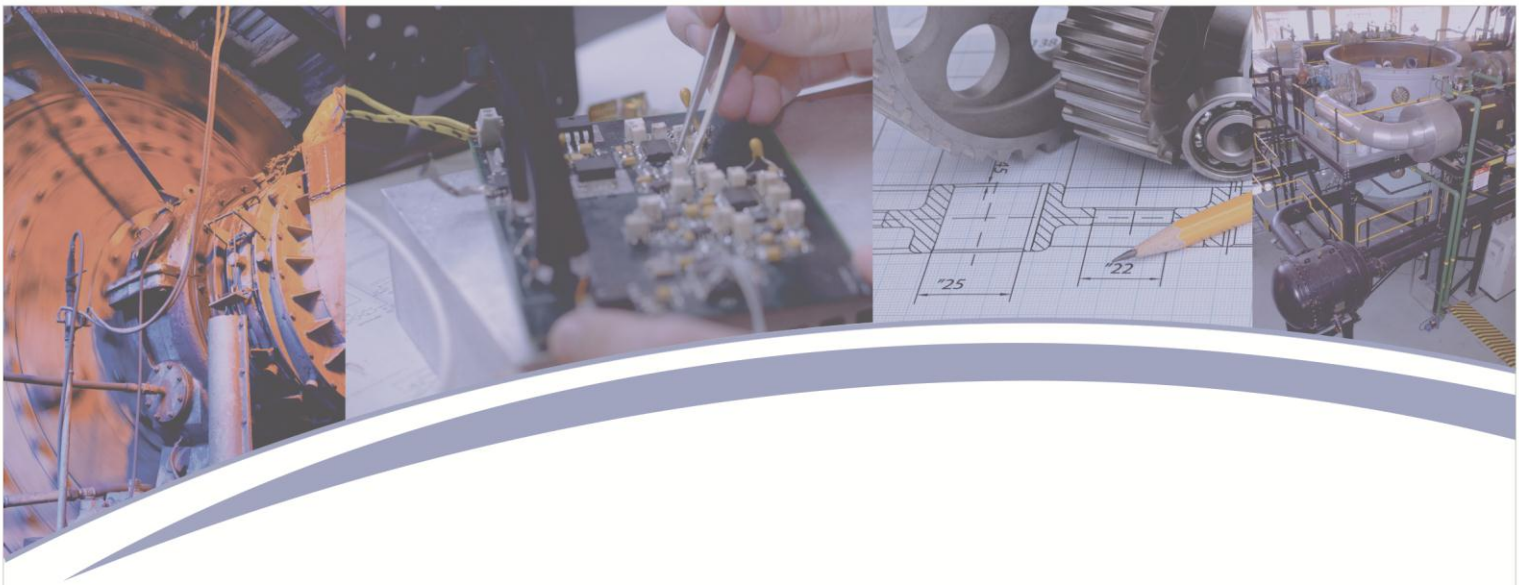

Simulation of the copper-chlorine thermochemical cycle

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(B.Eng)

This dissertation was submitted in fulfilment of the requirements of the degree Master in Chemical Engineering at the Potchefstroom campus of the North West University

Noordwes-Universiteit Potchefstroomkampus

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Potchefstroom, South Africa

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DECLARATION

Solemn declaration by student

I Liberty Sheunesu Mapamba, declare herewith that the dissertation entitled: “Simulation of the copper-chlorine thermochemical cycle”, which I herewith submit to the North-West University as partial completion of the requirements set for the MEng Chemical Engineering degree, is my own work and has not already been submitted by me to any other university.

Signature: _____

Signed at: Potchefstroom this 31st day of October 2011

ABSTRACT

The global fossil reserves are dwindling and there is need to find alternative sources of energy. With global warming in mind, some of the most commonly considered suitable alternatives include solar, wind, nuclear, geothermal and hydro energy. A common challenge with use of most alternative energy sources is ensuring continuity of supply, which necessitates the use of energy storage. Hydrogen has properties that make it attractive as an energy carrier. To efficiently store energy from alternative sources in hydrogen, several methods of hydrogen production are under study. Several literature sources show thermochemical cycles as having high potential but requiring further development.

Using literature sources, an initial screening of thermochemical cycles was done to select a candidate thermochemical cycle. The copper-chlorine thermochemical cycle was selected due to its relatively low peak operating temperature, which makes it flexible enough to be connected to different energy sources. Once the copper-chlorine cycle was identified, the three main copper-chlorine cycles were simulated in Aspen Plus™ to examine which is the best configuration. Using experimental data from literature and calculating optimal conditions, flowsheets were developed and simulated in Aspen Plus™. The simulation results were then used to determine the configuration with the most favourable energy requirements, cycle efficiency, capital requirements and product cost.

Simulation results show that the overall energy requirements increase as the number of steps decrease from five-steps to three-steps. Efficiencies calculated from simulation results show that the four and five-step cycles perform closely with 39% and 42%, respectively. The three-step cycle has a much lower efficiency, even though the theoretical calculations imply that the efficiency should also be close to that of the four and five-step cycles. The five-step reaction cycle has the highest capital requirements at US$370 million due to more equipment and the three-step cycle has the lowest requirement at US$ 275 million. Payback analysis and net present value analysis indicate that the hydrogen costs are highest for the three-step cycle at between US$3.53 per kg for a 5-10yr payback analysis and the five-step cycle US$2.98 per kg for the same payback period.

Key words: Aspen Plus™ Simulation, Thermochemical cycle, Hydrogen production, Efficiency, Economics

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LIST OF ABBREVIATIONS

Abbreviation	Description
CAPEX	Capital Expenditure
CEA	Commisariat à l'Énergi Atomique (French Atomic Energy Commission)
Cu-Cl	Copper-chlorine (Thermochemical cycle)
DST	Department of Science and Technology (South Africa)
H-5	5 reaction Hydrogen cycle
HyS	Hybrid sulphur (Thermochemical cycle)
HySA	Hydrogen South Africa
JAERI	Japanese Atomic Energy Research Institute
KAERI	Korean Atomic Energy Research Institute
MEA	Membrane Electrode Assembly
NASA	National Aeronautics and Space Administration
NHI	Nuclear Hydrogen Initiative(United States of America)
NPV	Net Present Value
SDE	Sulphur Depolarised Electrolysis
S-I	Sulphur Iodine(thermochemical cycle)
SMR	Steam Methane Reforming
US	United States(of America)
US-DOE	United States Department of Energy

NOMENCLATURE

Symbol	Description	Units
Greek		
η	Efficiency	-
ω_i	Acentric factor	-
γ_i	Activity coefficient for component i	-
Roman		
ΔH	Enthalpy change	kJ kg^{-1}
ΔG	Gibbs free energy change	kJ kg^{-1}
ΔS	Change in Entropy	kJ kg^{-1} K^{-1}
W	Work input (Electrical and Mechanical)	J mol^{-1} H_2
F	Faraday's constant	C mol^{-1}
Q	Thermal Energy input	J mol^{-1} H_2
E	Cell potential	V
R	Gas constant	J mol^{-1} K^{-1}
T	Absolute temperature	K
n	Amount of material being separated	Mol
y_i	Molar fraction of separated species	-
M	Mass flow rate	kg s^{-1} or kg hr^{-1}
Cp	Constant pressure specific heat capacity	kJ kg^{-1} $°C^{-1}$
a_i	Cubic equation constant specified for component i	
b	Overall cubic equation constant	-
b_i,b_j	Constants specified for components i, j	-
c	Cubic equation constant	-
c_i,c_j	Constants specified for components i, j	-
x	Liquid mole fraction	-
x_i,x_j	Liquid mole fraction of components i, j	-
y	Vapour mole fraction	-
y_i,y_j	Component vapour mole fractions	-
z_{RAi}	Compressibility factor	-
f_i^v	Vapour fugacity for component i	Atm
f_i^l	Liquid fugacity for component i	Atm

Symbol	Description	Units
P	Pressure	bar
P_{ci},P_{cj}	Critical pressure of component i, j	bar
T_i	Temperature of component i	K
T_{ci},T_{cj}	Critical temperature of component i, j	K
V_m	Molar volume	m^3 mol^{-1}

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CHAPTER 1 : INTRODUCTION

1.1 Background and motivation

According to the United Nations Department of Economic and Social affairs, energy is the key to economic development and renewable energy is the key to a future, with no dangerous climate change (United Nations, 2009). The scenario where the global economy is completely driven by renewable energy is still in the distant horizon. The world still has a major dependency on fossil energy in the form of oil, natural gas and coal (Forsberg,2007; Balat 2008). Fossil resource demand is fast outgrowing the supply from the known reserves and this is creating an energy gap which could threaten global development (United Nations, 2009) Besides dwindling reserves, environmental emissions from fossil fuels are exacerbating dangerous climate change.(United Nations,2009; Balat, 2008). Shortages and negative environmental contributions are key motivators for the world to seek alternative energy sources (Forsberg, 2007; Balat, 2008).

