2 are in case study 1, the ore consist of element of gold only while for case study 2, the ore consists other element. NaCN and HCl are 2 types of

alternative solvent will be used on leaching process. The equations being involved are:



3.3.4.2 Condition of Leaching Synthesis

The operating pressure is 1 bar while for temperature inlet is 30 °C and temperature outlet 60 °C. The conversion unit is 60% for both equation 25 and equation 26 reaction.

Table 8: Leaching flowrate of input and output

Feed Stream	Input	Output		
	Reagent	Ore	Air	Product
Temperature (°C)	30	30	25	60
Unit	Kg/hr	Kg/hr	Kg/hr	Kg/hr
Au	-	0.15	-	0.002
O ₂	-	-	113.45	-
CN ⁻	2.911	-	-	2.8719
OH ⁻	.9519	-	-	0.9519
Na ⁺	4.0397	-	-	4.0397
Au(CN) ₂	-	-	-	0.1907
H ₂ O	55994	-	-	55994
N ₂	-	-	426.80	-

3.3.5 Procedure of Leaching modelling using HSC Chemistry

The process of Leaching by using HSC Chemistry can be summarized by flowchart as shown below:

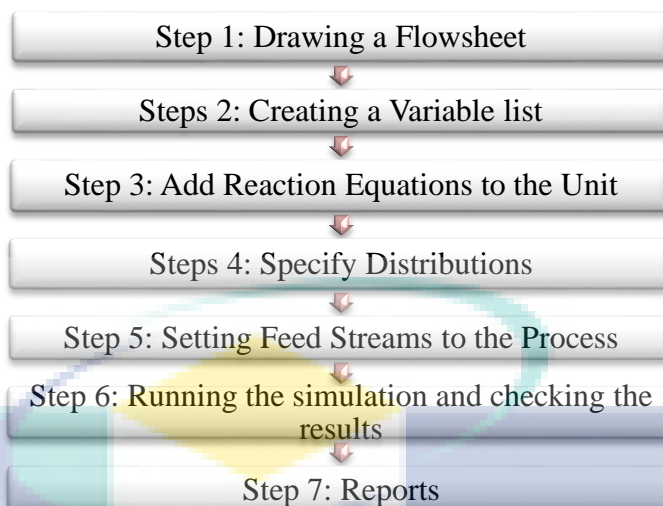


Figure 12: Flowchart of HSC Chemistry

Step 1: Drawing a Flowsheet

Select the reaction unit (blue) by left-clicking the unit icon. Select the stream icon with the mouse (left button). Choose the select icon and rename units and streams by double-clicking the name or click the name label and edit properties.

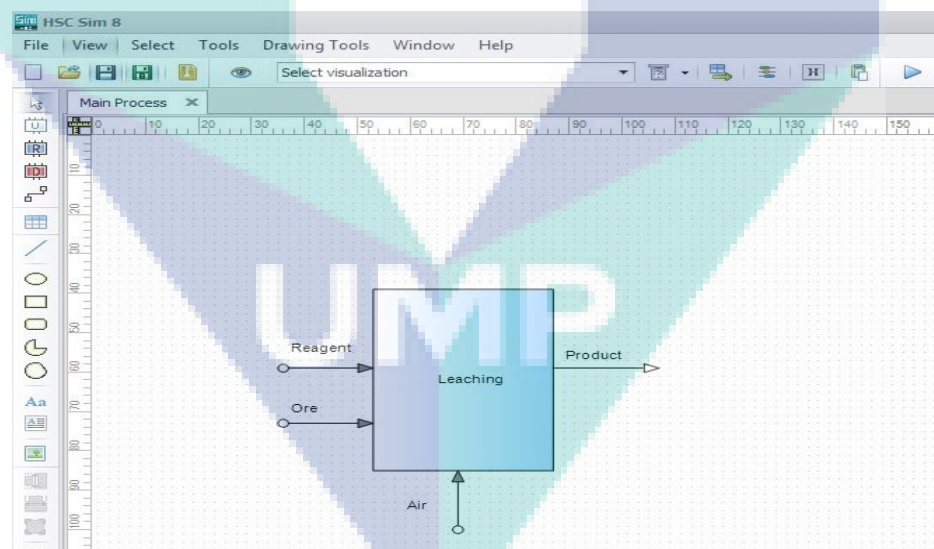


Figure 13: Drawing a Flowsheet

Steps 2: Creating a Variable list

A variable list editor is shown in Figure 14. The user should at least add some species to phases in this editor.

Specific the Species

First, specify the species are using in calculation. The species can be any combination of elements, solid species (Au), gases (O₂ (g), N₂ (g)) and liquids (Na(+a), CN(-a), Au(CN)₂(-a), OH(-a), H₂O, NaCN)