An acceptable alternative energy source should be technically feasible, economically competitive, environmentally acceptable and readily available (Balat, 2008). There are several alternative energy sources that satisfy these requirements and these include solar, wind, bio-energy, nuclear, geothermal energy, tidal energy and hydroelectric energy. Solar and wind have a minimal negative impact on the environment but are erratic in supply. Since the Fukushima accident in Japan, there have been rising concerns with nuclear plant safety and waste disposal, but developments in those areas which can mitigate the risks, are expected (AREVA, 2011). Hydroelectric energy and geothermal energy are good ways of generating electricity, the environmental impact being manageable, but raise issues with respect to storage of excess energy and application to mobile uses such as in transportation (Balat, 2008). Possible solutions for storage include the use of batteries, pumped hydroelectric schemes, compressed gas storage (FLATE, 2011) and hydrogen (Balat, 2008). Most of the storage solutions still have limitations with respect to application for mobile applications with the exception of hydrogen. Hydrogen has a high energy density and a relatively higher flexibility in comparison with electricity; hence it is a good energy transmission medium (Balat, 2008).

Hydrogen is a secondary source of energy which is produced from a hydrogen rich material such as hydrocarbons, ammonia and water (Schultz, 2003). The efficacy of hydrogen in addressing the challenges presented by the use of fossil fuels lies in its production method.

Most primary energy sources can be used in the manufacture of hydrogen(Schultz, 2003). Some of the processes which can be used to produce hydrogen include electrolysis, steam reforming of fossil hydrocarbons, biomass gasification, partial oxidation of hydrocarbons, algae liquefaction, thermochemical processes coupled with clean or renewable energy technologies, etc. Most of the production methods mentioned are either not technically feasible or economically uncompetitive on a large scale. The bulk of hydrogen used globally comes from conversion of fossil resources (Funk, 2001;Balat, 2008). Processes that produce hydrogen from conversion of fossil resources have a problem of emitting greenhouse gases which would eliminate the benefits of using hydrogen. Thermochemical processes have been developed that can be coupled with renewable or clean sources of energy to produce hydrogen (Schultz, 2003).

Thermochemical cycles are processes that primarily make use of heat and a series of intermediate chemical reactions to break down water into hydrogen and oxygen (Funk, 2001). More than 200 thermochemical cycles have been proposed for hydrogen production, but over the years many have been discarded for reasons ranging from feasibility to efficiency (Brown *et al.*,2000). Some of the most popular thermochemical cycles under study include the Hybrid Sulphur process, Sulphur Iodine cycle, Copper oxide-Copper sulphate cycle, Copper-chlorine cycle, Hybrid chlorine cycle and the Magnesium iodide cycle. Some of the key criteria in literature for selection of a thermochemical cycle for commercialization include cycle efficiency, capital requirements and peak temperature (Brown *et al.*, 2000). A basic comparison of the five most popular cycles (Using time adjusted data) is shown in Table 1.1

Table 1.1: Thermochemical cycle comparison [Sources:(Gorensek and Summers, 2009;Gooding, 2009;Wang *et al.*, 2009;Law *et al.*, 2008)]

Cycle	Efficiency %	Capital Requirement($millions)	Peak Temperature(°C)
Hybrid Sulphur	36.6	400	870
Hybrid Chlorine	36	800	850
Hybrid CuO-$CuSO_4$	52.4	360	870
Sulphur- Iodine	52	660	870
Copper-Chlorine	52	370	550

From Table 1.1 the copper oxide-copper sulphate reaction seems to have the highest efficiency and lowest high temperature heat source free capital requirement. It, however, has

a high peak temperature which will raise the overall capital cost associated with the cycle. The hybrid copper-cycle however, has a relatively high efficiency and slightly higher capital requirement. The peak temperature of the copper-chlorine is much lower and has more flexibility on the high temperature heat source it can be coupled with, and as such has a lower overall capital requirement.

Literature reports several copper-chlorine cycles ranging from three-step to five-step cycles. Wang *et al.*(2009) state that the different forms are a result of combining different reaction steps into one reaction. Furthermore, different forms of the copper-chlorine cycle perform differently in terms of the overall efficiency, energy requirements and capital requirements. Canadian researchers (Chukwu, 2008;Law *et al.*, 2008;Lewis *et al.*, 2009) have simulated the three and four reaction cycles assuming coupling with a nuclear heat source, all with different results. Wang *et al.* (2009) suggest that the five reactions cycle is theoretically more efficient than the four and three reactions cycles. Conclusive determination of the most effective cycle configuration has not been done, hence the need to simulate and determine it.

In 2007, the Department of Science and Technology developed the national hydrogen and fuel cells research development and innovation strategy, which was later branded as Hydrogen South Africa (HySA, 2010). The HySA mandate was split into Systems, Catalysis and Infrastructure. North-West University is co-hosting the Infrastructure group which is responsible for developing a knowledge base on the production of hydrogen from different energy generators (HySA, 2010). The simulation of the copper-chlorine cycles is intended to contribute to the HySA infrastructure's knowledge base on centralised hydrogen production.

1.2 Objectives

In this study three Aspen Plus™ simulations will be developed for the three, four and five-step copper-chlorine cycles. The main objective is therefore to determine the most effective configuration of the three different copper-chlorine cycles. The key outputs to be measured from the different cycle's configurations are

- overall energy requirements of the cycle;
- thermal efficiency of the cycle;
- capital requirements of the cycle; and
- hydrogen production price.

Using these key outputs, the best configuration of the copper-chlorine cycle will be determined.

1.3 Scope of study

Figure 1.1 summarizes the scope of study of the simulation of the copper-chlorine cycle.

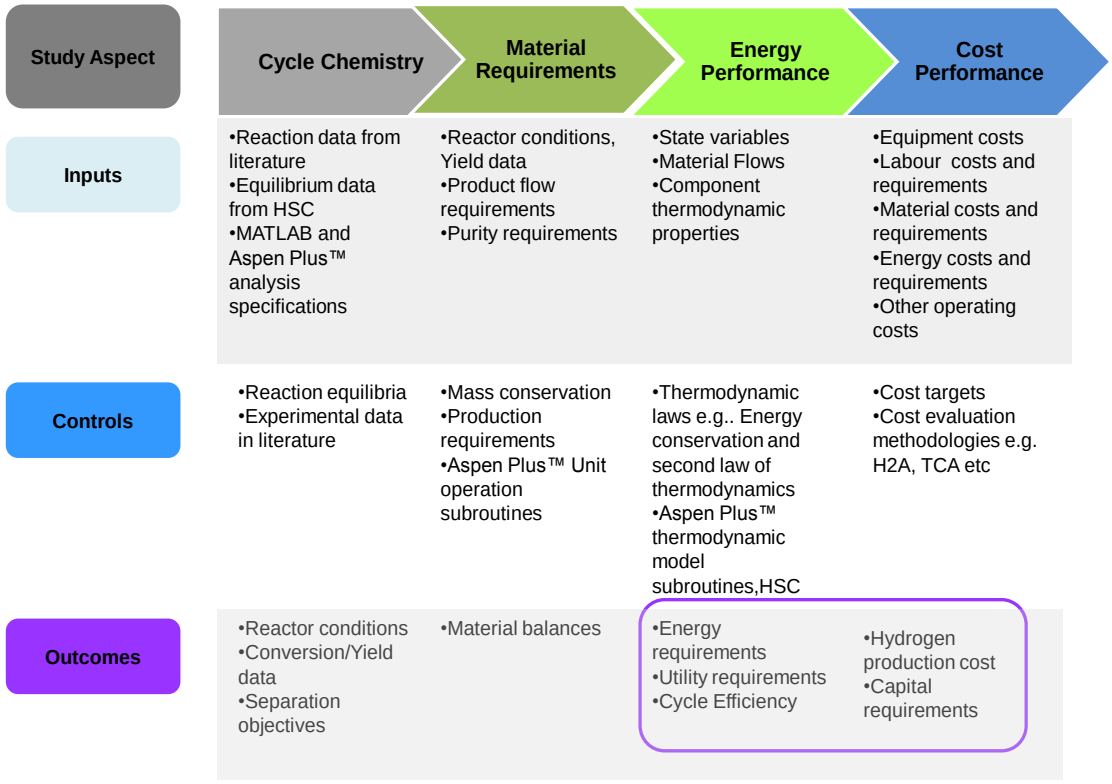

Figure 1.1: Scope of study

Using Aspen Plus™, a flowsheet of the five-reactions copper-chlorine cycle will be developed and analysed according to the framework and scope outlined in Figure 1.1. Intermediate outcomes expected, include optimal reactor conditions and conversion/yield data on individual reactions which will provide guidelines for the development of separation systems. The intermediate outcomes will then enable further development of the flowsheet to obtain material balances, energy requirements and efficiencies, capital requirements and hydrogen production cost estimates. The final outcomes will form the basis of comparison with the other forms of the copper-chlorine cycle.

1.4 Scope of dissertation

- Chapter 1: Introduction
- Chapter 2: *Research approach*

  In Chapter 2 the approach to bridge the problem statement and the presentation of a viable solution is discussed. Chapter 2 covers the conceptual framework of the study, the approach to design aspects of the simulation and the analysis of results.

- *Chapter* 3*: Literature review*

  In Chapter 3 literature is reviewed to get a holistic understanding of the methods of hydrogen production. Comparisons of the most popular thermochemical cycles are done based on publicised information. A discussion of the copper-chlorine cycle is presented along with the simulation work done by other researchers on those cycles is also covered in this chapter.

- *Chapter 4: Simulation selection and design*

  This chapter outlines the approach to different aspects of the simulation design. The chapter covers methods used in pre-simulation preparation and methods used in the design of the simulation.

- *Chapter 5: Energy and Cost analysis*

  In Chapter 5 the simulation results are used to carry out an energy and cost analysis of the three copper-chlorine cycle flowsheets.

- *Chapter 6: Conclusions and recommendations*

  The findings of the study are discussed in this chapter. A review of the comparisons and the findings is discussed and the conclusions are presented.

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CHAPTER 2 : RESEARCH APPROACH

Overview

In Chapter 2 the approach used to bridge the clean hydrogen production problem and a viable possible solution are discussed. Section 2.1 gives an introduction and discusses the research conceptual framework. Section 2.1 also has two sub-sections to allow more detail to be given on design approach in Section 2.1.1 and the approach to analysis in Section 2.1.2. Section 2.2 summarizes the accomplishments of Chapter 2 and Section 2.3 is a reference list.

2.1 Conceptual Framework

According to John Curry (2010), if the engineering method is applied to problem solving, once the problem has been identified and objectives have been clarified, there are three key steps between the problem and the final solution. The three steps are: to generate possible solutions, testing the solutions, and implementing the most viable solution. With respect to a process conceptualisation problem, the steps can be translated to identification of candidate processes, evaluating the processes and presenting the most viable option. In the past, once candidate processes had been identified, the most promising plant would be evaluated using a pilot plant. Though this had an advantage of proving that the process really worked, it was costly and not very flexible with regard to major changes in the process. Nowadays evaluation of candidate processes can be done using process simulators which allow virtually all options to be explored, time permitting. Simulation applies computational models and computing power to the prediction of system behaviour (Oden *et al.*, 2006). Prior to simulation, there is some preparatory work that needs to be done in order to allow smooth flow of work and to ensure that everything is done systematically to reduce oversight (Howat, 1997). If simulation is not approached systematically, the output from the simulation might be misleading or meaningless (Oden *et al.*, 2006).

In this chapter the research approach outlines the systematic approach taken in closing the gap between problem identification and presentation of a viable solution. Since the hydrogen production problem is an open ended problem, the approach taken in this study produces one of many possible and viable solutions.

A framework in general terms can be defined as a structure or the construction of interlinked concepts which support an approach to a specific objective and serves as a flexible guide (WebFinance Inc, 2011). Applied to the current study, the conceptual framework is a skeletal summary of the activities covered in approaching a viable process solution to hydrogen production. Figure 2.1 is a diagrammatic representation of the approach taken in this study. Selection of process examines possible process solutions reported in literature and applies criteria to select a candidate process which will be evaluated using a steady state simulator. The simulation design and selection give detail of the preparatory activities which have to be done prior to simulation. The remaining sections cover the actual simulation, results analysis and the presentation of process findings.

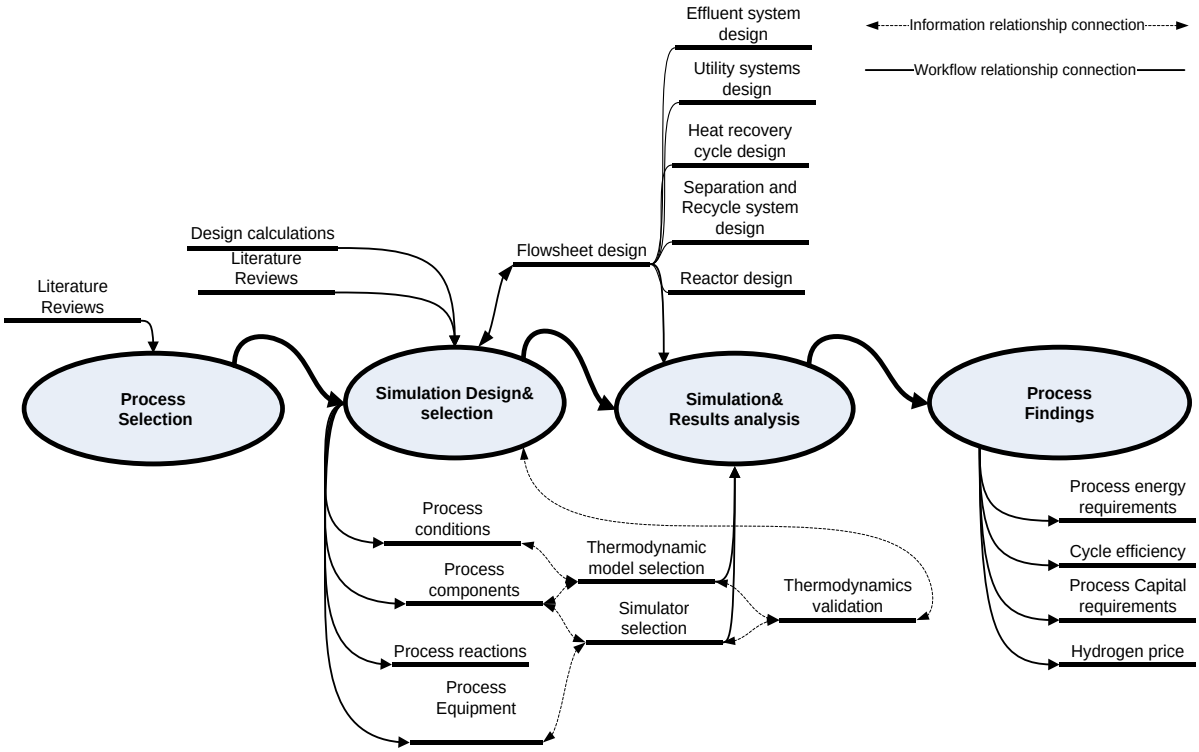

Figure 2.1: Conceptual framework

As shown in Figure 2.1, the conceptual framework, the process selection will be done by review of the literature. The simulation design and selection stage is a combination of literature reviews and some design. In some cases it would be necessary for some lab-work to be done to provide information for the selection and design process but lab-work is out of the scope of the current study. For the reason that the design can be approached in many ways, it is necessary to consider more deeply the design approach to be used. Section 2.1.1 is a discussion of the design approach taken in this study. A brief discussion of the simulation and analysis stage will also be done in Section 2.1.2.

2.1.1 Design approach

Foo *et al.*(2005) defined process design as the systematic creation of a process which is capable of transforming feed to product. The process design principles may be applied in designing a physical process or a virtual process in which case it becomes simulation design. According to Smith (2005) there are two basic approaches to process design, i.e. creating an irreducible structure and creating a superstructure and then optimizing the flowsheet. The irreducible structure approach justifies economically all equipment to be included in the flowsheet before including it. Several methods can be used to develop an irreducible process structure but two methods of note include the Onion model and the Douglas method (Douglas, 1988;Foo *et al.*, 2005) as shown in Figures 2.2 and Figure 2.3, respectively. The superstructure approach includes all possible pathways to form a super-

complex flowsheet and then redundant equipment is eliminated through optimization (Smith, 2005).

Figure 2.2 shows the Onion model approach to process design and shows that process design starts at the reactor and is a multi-layered process which ends with the utility system design (Smith, 2005). The Douglas approach shown in Figure 2.3 is also hierarchical like the Onion approach but has a different design starting point (Emets *et al.*, 2006). The Douglas method starts by a decision of the operation mode of the process and then builds on from there to design the input output-structure, recycle, separation and heat recovery structures.