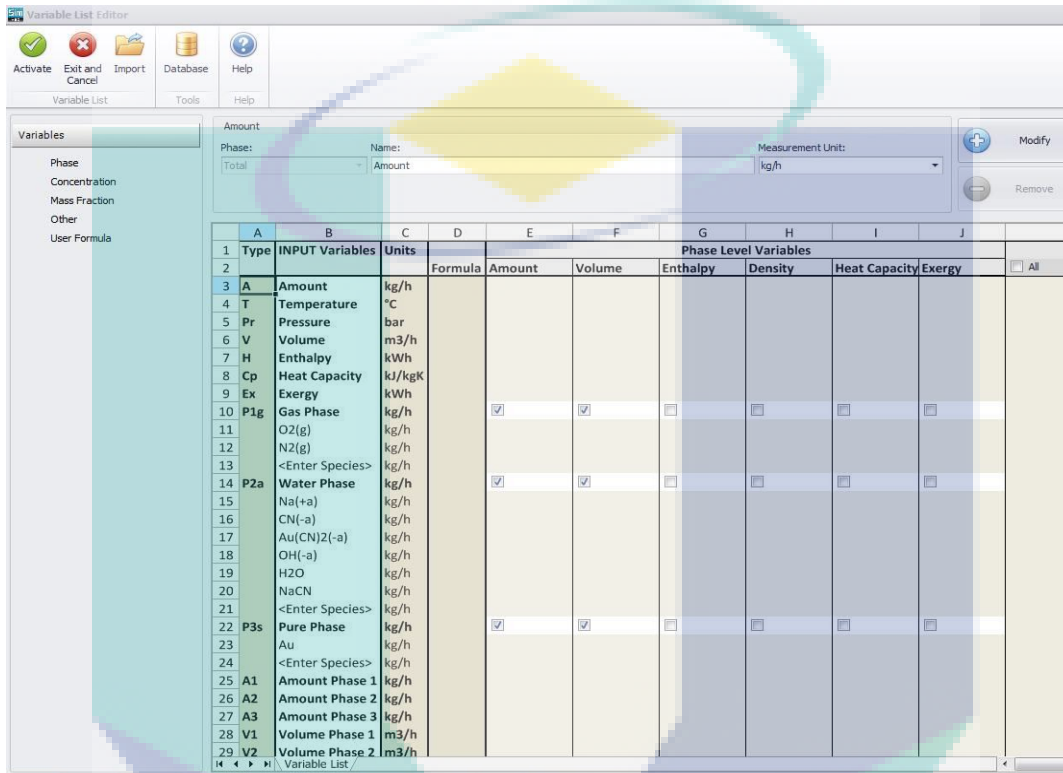


Figure 14: Creating a Variable List

Special case: species that are not found in HSC database

If the compound is not found from the HSC database, we need to add it to the own database. Here are instructions what need to take into account when need add the compound: The compound needs to have a chemical formula. Molecular weight is calculated from the formula. For mixtures use formula that gives average molecular weight. We need to added properties to the compound manually, for example enthalpy (kJ/mol), entropy (J/mol.K), heat capacity (J/mol.K) and density (kg/l).

Specify the Variable

Concentrate (Concentration): Measurement units of different phases.

- a. Gas (wt %, vol % or ppm)
- b. Water (wt%, vol % or ppm)
- c. Pure (wt%, vol % or ppm)

*For case study 2, concentrations of difference amount need to be including in the variable list..

30		K	kg/h	2.14	2.14		
31		Mg	kg/h	0.44	0.44		
32		Na	kg/h	5.37	5.37		
33		P	kg/h	0.04	0.04		
34		S	kg/h	0.29	0.29		
35		Ti	kg/h	0.34	0.34		
36		Mn	kg/h	0.08	0.08		
37	A1	Amount Phase 1	kg/h	540.25	0.00	540.25	0.00
38	A2	Amount Phase 2	kg/h	56001.90	0.00	0.00	56001.90
39	A3	Amount Phase 3	kg/h	96.53	96.53	0.00	0.00
40	V1	Volume Phase 1	m3/h	420.95	0.00	420.95	0.00
41	V2	Volume Phase 2	m3/h				
42	V3	Volume Phase 3	m3/h	0.04	0.04	0.00	0.00
43	C3	Au	ppm	1553.92	553.92	0.00	0.00
44	C3	Si	wt-%	68.37	68.37	0.00	0.00
45	C3	Al	wt-%	15.64	15.64	0.00	0.00
46	C3	Ca	wt-%	2.15	2.15	0.00	0.00
47	C3	Fe	wt-%	4.66	4.66	0.00	0.00
48	C3	K	wt-%	2.22	2.22	0.00	0.00
49	C3	Mg	wt-%	0.46	0.46	0.00	0.00
50	C3	Na	wt-%	5.56	5.56	0.00	0.00
51	C3	P	wt-%	0.04	0.04	0.00	0.00
52	C3	S	wt-%	0.30	0.30	0.00	0.00

Figure 15: Concentration of others element

Step 3: Add Reaction Equations to the Unit

The following leaching reaction equation 1 can be added with the Chemical Reaction Wizard. In the Leaching unit, open the Excel editor “Chemical Reaction Wizard”. The progress %, Reactants, Products and press the Balance button, which checks the coefficients for the reactions, see Table 7.

1	Progress	Reactants	Products	Balance	H	K
2	%	Separated with +		Separated with +		25 °C
3	60	4Au + 8CN(-a) + O2(g) + 2H2O	= 4Au(CN)2(-a) + 4OH(-a)	OK	-139.5904844 kcal	5.54721E+68
4			=			

Figure 16: Reaction sheet in Chemical Reaction Wizard

Steps 4: Specify Distributions

Remember to complete the Distribution sheets of the units. In the Leaching unit, 100% of the gas, solid and liquid phase produces to the product stream. Fill in the percentages.

5	Type	Dist Variables	Units	Total % Sum	product
14	P1g	Gas Phase	kg/h	100.00	100.00
15		O2(g)	kg/h	100.00	100.00
16		N2(g)	kg/h	100.00	100.00
17	P2a	Water Phase	kg/h	100.00	100.00
18		Na(+a)	kg/h	100.00	100.00
19		CN(-a)	kg/h	100.00	100.00
20		Au(CN)2(-a)	kg/h	100.00	100.00
21		OH(-a)	kg/h	100.00	100.00
22		H2O	kg/h	100.00	100.00
23		NaCN	kg/h	100.00	100.00
24		O2(g)	kg/h	100.00	100.00
25	P3s	Pure Phase	kg/h	100.00	100.00
26		Au	kg/h	100.00	100.00

Figure 17: Distribution Sheet for Leaching Units

Step 5: Setting Feed Streams to the Process

All the feed streams to the process should be set. If the feed to the process is not set, the stream will be ignored.

Input sheets of Leaching unit:

a) Reagent stream consists of Na(+a), CN(-a), Au(CN)₂(-a), OH(-a), H₂O.
Temperature of reagent streams should be set to 30°C.

b) Air stream consists of 21 vol.% of O₂(g) and 79% vol.% of N₂(g).
Temperature of air streams should be set to 25°C.

c) Ore streams consists of solid Au

Output sheets of Leaching unit:

a) Temperature of product streams should be set to 60 °C.

Type	INPUT Variables	Units	Total Sum	Reagent	Air 1	Ore
A	Amount	kg/h	56546.35	0.15	540.25	56005.95
T	Temperature	°C		20.00	25.00	20.00
Pr	Pressure	bar		1.00	1.00	1.00
V	Volume	m ³ /h				
H	Enthalpy	kWh	-247127.79	0.00	0.00	-247127.79
Cp	Heat Capacity	kJ/kgK	5.31	0.13	1.01	4.17
Ex	Exergy	kWh	834.95	0.01	6.96	827.98
P1g	Gas Phase	kg/h	540.25	0.00	540.25	0.00
	O2(g)	kg/h	113.45		113.45	
	N2(g)	kg/h	426.80		426.80	
P2a	Water Phase	kg/h	56005.95	0.00	0.00	56005.95
	Na(+a)	kg/h	4.04		0.00	4.04
	CN(-a)	kg/h	2.91		0.00	2.91
	Au(CN) ₂ (-a)	kg/h	0.00		0.00	
	OH(-a)	kg/h	5.00		0.00	5.00
	H2O	kg/h	55994.00		0.00	55994.00
	NaCN	kg/h	0.00			
P3s	Pure Phase	kg/h	0.15	0.15	0.00	0.00
	Au	kg/h	0.15	0.15	0.00	
A1	Amount Phase 1	kg/h	540.25	0.00	540.25	0.00
A2	Amount Phase 2	kg/h	56005.95	0.00	0.00	56005.95
A3	Amount Phase 3	kg/h	0.15	0.15	0.00	0.00
V1	Volume Phase 1	m ³ /h	420.95	0.00	420.95	0.00
V2	Volume Phase 2	m ³ /h				
V3	Volume Phase 3	m ³ /h	0.00	0.00	0.00	0.00