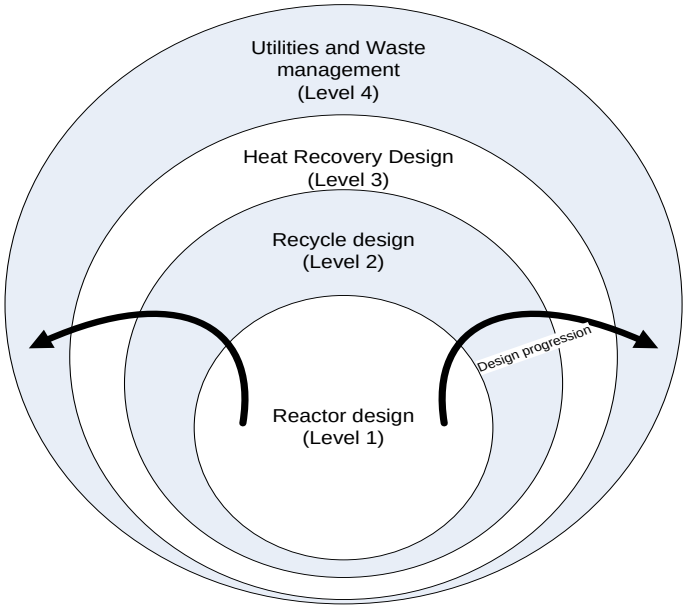

Figure 2.2: Adapted Onion Model of process design

The same methods applied in process design can be applied to simulation design. When applied to simulation design, the Douglas and Onion methods demonstrate the sequential and hierarchical nature of flowsheet design (Foo *et al*., 2005). Applying either method has its strengths and drawbacks. For both methods, fault diagnostics is relatively easy as there is a level by level approach to the design of the process or of the simulation – hence detection of sources of error is made easier(Foo *et al.*, 2005; Smith, 2005). In the case of use of equation oriented simulators, the modular nature of both process design methods allows verification, validation and debugging to be done faster. A layered approach also adds flexibility to the optimization process as it needs not wait for completion of the flowsheet, but can be done for each additional layer added to the flowsheet. One challenge with the Douglas method cited by Emets *et al.*(2006) is the absence of a distinct reactor design stage. The reactor, separation and recycle stages dictate the bulk of the energy

requirements of the system – hence it is important to deal with the design in the early stages of process or simulation design (Emets *et al*., 2006)

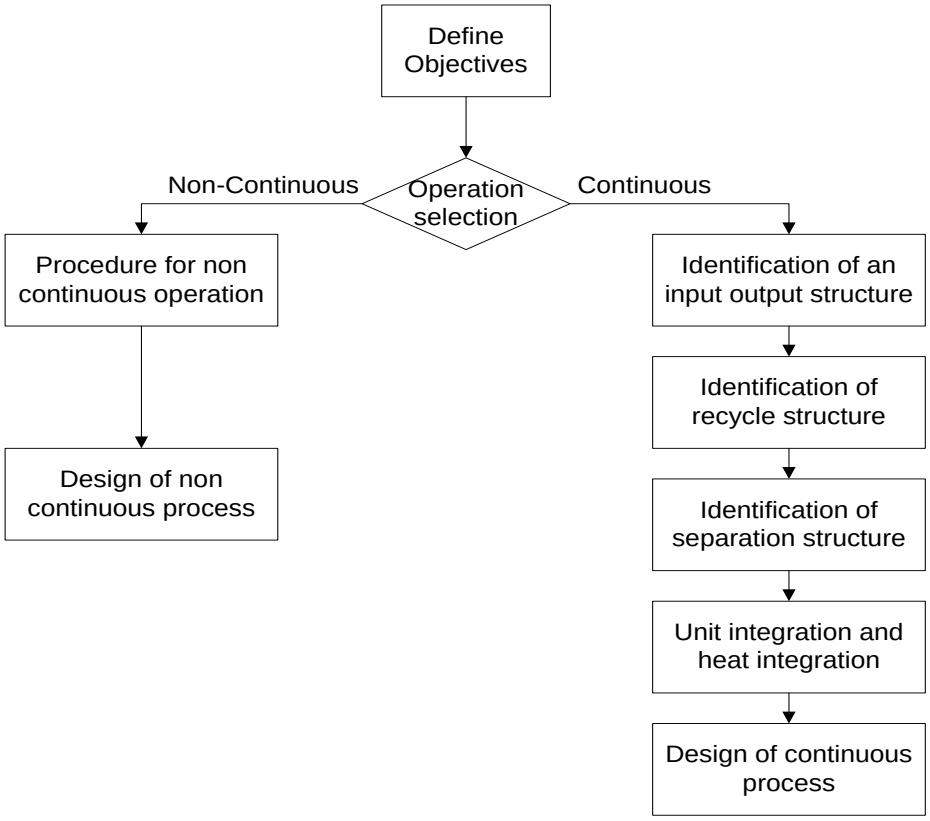

Figure 2.3: Douglas method of process design [Source: Douglas (1988)]

Creating a process using the irreducible structure approach gives more control to the designer. The approach tends to be blindsided in the sense that optimization of early layers tends to be done with an incomplete picture necessitating iterative development. The process of creating an irreducible structure explores alternatives but cannot guarantee finding the best process. Superstructure approach is suitable for design companies which need to develop a high number of flowsheets fast (Smith, 2005).Some of the drawbacks associated with superstructures include the complexity of such flowsheets for advanced processes which makes it more difficult to arrive at the optimal solution. As a consequence of optimization being done via killing redundancies, if the optimal solution is not in the original superstructure, then an optimal solution might not be found.

The thermochemical production of hydrogen using the copper-chlorine cycle to be simulated in the scope of this work is desired to be continuous. After all considerations are made on the different approaches to the process design, the irreducible structure approach with mostly onion logic approach is chosen. A sequence of the adapted approach used for the design of the copper-chlorine flowsheets is shown in Figure 2.4. Key motivators for the

choice were the need or strong control of the flowsheet design, simplicity and the flexibility to allow different design scenarios to be explored easily.

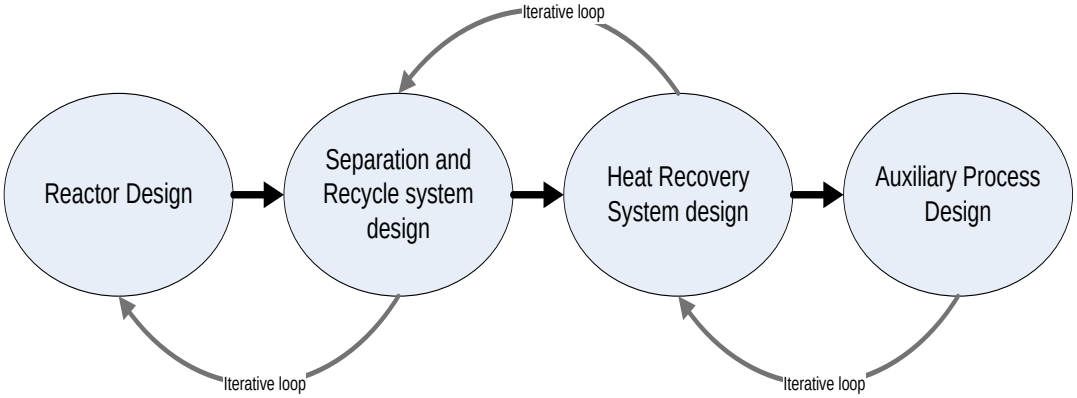

Figure 2.4: Adopted design approach

2.1.2 Simulation and Results analysis approach

After the flowsheets designed in the simulation design and selection stage have been set up in the selected steady state simulator, the simulation will be run and results collected and analysed. Primary results from the simulation will be used to calculate the energy requirements, efficiencies and preliminary economic data. Information obtained, especially preliminary economic data from these calculations, will be analysed for sensitivity to various input parameters and the trends documented. The analysis results will then form a platform on which the process findings will be presented.

2.2 Summary

In this chapter the research approach charts the progression of this simulation study. Thus far, the approach has been left generic which is consistent with the open-ended nature of the study. In Chapter 3 possible solutions to the hydrogen production process problem are reviewed and the conceptual framework, discussed in the preceding sections, applied to it in order to arrive at a viable process solution.

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CHAPTER 3 : LITERATURE REVIEW

Overview

Chapter 3 reviews thermochemical processes from literary sources to select a candidate process. After an introduction in Section 3.1, Section 3.2 discusses the target market. Section 3.3 briefly discusses possible solutions and Section 3.4 is a comparison of the promising process. Section 3.5 discusses the most promising process and previous simulations on it are discussed in Section 3.6 and Section 3.7 summarizes the conclusions drawn from the literature review.

3.1 Introduction

Many countries have been interested in production of hydrogen as an alternative fuel for a number of years. There are a lot of production methods which have been proposed and developed over the years. The production method is, however, strongly influenced by the final consumers of the product, the market. The market requirements influence the levels of purification, the state of the product and these in turn influence the process equipment and other costs (Seider *et al.*, 2004). Process equipment costs and the other costs affect the product price and economic viability of the process. It is therefore necessary to understand the market of the product. Section 3.2 gives a short discussion of the South African market which will serve as a guide to the hydrogen production process selection.

3.2 South Africa's hydrogen market

The bulk of hydrogen produced in South Africa is currently used for industrial purposes such as in iron reduction for the steel industry, production of ammonia for the fertilizer industry, production of hydrogen chloride, production of sorbitol and refining of crude petroleum. Very little hydrogen is being used in transportation and stationary fuel cell applications as fuel cell driven engines are still a novelty. Considerable investment has been made by the South African government towards making hydrogen fuel cell driven vehicles a reality (HySA, 2010). Optimistic projections predict supply of 25% of global fuel cell technologies by year 2020. South Africa also has a target to reduce carbon dioxide emissions by a third within the same period and this would call for production of hydrogen to be constituted of more than 60% non-fossil-based technologies (HySA, 2010).

No explicit information is available on the current demand of hydrogen in South Africa. The main drivers in the local market are value addition to platinum extracted, need for better power supply stability, emission reduction targets and job creation initiatives (HySA, 2010). Frost and Sullivan growth consultants estimate that the South African clean energy industry will grow at an average of 3.75% a year in the next 10-15years (Waal, 2011). Using these figures and information about the national Gross domestic product of South Africa (Statistics Council, 2010) and a country with more explicitly defined hydrogen demands such as the United States (Central Intelligence Agency, 2011), an estimated demand can be derived and used as a working demand capacity. Table 3.1 is a summary of the estimation calculations done to obtain a design basis for the South African case.

Table 3.1: Estimation of South African demand for hydrogen

Gross Domestic Products (GDP)			
Description		*Value*	*Units*
United States of America (USA)		14,500,000,000,000	US$
South Africa (RSA)		527,500,000,000	US$
GDP Ratio		27.49	
Current Demand Estimates			
USA		**RSA**	
Sector	*Demand (tpa)*	*Sector*	*Demand (tpa)*
Agriculture	2,271,000	Agriculture	206 544
Oil	7,444,000	Oil	157 001
Chemicals	952 000	Chemicals	35 955
Total	10,700,000	*Total*	399 500

If an estimate is made based on the ratio of gross domestic product, the projected demand is 399 500tons per annum. For the purpose of the current study, a plant to meet an eighth of the market requirements will be used. This is because it is not practical for a single plant will be able to produce the national demand single handed as such a design basis of 53 914 tons per annum. This capacity is also convenient for process analysis as it is approximately equal to a 1kmol s^{-1} capacity for a plant which runs continuously for 312 days a year.

Different users of hydrogen require the hydrogen at different specifications and this influences the production process used. Typical user specifications include the hydrogen purity, temperature and pressure. The temperatures and pressures tend to be varying with the delivery or storage method to be used and are relatively easily adjustable post production. Purity requirements are more influenced by the production and are harder to adjust post production. Table 3.2 is a summary of the purity requirements of the key industry sectors that consume hydrogen.

Table 3.2: Product purity requirements per user group

User class	**Purity (%)**	**Reference**
Petroleum refinery	99.95	(Kubek *et al.*, 2008)
Fertiliser production	99.95	(Kubek *et al.*, 2008)
Iron reduction	99.9	(Carmo de Lima *et al.*, 2004)
Fuel cells	99.97	(Reijerkerk, 2009)

From Table 3.2 the fuel cell sector has the highest purity requirement. If a hydrogen production facility which is not dedicated to a particular segment of the market is to be

established, it should be capable of producing hydrogen to meet a 99.97% purity requirement. From the quantities required, centralized hydrogen production located close to point of use would be ideal. Some of the candidate processes for the central production of hydrogen for the South African market are discussed in Section 3.3

3.3 Centralized hydrogen production

Centralized hydrogen production has been carried out since the 1960s using different methods ranging from electrolysis, gasification and reforming of hydrocarbons, and novel water splitting methods (Sorensen, 2005). Currently reforming of hydrocarbons is applied on large scale applications (Forsberg, 2007). Reforming of hydrocarbons, however, is associated with the release of carbon dioxide and other gases with global warming potential. The release of greenhouse gases has made reforming less desirable in the recent years as climate change issues have become a major concern globally (Forsberg, 2007). Alternative methods of producing hydrogen are therefore being investigated by researchers.

Alternative hydrogen production methods being sought, are typically those that will result in a lower carbon footprint associated with the production of hydrogen. Some of the alternative hydrogen production methods include water electrolysis, photo-biological water splitting, photovoltaic water splitting and thermochemical water splitting (Sorensen, 2005). Most of the aforementioned technologies are still on lab scale development. Electrolysis of water is a good example of a commercialised method with a low carbon footprint if the source of power is clean (Duigou *et al.*, 2005). Electrolysis has been done using nuclear generated electricity or electricity from renewable sources such as wind, hydro-power and solar which all have low carbon footprints (Duigou *et al.*, 2005). Electrolysis of water, however, has cost sustainability issues brought about by low efficiencies (Funk, 2001:185). Balat (2008:4013) in comparing electrolysis to gasification suggests that gasification has higher efficiency than electrolysis. Considering the overall costs, the higher efficiency of gasification is significant only when the price of electricity is high and so efficiency of the more polluting gasification ceases to be of real economic advantage (Balat, 2008).

The success of adoption of hydrogen as a fossil replacement depends on the price of hydrogen being sustainable and competitive when compared to traditional energy sources such as fossil fuels (Forsberg, 2007). Low efficiencies are associated with higher costs and a high price of hydrogen is a major drawback to the wide acceptance of hydrogen use as a clean energy carrier. The need to find methods of producing hydrogen at sustainable prices has led to restoration of interest in research of various electrochemical and thermal methods of producing hydrogen more efficiently than electrolysis.

3.3.1 Electrochemical water splitting processes

Most electrochemical methods of producing hydrogen from water are built on direct water electrolysis and some of these include alkaline electrolysis and high temperature water electrolysis (Bilgen, 2004). Until early 1980s electrolysis was thought to be the cheapest option of manufacturing hydrogen from water (Shinnar *et al.*, 1981), which is not true when compared to reforming. Electrolysis has challenges associated with it including low efficiencies leading to a high hydrogen cost. High cost among other factors has motivated investigation of alternative means of producing hydrogen in a clean and sustainable way. The use of electrical energy in splitting water is undesirable as the thermal to electric power conversion has to be considered in the determination of the overall efficiency of the process (Funk, 2001). On average conversion efficiency is 30% which would make the overall process efficiency 24% for a process which has cell efficiencies of around 80% (Funk, 2001:185). The main challenge with electrolyzing water directly is the high overpotential requirement (Suffredini *et al.*, 2000). The biggest overpotential would be the reaction overpotential in a properly designed electrolytic cell (Suffredini *et al.*, 2000). High overpotential requirements are due to the low self-polarization capability of pure water (Sorensen, 2005). Use of alkaline electrolysis and high temperature electrolysis has been seen to improve the efficiency characteristics of the electrochemical processes but still has much room for development (Ganley, 2009).

From an economic viewpoint it would be desirable to find better performing processes by which water splitting can be done. Processes being investigated so far have been biased towards thermal systems whose efficiency ratings are not lowered by conversion to electricity losses (Funk, 2001).

3.3.2 Thermochemical water splitting

In the same way that water splitting can be done using a completely electrical process which requires high electrical work, thermal energy can be used to achieve the water splitting using decomposition. The simplest thermochemical water splitting method is to decompose water directly by the following reaction (Funk, 2001):

$$H_2O(g) \leftrightarrow H_2(g) + \frac{1}{2}O_2(g) \qquad (3.1)$$

Data for the reaction show that ΔH=285.76kJ mol^{-1}, ΔG=237.24kJ mol^{-1} and ΔS=1.6kJ mol^{-1} K^{-1}.

The Gibbs energy (ΔG) for this reaction only zeroes out at a temperature of 4 700K (Funk, 2001:185). High temperatures result in materials of construction selection challenges in the

design of the plant. Pursuit of a process with high temperatures would result in a high capital production facility which will result in high final product cost which is undesirable. To reduce the high thermodynamic work requirement, the equilibrium of the water splitting reaction has to be improved. This can be done in several ways including use of multiple reactions whose overall work requirement is equal to the requirement for the water splitting reaction (Funk, 2001:185). A generalized expression of such a reaction arrangement would be as given in Reactions 3.2-3.4

$$\text{r1:} \qquad H_2O + X \rightarrow H_2 + XO \tag{3.2}$$

$$\text{rn:} \qquad XO \rightarrow X + \frac{1}{2}O_2 \tag{3.3}$$

$$\text{net reaction:} \quad H_2O \rightarrow H_2 + \frac{1}{2}O_2 \tag{3.4}$$

The total work requirement in such a case is the summation of the individual reaction work (Funk, 2001) requirements, which can be expressed as,

$$\Delta G_{Ov} = \sum_{i=1}^{i=n} \Delta G_{ri} \tag{3.5}$$

where subscript ri is indicative of the reaction number e.g. r1, r2…rn

If reactions can be found that have the net reaction being equivalent to the water splitting reaction without requiring the same stringent conditions of the water decomposition reaction, accomplishing a higher overall efficiency than direct electrolysis of water, then the chance of commercialization of hydrogen as an energy carrier for common uses becomes higher. Some of the processes that are considered as key candidate thermochemical processes to achieve water splitting are listed in Section 3.4, in the comparison of thermochemical cycles.