Figure 18: Feed stream amounts of the Leaching unit

	A	B	C	D	E
4					
5	Type	OUTPUT	Units	Total	
6		Variables		Sum	product
7	A	Amount	kg/h	56546.35	56546.35
8	T	Temperature	°C		60.00
9	Pr	Pressure	bar		1.00
10	V	Volume	m3/h		
11	H	Enthalpy	kWh	-244520.73	-244520.73
12	Cp	Heat Capacity	kJ/kgK	4.16	4.16
13	Ex	Exergy	kWh	956.58	956.58
14	P1g	Gas Phase	kg/h	540.25	540.25
15		O2(g)	kg/h	113.45	113.45
16		N2(g)	kg/h	426.80	426.80
17	P2a	Water Phase	kg/h	56006.04	56006.04
18		Na(+a)	kg/h	4.04	4.04
19		CN(-a)	kg/h	2.89	2.89
20		Au(CN)2(-a)	kg/h	0.11	0.11
21		OH(-a)	kg/h	5.01	5.01
22		H2O	kg/h	55994.00	55994.00
23		NaCN	kg/h	0.00	0.00
24	P3s	Pure Phase	kg/h	0.06	0.06
25		Au	kg/h	0.06	0.06
26	A1	Amount Phase 1	kg/h	540.25	540.25
27	A2	Amount Phase 2	kg/h	56006.04	56006.04
28	A3	Amount Phase 3	kg/h	0.06	0.06
29	V1	Volume Phase 1	m3/h	420.95	420.95
30	V2	Volume Phase 2	m3/h		
31	V3	Volume Phase 3	m3/h	0.00	0.00
32					

Figure 19: Output stream temperature is put at 60C

Step 5: Saving the Process

Processes should always be saved in their own folder. Changing the process name is not enough since every unit is an Excel file that is saved in the same folder as the flowsheet. The name of these files is the same as the name of the units. Therefore, save different scenarios in different folders.

Step 6: Running the simulation and checking the results

When we have finished the model, we can run the simulation.

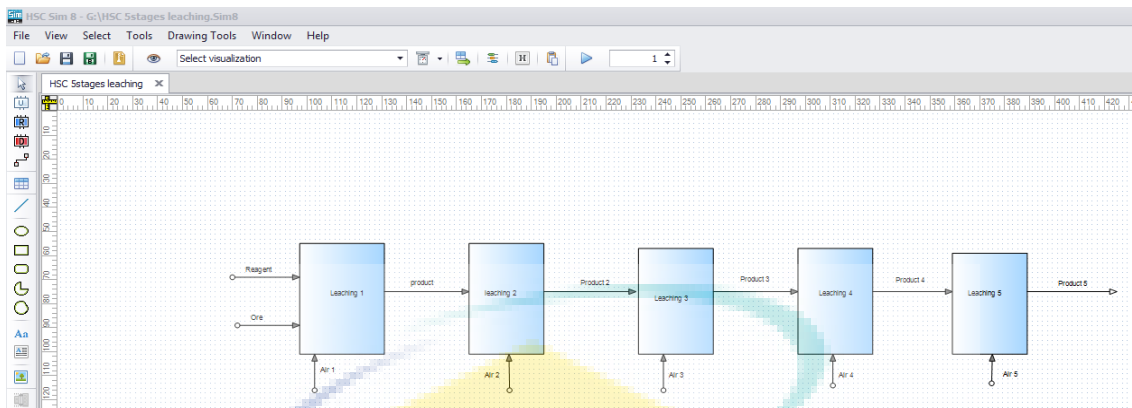


Figure 20: Selecting visualization from the list

The Stream Table Editor window displays the following variables:

- Available variables:** Amount Phase 1 (kg/h), Amount Phase 2 (kg/h), Amount Phase 3 (kg/h), Au (ppm), Enthalpy (kWh), Exergy (kWh), Gas Phase (kg/h), Heat Capacity (kJ/kgK), Pressure (bar), Pure Phase (kg/h), Volume Phase 1 (m3/h), Volume Phase 2 (m3/h), Volume Phase 3 (m3/h), Volume (m3/h), Water Phase (kg/h), Au (kg/h).
- Visible variables:** Amount (kg/h), Temperature (°C), Au(CN)2(-a) (kg/h), Au (kg/h), CN(-a) (kg/h).

Amount	123.45
Temperature	234.56
Au(CN)2(-a)	345.67
Au	456.78
CN(-a)	567.89

Check all the stream tables visible
 View mode: Name and value Column 1 Color: 255, 255, 255 Column 2 color: 255, 255, 255 Number Format: 0.00
 OK Cancel

Figure 21: Stream table editor to modify Stream Tables

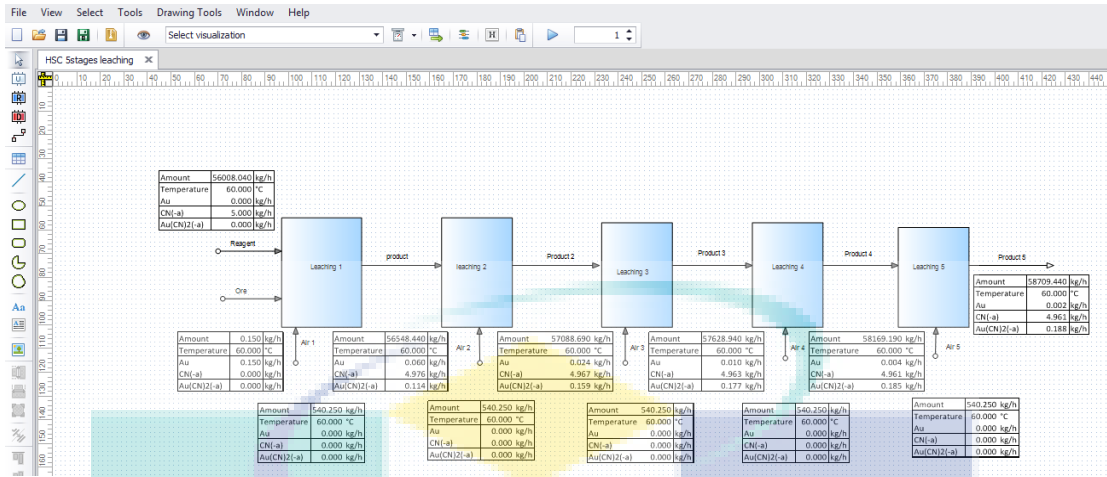


Figure 22: Stream Tables to visualize calculation results

Step 7: Reports

A summary of flowsheet results can be saved and printed here. There are two pages in this report sheet. One for units balance and one for streams balance.