3.4 Comparison of thermochemical cycles

Thermochemical water splitting cycles are ideally sets of reactions that split water into hydrogen and water, with the intermediate reactions being able to sustain themselves without further raw material input (Funk, 2001).To enable comparison of thermochemical cycles, a performance criterion has to be developed which will create an equal platform upon which performance of the cycle can be measured. There are a number of articles reviewed with respect to the criteria for comparison of thermochemical cycles but the most notable being Brown *et al.* (2000), (Lewis and Masin, 2009) and Bagajewicz *et al.* (2009). Conceding the differences in semantics the general consensus is that for comparison the key factors to consider are:

i. Cost: capital, raw materials, output product cost, etc.
ii. Chemical viability: the chemical viability of a cycle is assessed by the number of reactions, availability and abundance of chemicals, number of competing reactions, severity of conditions (Lewis and Masin, 2009).
iii. Engineering feasibility: This is seen by the existence of a complete flowsheet which is demonstrable, materials of construction, heat transfer, energy utilization, availability of thermodynamic data (Lewis and Masin, 2009).
iv. Safety, health and environmental factors: where some of the considerations include the toxicity of materials, controllability of process in event of accident (Brown *et al.*, 2000)

On application of these criteria to the hundreds of cycles, the following were considered to have the most potential for development to commercialization by different research groups around the world (Bagajewicz *et al.*, 2009):

- Hybrid copper-chlorine
- Westinghouse (Hybrid sulphur)
- Hybrid copper oxide-copper sulphate cycle
- Sulphur Iodine
- Hallet Air Products (Hybrid Chlorine)
- Gaz de France (Potassium cycle)
- Ispra Mark 13 (Sulfur bromide)
- Julich (Iron chloride – sulphate)
- UT-3 Tokyo (Hybrid calcium bromide)
- Ispra Mark 9 (Iron chloride)

For the purpose of this research a comparison of the first five cycles was done to yield the results summarized in Table 3.3.

Table 3.3: Thermochemical cycle comparison

Parameter	HyS	S-I	Hybrid Cl	CuO-CuSO4	Cu-Cl
COST:					
Capital($millions)	400	660	800	360	370
Product($/kg)	1.60	1.90	3.00	2.50	1.90
ENERGY REQUIREMENTS:					
Input(kJ/mol)	685	674.9	776.9	668	554.7
Efficiency (%)	36.6	52	36	52.4	52
Peak T(°C):	870	850	850	850	550

The numerical data in Table 3.3 was drawn from several sources and capacity normalised to 2010 dollars to enable the comparison to be done on a uniform basis. The hybrid sulphur data is reported by Gorensek and Summers(2009) , the Copper-chlorine data by Wang *et al.*(2009), Hybrid chlorine by Gooding (2009), Hybrid Copper oxide-copper sulphate by Gonzales *et al.* (2009) and sulphur iodine extracted from Wang *et al.* (2009)

The results in Table 3.3 indicate that the prices of hydrogen produced from the sulphur iodine, hybrid sulphur and hybrid copper-chlorine cycles are theoretically relatively closely comparable. The peak temperatures, energy input and capital requirements of the sulphur iodine and hybrid sulphur cycles are, however, higher than that of the hybrid copper-chlorine cycle. These results suggest that the hybrid chlorine cycle is an excellent candidate for study with the intention to commercialize. The efficiency of the cycle is also sufficiently high with opportunity for further development (Lewis *et al.*, 2009). The rest of this report study focuses more on the hybrid copper-chlorine cycle as a result of these findings.

3.5 The hybrid Copper-chlorine cycle

The literature reviewed for this hybrid thermochemical cycle mostly originated from the USA and Canada, with the most publications coming from Canadian institutions. Notable publishing institutions on this cycle include the University Of Ontario Institute Of Technology, Argonne National Laboratory, and other partner institutions. Authors Lewis *et al. (2009a)*, Rosen M. A *et al.* (2008), Naterer *et al.* (2009) and Wang *et al.* (2009) seem to be in agreement that the most attractive attribute of this cycle is the low peak temperature which makes the cycle very versatile in terms of the heat source that can be applied to energise the water splitting process. With recent developments in the Canadian research field it is

also emerging that the kinetics and yields of the Cu-Cl cycle are much more favourable in comparison with most other cycles (Naterer *et al.*, 2009).

The copper-chlorine thermochemical cycle consists of intermediate reactions which utilise compounds of copper and chlorine to facilitate the breakdown of water into hydrogen and oxygen. There are a number of different copper-chlorine cycles in existence, differentiated by the number of intermediate reactions utilised to achieve the breakdown of water to produce hydrogen and oxygen (Lewis *et al.*, 2009;Wang *et al.*, 2009). There are three main groups of cycles as grouped by the number of steps and these are the three, four and five-step cycles.

There are basically two pathways by which hydrogen can be produced by Cu-Cl cycle, the first being chlorination of elemental Cu and the second being the chlorination of CuCl (Law *et al.*, 2008). The first is the pathway used in the four and five-step cycles and the latter is seen in the three-step version (Wang *et al.*, 2009) A summary of the reactions summarising the three versions of the Cu-Cl cycle that are most reported in literature is:

Three-step cycle:

$$2CuCl_{(s)}+2HCl_{(aq)}\rightarrow 2CuCl_{2(aq)}+H_{2(g)} \quad (3.6)$$

$$2CuCl_{2(aq)}+H_2O_{(g)}\leftrightarrow Cu_2OCl_{2(aq)}+2HCl_{(aq)} \quad (3.7)$$

$$Cu_2OCl_{2(aq)}\rightarrow 2CuCl_{(s)}+\frac{1}{2}O_{2(g)} \quad (3.8)$$

Four-step cycle:

$$4CuCl_{(s)}\rightarrow 2CuCl_{2(aq)}+2Cu_{(s)} \quad (3.9)$$

$$2Cu_{(s)}+2HCl_{(aq)}\rightarrow 2CuCl_{(l)}+H_{2(g)} \quad (3.10)$$

$$2CuCl_{2(aq)}+H_2O_{(g)}\leftrightarrow Cu_2OCl_{2(aq)}+2HCl_{(aq)} \quad (3.11)$$

$$Cu_2OCl_{2(aq)}\rightarrow 2CuCl_{(s)}+\frac{1}{2}O_{2(g)} \quad (3.12)$$

Five-step cycle:

$$2Cu_{(s)}+2HCl_{(aq)}\rightarrow 2CuCl_{(l)}+H_{2(g)} \quad (3.13)$$

$$4CuCl_{(s)}\rightarrow 2CuCl_{2(aq)}+2Cu_{(s)} \quad (3.14)$$

$$CuCl_{2(aq)}+n_fH_2O_{(g)}\leftrightarrow Cu_2Cl_{2(aq)}\cdot n_hH_2O_{(s)}+(n_f-n_h)H_2O_{(g)} \quad (3.15)$$

$$2Cu_2Cl_{2(aq)}\cdot n_hH_2O_{(s)}+H_2O_{(g)}\leftrightarrow Cu_2OCl_{2(aq)}+2HCl_{(aq)}+n_hH_2O_{(g)} \quad (3.16)$$

$$Cu_2OCl_{2(aq)}\rightarrow 2CuCl_{(s)}+\frac{1}{2}O_{2(g)} \quad (3.17)$$

All these reactions have complete proof of reaction concept work done and confirmed in the recent past (Lewis and Masin, 2009). More detail of the different forms of the copper-chlorine cycle are done in Sections 3.5.1-3.5.3.