The table below is a simplified representation of the 'Stream Balance' sheet shown in the screenshot. It lists 30 streams and their properties across various stages.

Streams	BALANCE TOTAL	INPUT:	Reagent	Air 1	Ore	Air 2	Air 3	Air 4	OUTPUT:	Product 4	INTERMEDIATE:	product	Product 2	Product 3
Destination	?	Leaching	Leaching	Leaching	Leaching 2	Leaching 3	Leaching 4	?	Leaching 4	?	Leaching	Leaching 2	Leaching 3	Leaching 4
5 Amount kg/h	0.00	58167.10	0.15	540.25	56005.95	540.25	540.25	540.25	58167.10	58167.10	56546.35	57086.60	57626.85	
6 Temperature °C	-100.00	160.00	30.00	25.00	30.00	25.00	25.00	25.00	60.00	60.00	60.00	60.00	60.00	60.00
7 Pressure bar	-5.00	6.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
8 Volume m3/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9 Enthalpy kWh	1973.64	-246478.39	0.00	0.00	-246478.39	0.00	0.00	0.00	-244504.74	-244504.74	-244520.73	-244515.40	-244510.07	
10 Heat Capacity kJ/kgK	-4.29	8.36	0.13	1.01	4.18	1.01	1.01	1.01	4.07	4.07	4.16	4.13	4.10	
11 Energy kWh	122.55	855.76	0.01	6.96	827.92	6.96	6.96	6.96	978.32	978.32	956.58	963.82	971.07	
12 Gas Phase kg/h	-0.01	2161.00	0.00	540.25	0.00	540.25	540.25	540.25	2160.99	2160.99	540.25	1080.49	1620.74	
13 O2(g) kg/h	-0.01	453.80	0.00	113.45	0.00	113.45	113.45	113.45	453.79	453.79	113.45	226.89	340.34	
14 N2(g) kg/h	0.00	1707.20	0.00	426.80	0.00	426.80	426.80	426.80	1707.20	1707.20	426.80	853.60	1280.40	
15 Water Phase kg/h	0.15	56005.95	0.00	0.00	56005.95	0.00	0.00	0.00	56006.10	56006.10	56006.04	56006.08	56006.10	
16 Na(+a) kg/h	0.00	4.04	0.00	0.00	4.04	0.00	0.00	0.00	4.04	4.04	4.04	4.04	4.04	
17 Ni(-a) kg/h	-0.04	2.91	0.00	0.00	2.91	0.00	0.00	0.00	2.87	2.87	2.89	2.88	2.87	
18 Au(CN)2(-a) kg/h	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.18	0.11	0.16	0.18	
19 OH(-a) kg/h	0.01	5.00	0.00	0.00	5.00	0.00	0.00	0.00	5.01	5.01	5.01	5.01	5.01	
20 H2O kg/h	-0.01	55994.00	0.00	0.00	55994.00	0.00	0.00	0.00	55993.99	55993.99	55994.00	55993.99	55993.99	
21 NaCN kg/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
22 Pure Phase kg/h	-0.15	0.15	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.02	0.01	
23 Au kg/h	-0.15	0.15	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.02	0.01	
24 Amount Phase 1 kg/h	-0.01	2161.00	0.00	540.25	0.00	540.25	540.25	540.25	2160.99	2160.99	540.25	1080.49	1620.74	
25 Amount Phase 2 kg/h	0.15	56005.95	0.00	0.00	56005.95	0.00	0.00	0.00	56006.10	56006.10	56006.04	56006.08	56006.10	
26 Amount Phase 3 kg/h	-0.15	0.15	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.02	0.01	
27 Volume Phase 1 m3/h	0.00	1683.80	0.00	420.95	0.00	420.95	420.95	420.95	1683.80	1683.80	420.95	841.90	1262.85	
28 Volume Phase 2 m3/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
29 Volume Phase 3 m3/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
30 Volume Phase 3 m3/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	

Figure 23: Stream balance sheet of the report file

3.4 Result and Discussion

3.4.1 Overview

In this part, comparison of gold (Au) dissolution between experiment and simulation is discussed. Next, the results using different simulator i.e. Aspen Plus and HSC Chemistry will be elaborated. In addition, the discussion will covers effect of conversion on gold flowrate and gold-cyanide complex flowrate, effect of inlet flowrate to outlet flowrate of gold, effect of sodium cyanide (NaCN) as reagent to the Au outlet flowrate, effect of other elements in leaching process and effect of temperature based on thermodynamic equilibrium of solid-liquid extraction.

3.4.2 Result and Discussion from journal

3.4.2.1 Comparison of Results between Aspen Plus in literature and HSC

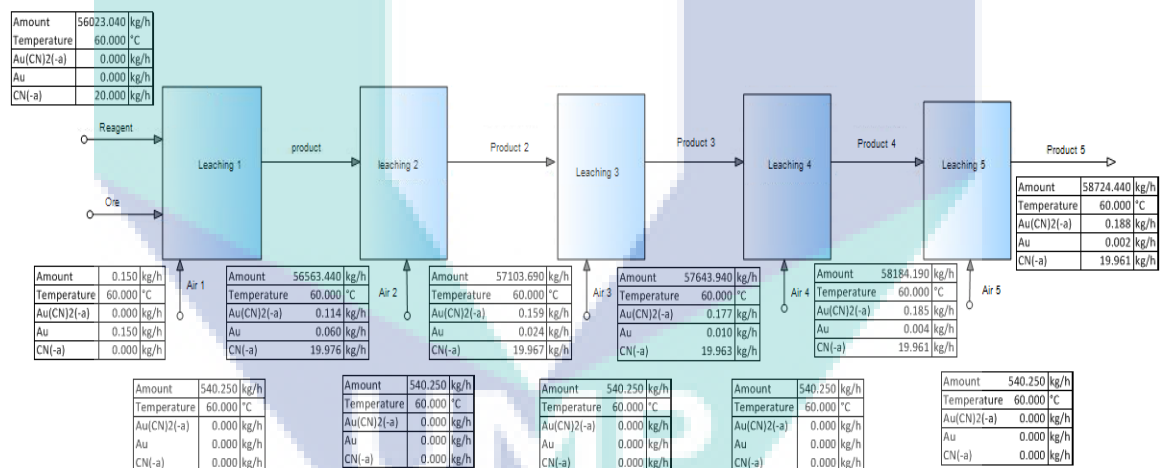


Figure 24: Block flow Diagram of leaching process by HSC

Figure 10 shows the leaching process of gold by Aspen Plus while on Figure 25 shows the leaching process of gold by HSC Chemistry 8.

From the Table 10, it can be seen that there are no significant differences in results between Aspen Plus simulation and HSC Chemistry simulation. Both of them are assumed in steady state condition. The reaction between gold and sodium cyanide

is the extraction between solid and liquid phase by leaching process. Therefore, HSC Chemistry is more suitable and easier to handle in processing of solid-liquid extraction compared to Aspen Plus. Furthermore, in HSC Chemistry it is easier because there is no need to identify the thermodynamic dynamic model, whereas in Aspen Plus, we need to choose a suitable thermodynamic model for the reaction. In HSC also, the overall reaction in term of dissolution of gold with cyanide is faster than Aspen Plus because via Aspen Plus simulation resulted in be utilized 6 CSTR reactors to dissolve it while HSC only needed 5 CSTR reactors. In addition, air was function as to remove undesirable gases dissolved in water.

Table 9: Comparison of results between Aspen Plus in literature and HSC simulation

Components	Output Stream		
	Aspen Plus (Benjamin, 2014)	HSC Chemistry	Error (%)
Au	0.002	0.002	0
O₂	-	-	-
CN⁻	2.8719	2.87	0.066
OH⁻	0.9519	0.96	0.844
Na⁺	4.0397	4.04	0.007
Au(CN)₂	0.1907	0.19	0.368
H₂O	55994	55993.99	0
N₂	-	-	-

3.4.2.2 Comparing Result Experimental and Simulation

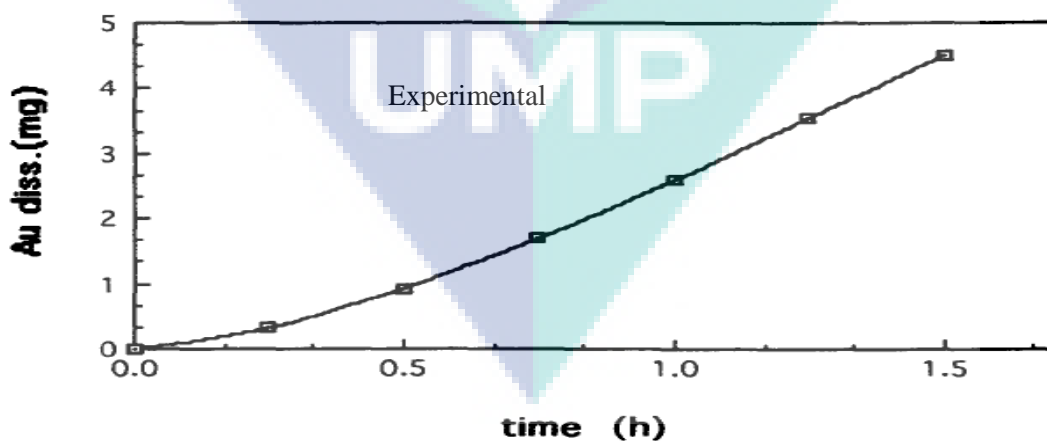


Figure 25: Gold dissolution by time in experiment

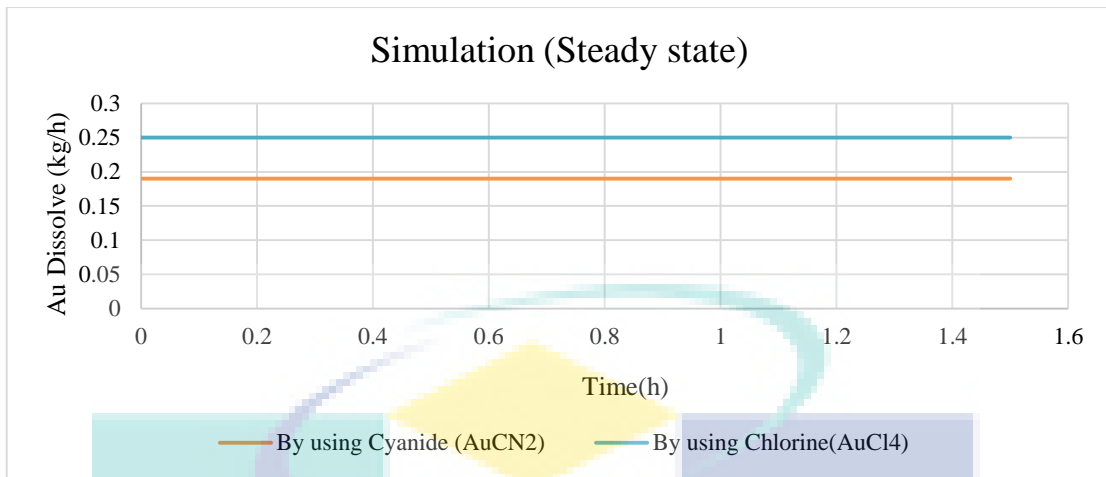


Figure 26: Gold dissolution by time in simulation with difference solvent which are cyanide and chlorine

From Figure 26 shows gold dissolution by time in experiment while in Figure 27, gold dissolution by time in simulation with difference solvent which are cyanide and chlorine. Both graph shows that at the end of time, gold dissolution will increase and approaches to the same value.

Based on Figure 27, according to Aylmore (2005), the flowrate loss of gold strips immersed in chloride mixtures was much faster than that achieved by cyanidation under similar condition. The stability of the AuCl_4 is strongly dependent on the solution pH and requires high chloride and chlorine levels and high ore surface area. But, as usual the ores possibly has high silver contents was dissolve slowly in low-chloride solutions because formation of a passivating film of insoluble silver chloride. Consequently higher concentrations of chloride in solution are required to solubilize the relatively insoluble silver chloride. Therefore, the chloride system is not ideally suited to treatment of ores to produce gold. (Aylmore M. G., 2005)