3.5.1 The five-step copper-chlorine cycle

The four and five-step cycles are two very similar cycles. The five-step cycle consists of copper chlorination (hydrogen production), disproportionation (electrolytic), drying, hydrolysis and decomposition (oxygen production step). These intermediate reaction steps interact as illustrated in Figure 3.1:

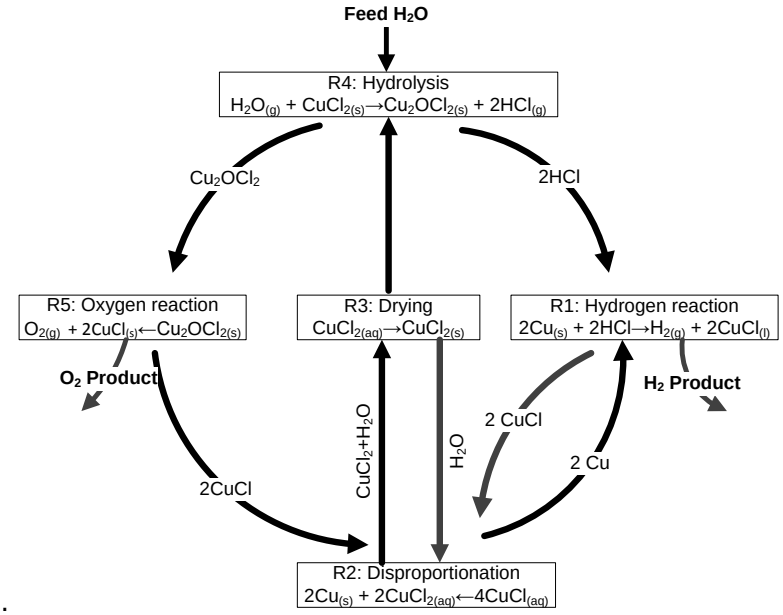

Figure 3.1: The five-step copper-chlorine cycle [Adapted from(Orhan *et al.*, 2010)]

As shown in Figure 3.1 almost all five reaction steps need to have heat supplied at different grades but the peak heat grade is relatively low at 530°C (Wang *et al.*, 2009) compared to 850°C for the sulphur-based cycles. The electrolytic disproportionation step occurs at ambient temperatures and only requires supply of electrical energy to facilitate the disproportionation step. A short discussion of individual reaction steps will be done.

Step 1: Hydrogen production

$$Cu_{(s)} + 2HCl_{(g)} \rightarrow H_{2(g)} + 2CuCl_{(l)} \text{ at } 450°C \qquad (3.13)$$

The hydrogen production step is an exothermic reaction where hydrogen chloride gas reacts with copper metal to produce cuprous chloride. The reactions happen spontaneously at temperatures higher than 300°C (Chukwu, 2008). For ease of transportation between stages, the cuprous chloride is preferred to be in molten state and so the temperature used should exceed 430°C, which is the melting point of cuprous chloride (Serban *et al.*, 2004). As a result heat is supplied to the step. The reaction generally proceeds to completion if

small copper particles of size less than 3µm are used and the activation energy is 63kJ mol^{-1}, which is low enough to initiate with no catalysis (Serban *et al.*, 2004:3).

Step 2: Disproportionation

$$4CuCl_{(aq)} \rightarrow Cu_{(s)} + CuCl_{2(aq)} \text{ at } 30\text{-}80°C \quad (3.14)$$

The disproportionation reaction occurs when cuprous chloride is dissolved in hydrochloric acid and a potential difference applied across the solution. In the reaction copper is deposited on the cathode and copper (II) chloride remains in solution mixed with hydrochloric acid. The reaction occurs at ambient conditions. From experimental work done at Argonne National Laboratory, the potential difference required is between 0.4V and 0.6V per cell (Lewis *et al.*, 2009b). In practice there is industrial expertise available to make disproportionation a reality, such as is outlined in US Patent 3,692,647 (Chambers and Chambers, 1972).

Step 3: Drying

Drying converts aqueous copper (II) chloride from disproportionation to solid copper (II) chloride. There are many methods that can be used to effect drying, some of which include spray drying, crystallisation combined with evaporative drying or with spray drying. The method used for drying determines whether solid copper (II) chloride is anhydrous or hydrated. According to Wang *et al. (2009)* crystallisation allows for lower grade and quantity of heat to be used for the drying step.

Step 4: Hydrolysis

$$H_2O_{(g)} + CuCl_{2(s)} \rightarrow Cu_2OCl_{2(s)} + 2HCl_{(g)} \text{ at } 375°C \quad (3.16)$$

Hydrolysis is the step where copper (II) chloride reacts with steam to form copper (II) oxy-chloride. According to most literature reviewed, the hydrolysis step is the most challenging reaction of the copper-chlorine cycle reactions. The reaction is plagued by side reactions which result in the formation of cuprous chloride and chlorine instead of copper oxychloride by thermolysis. Lewis *et al.* (2009) report that this reaction becomes significant at temperatures in excess of 390°C with cuprous chloride approaching 5wt% of products. As this reaction is a solid fluid reaction, the contact area between reactants is critical to conversion; hence size of feed copper (II) chloride is very important. The amount of steam used in the reaction also influences the extent of reaction with copper to steam ratios above 14 producing better than 90% conversion (Ferrandon *et al.*, 2010).

Step 5: Decomposition (Oxygen production reaction)

$$Cu_2OCl_{2(s)} \rightarrow 0.5O_{2\,(g)} + 2CuCl_{(s)} \text{ at } 530°C \qquad (3.17)$$

Decomposition of copper oxy-chloride to form oxygen and cuprous chloride has the highest heat grade requirement with an operating temperature of 530°C. Carryover of copper (II) chloride could result in the production of chlorine gas which can damage equipment (Wang *et al.*, 2009). The activation energy of the reaction is relatively low at 50kJ mol^{-1}, allowing the reaction to proceed without catalysis (Serban *et al.*, 2004). Heat can be recovered from the molten cuprous chloride as it will be used in a reaction that requires it to be much lower than 530°C.

3.5.2 The four-step cycle

This cycle is almost the same as the five-cycle step with the exception of the drying step which is absent in the four-step cycle. Figure 3.2 illustrates the four-step copper-chlorine cycle

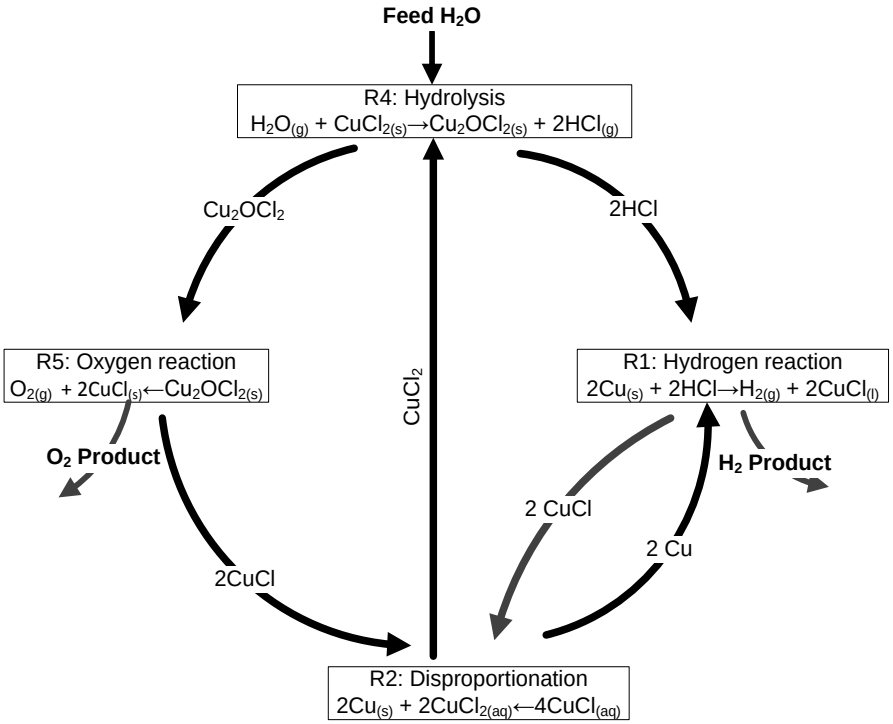

Figure 3.2:The four-step copper-chlorine cycle

As Figure 3.2 shows, the four-step cycle is almost the same as the five-step cycle but utilizes aqueous copper (II) chloride rather than using solid copper (II) chloride. Figure 3.3 is an illustration of a process flow diagram of the five-step cycle and shows the resemblance between it and the four-step cycle. Some researchers suggest that the four-step cycle is a

more efficient cycle (Chukwu, 2008), whereas Wang *et al.* (2009)suggest that the five-step version is better. In equipment terms, the four-step cycle requires less than the five-step cycle and this should result in lower capital requirements.