3.4.2.3 Effect of Cyanidation

Effect of Conversion to Gold flowrate in Cyanidation Process

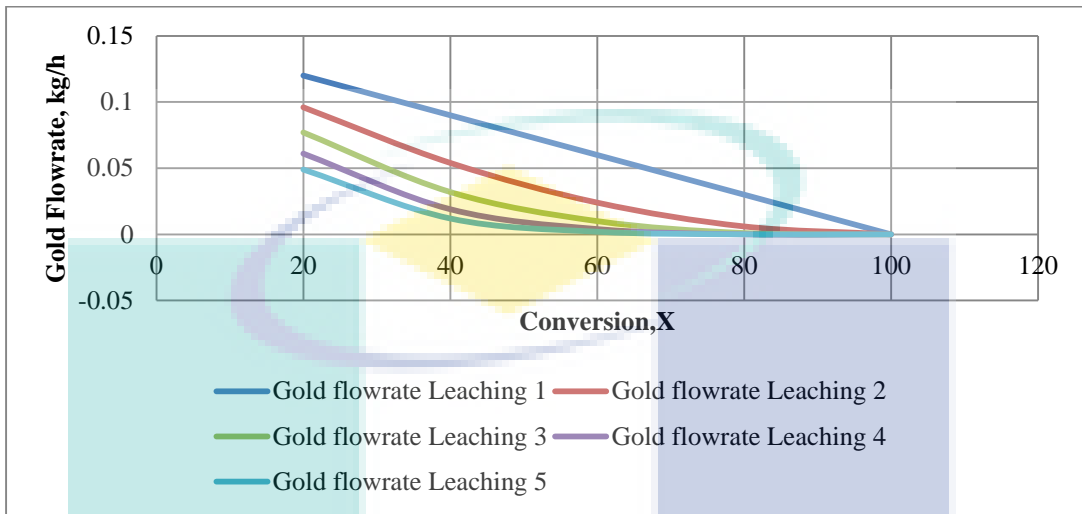


Figure 27: Effect of conversion on Gold Flowrate

Effect of Conversion to Gold Cyanide Complex flowrate in Cyanidation Process

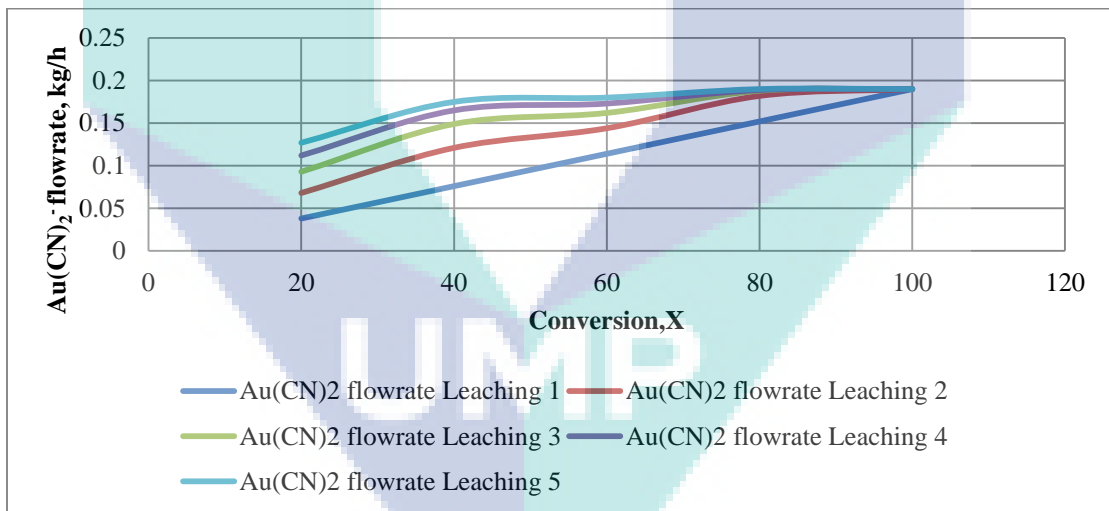


Figure 28: Effect of conversion to gold cyanide complex

From Figure 4.3, it is shown that when the conversion increases, the outlet flowrate of gold (Au) decreases while from Figure 4.4, the increase of conversion increases the gold-complex cyanide. As can be seen in both Figure 4.3 and 4.4, there are only 60% conversion and above can achieve the exact data 0.0002 for gold flowrate and 0.19 for gold-complex cyanide. It is because of the dissolution of gold

in reaction between gold and sodium which gold is oxidized and dissolved to form the stable gold-cyanide complex ion. In addition, increases of conversion will increase the dissolution reaction and the cost of leaching reactor.

Effect of Inlet Flowrate to Outlet Flowrate of Gold

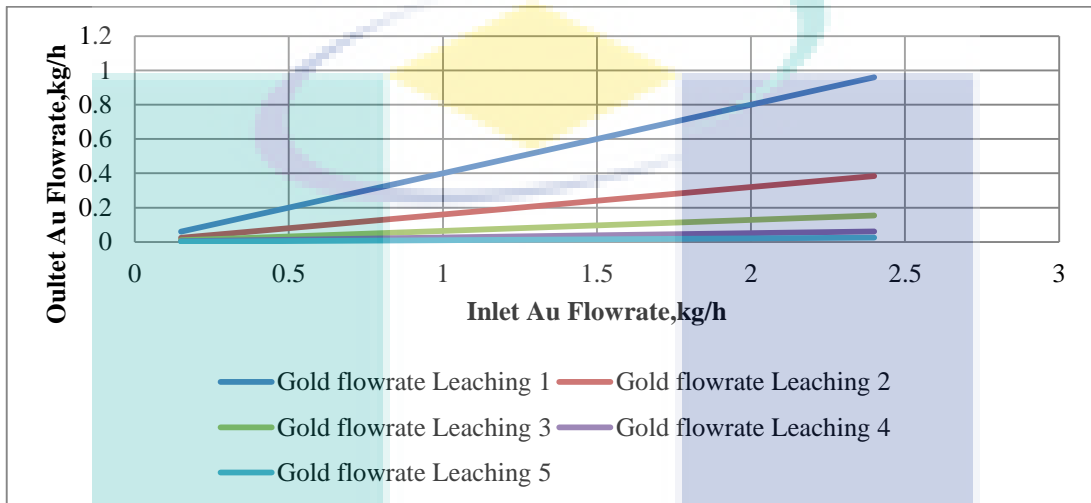


Figure 29: Effect of Inlet Flowrate to Outlet Flowrate of Gold

Effect of Sodium Cyanide (NaCN) as reagent to the Au Outlet Flowrate

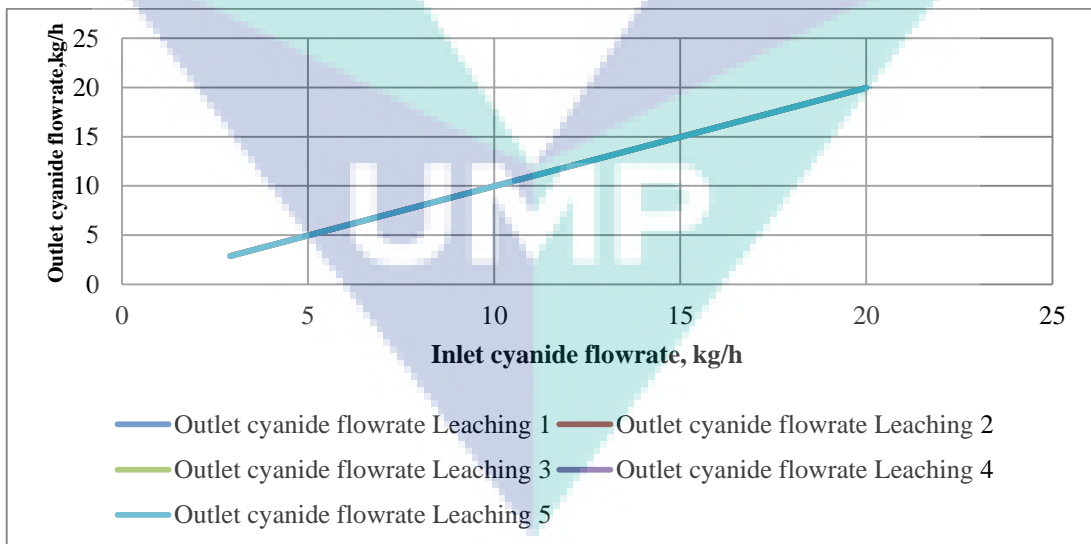


Figure 30: Effect of Sodium Cyanide (NaCN) as reagent to the Au Outlet Flowrate

Figure 4.6 and 4.7 shows increases of outlet flowrate of gold because due to the fact that increases of inlet flowrate of gold and increases of sodium cyanide. It is because solubility of cyanide salts to dissolves and ionize in water to form their respective metal cation and free cyanide ions (CN^-). Increases of inlet gold and sodium cyanide, increasing the rate of diffusion because of dissolution involves in gold oxidation which is anodic reaction. Consequently the majority of the mills operate at cyanide level dependent on the dissolved oxygen level. De Andrade Lima and Hodouin (2005) also investigated the kinetic model for the cyanide consumption as function of cyanide concentration.

Effect of Other Elements in Leaching Process

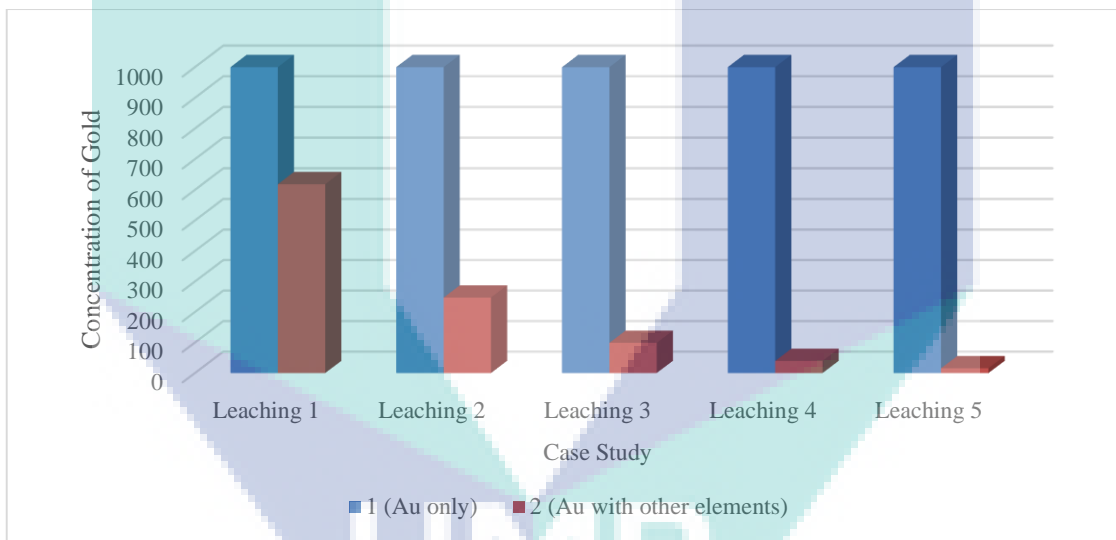
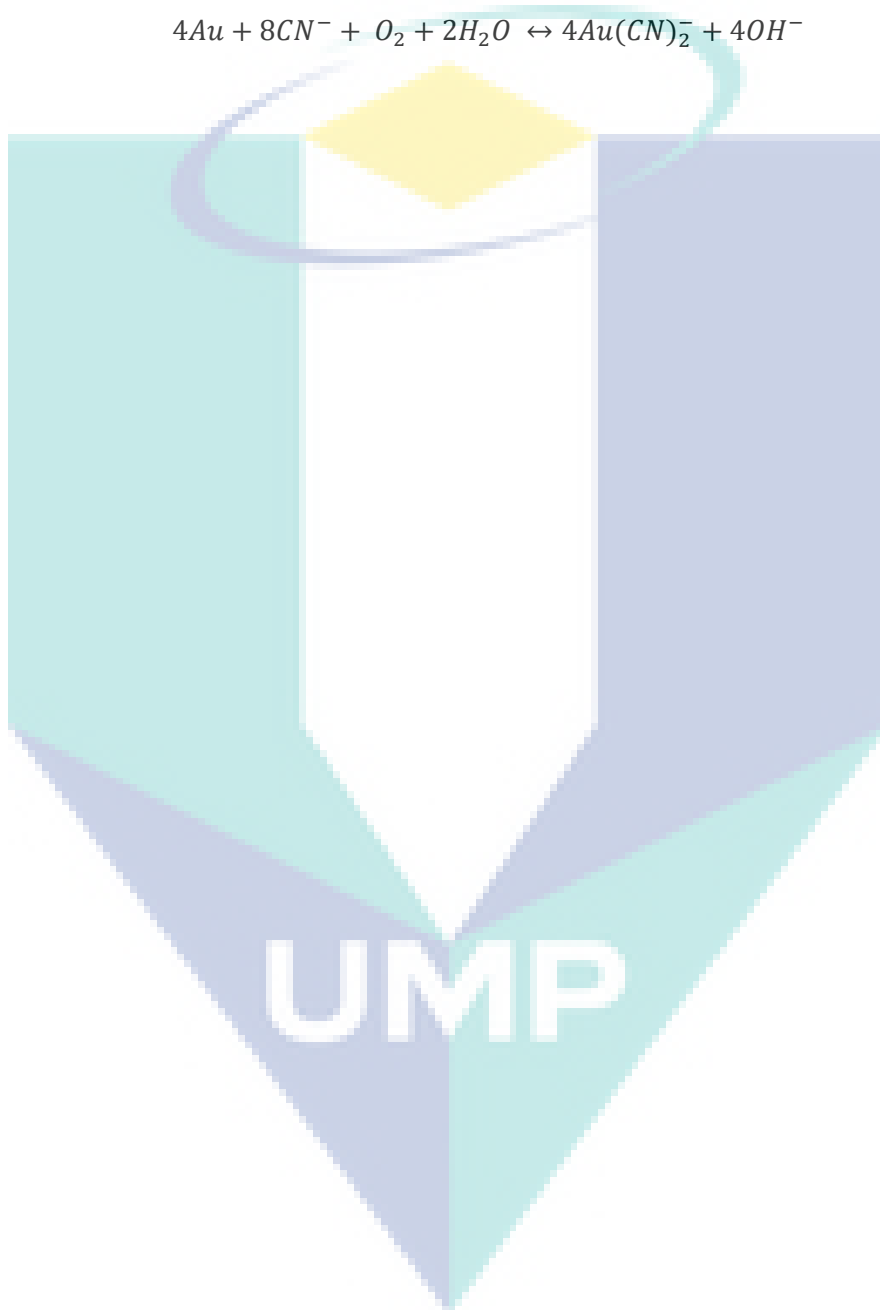
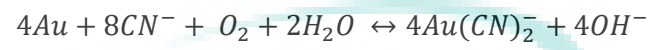


Figure 31: Effect of other elements by units weight/weight in leaching process to the gold concentration

Figure 4.8 shows a different case study which are case study 1, the ore consists of element of gold only while for case study 2, the ore consists other element such as gold(Au), silica(Si), ferum(Fe), aluminium(Al) and other which are already state in Table 1. As we can see, case study of 1 has no change of concentration of gold while for case study 2, concentration of gold decreases from leaching 1 to leaching 4. It is because effects from the competitive reactions may increase in the consumption of cyanide and reduce the efficiency of gold leaching. According

to Mudder, another effects of case study 2 are waste water that may be difficult to treat and complications in the analysis of cyanide solution. (Mudder, 2001)

Thermodynamic Equilibrium of Solid-Liquid Extraction



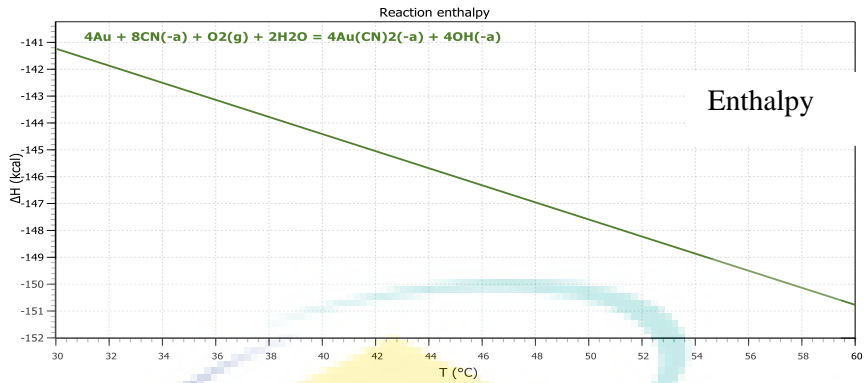


Figure 32: Cyanidation of enthalpy

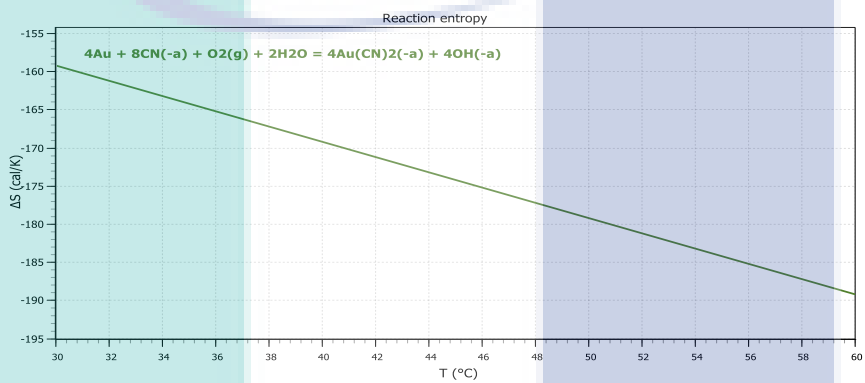


Figure 33: Cyanidation of entropy

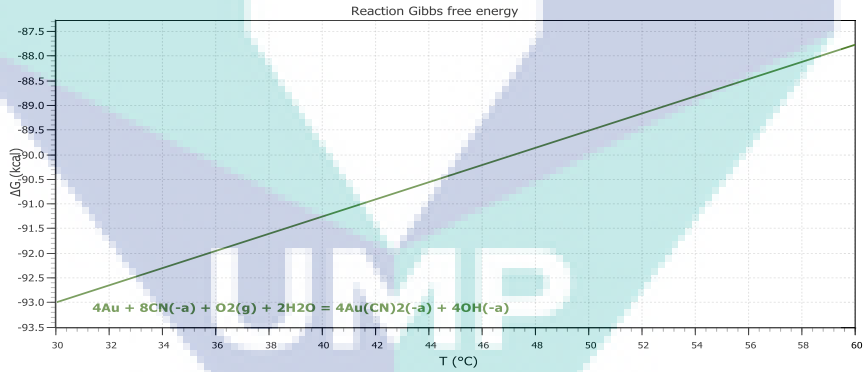


Figure 34: Cyanidation of Gibbs energy

Reaction simulations were carried out to understand the thermodynamic equilibrium of reactions and to analyze the optimum condition for the extraction. The reaction simulation study was done by using HSC Chemistry 8 software to analyze the properties of reaction enthalpy, entropy and Gibbs energy.

Simulation equation from 30°C to 60°C have negative enthalpy which indicate the reaction are exothermic reaction which release energy. This negative enthalpy

indicate that product enthalpy is lower than the reactant enthalpy of the system. Simulation data from temperature 30°C to 60°C show the enthalpy value decreases as the temperature increase as showed by figure 4.9.

The reaction entropy indicate either reaction is in order or disorder. When gold react with sodium cyanide, water and air, the reaction has negative entropy and therefore indicate the reaction are ordered.

3.5 Conclusion

The cyanidation of gold processing was successfully developed by using leaching process in HSC Chemistry 8. This work found that when comparing data from case study 1, the data for input and output via simulation in HSC Chemistry almost similar. From this simulation, it is found the dissolution on cyanide concentration have a dominant effect on gold leaching. Increasing the reagents concentration can improve gold dissolution rate. However, the reaction also depends on the gold concentration in the particles. Next, effect of other elements in leaching process contribute to the decreasing of gold concentration.

As recommendation, more experimental data should be obtained in order to improve the simulation in HSC via comparison it is also recommend to stimulate the full process of gold extraction such as grinding, leaching, filtering, carbon absorption and recovery. In addition, a study on another alternative to cyanide, in extracting gold should be carried out.

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