Wang *et al.*(2009), in a comparison of the Cu-Cl cycle and the S-I cycle, gave the estimated cost of Cu-Cl produced hydrogen to be $1.60-$2.25/kg of hydrogen at output. This hydrogen price calculation was done, based on capital requirements obtained by the eight times basic equipment cost rule for capital estimation (Law *et al.*, 2008)

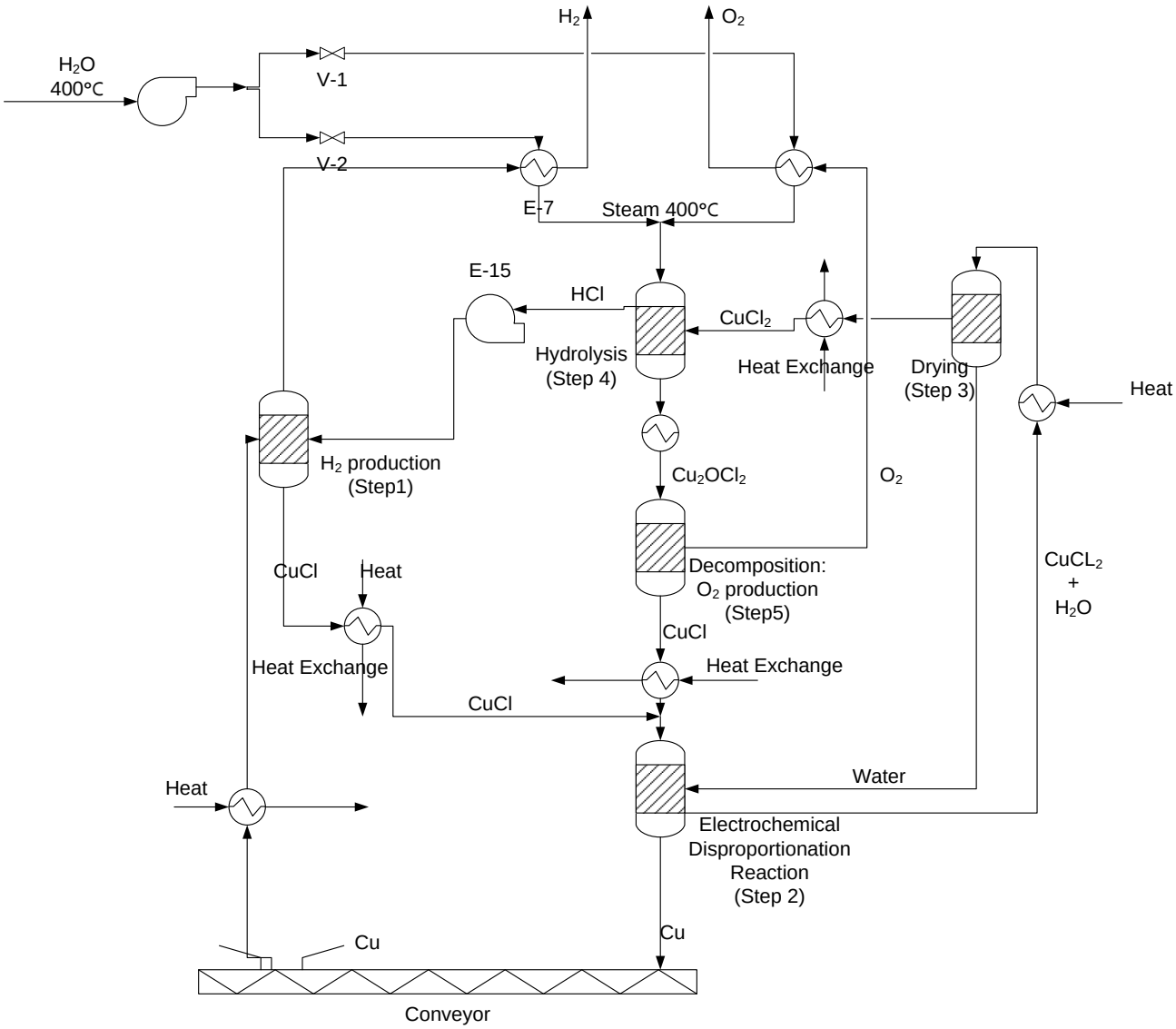

Figure 3.3: Hybrid copper-chlorine (five-step) process flow diagram (Orhan *et al*., 2010a)

3.5.3 Three-step cycle

The three-step copper-chlorine is different compared to the four and five-step cycles. The major difference is that hydrogen is produced in the electrolytic step as compared to the four

and five-step cycles which produce hydrogen in thermal reactions (Wang *et al.*, 2009). The hydrogen step in the three-step cycle is equivalent to a combination of step 1, 2 and 3 in the five-step cycle (Wang *et al.*, 2009).

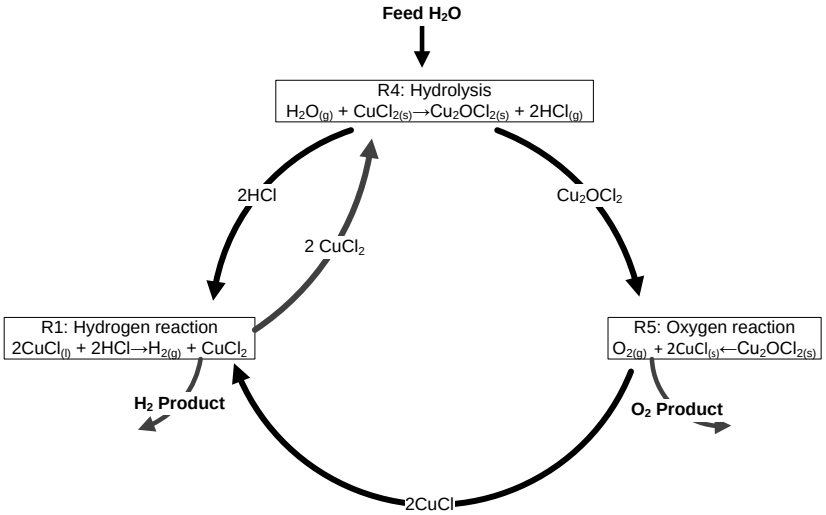

Figure 3.4: Three-step copper-chlorine cycle

According to Lewis the reaction happens under high pressure of 24 bar as compared to the reactions in the four and five-step which require atmospheric pressure. The hydrolysis and decomposition steps are also reported by Law(2008) and Lewis (2009) to require slightly higher temperatures, requiring 400 and 540°C as compared to 375 and 530°C for the four and five-step cycles. Due to less equipment required, the cycle could have lower capital costs than the four and five-steps cycles.

3.6 Previous simulations of the Cu-Cl thermochemical cycle

The Cu-Cl cycle has been simulated in Aspen Plus™ by three main workers Michelle A. Lewis, Cletus Chukwu and Victor Law. Their reports of the simulation work show that Lewis's (2009) and Law's(2008) simulations were of the three-step Cu-Cl cycle, Cletus Chukwu (2008) simulated the four-step cycle. There is no indication in the literature reviewed so far that indicates any complete Aspen Plus™ simulations of the five-step cycle. The lack of complete simulations may be due to the complications of handling solids used in the five-step cycle. Rosen (2008) and Wang *et al.* (2009) in their comparison of different Cu-Cl cycles are biased to the five-step cycle being the best option from a practical standpoint as the engineering complications increase with the reduction of steps.

Of the reported Aspen Plus™ simulations of the Cu-Cl cycle, the areas of focus were:

i. Victor Law (2008)

Simulation of the three-step Cu-Cl cycle in three stages:

a. Stage 1: Use stoichiometric reactors allowing the reactions to go to completion.
b. Stage 2: Using some of the results from stage 1, use an equilibrium reactor for the hydrolysis step.
c. Stage 3: Optimise the flowsheet, using a user customised model with FORTRAN code of the electrolyser model and simulate.

The results of the simulation work are not reported in the progress report as the work was still on-going. The focus on customising and improving the accuracy of results of the electrolyser model is emphasised in this report.

ii. Lewis *et al.* (2009)

Summarized report of the work published in the International Journal of Hydrogen Energy. The setup of the Aspen simulation shows that the major focus was to enhance and cross-check the accuracy of the data and models used in the simulations and as such is thorough about the work done in updating the thermodynamic database. In terms of the flowsheet setup used, simple reactor models were used for the electrolyser with specification of inlet and outlet conditions of streams being done. The results of this simulation effort are yet to be published.

iii. Cletus Chukwu (2008)

This report is of a simple simulation of the Cu-Cl three and four-step cycles using stoichiometric reactor models, all reaction steps and experimental data generated by Argonne National Laboratory. The results of the simulation are available in this report and the main focus seems to be on optimising the energy consumption and yields and to predict the cycle thermal efficiencies.

3.7 Summary

From the findings of the literature study carried out, it is apparent that the copper-chlorine hybrid thermochemical cycle is a high potential candidate. The copper-chlorine cycle is attractive because of its low peak temperature and versatility with heat sources due to its ability to utilize low grade waste heat to produce hydrogen (Law *et al.*, 2008;Lewis and Masin, 2009;Wang *et al.*, 2010). Specific opportunities could lie in the optimization study of the five-step Cu-Cl cycle as little simulation work is reported in literature. The results of these simulation studies can then be referenced or compared to the more simulated four and

three-step cycles to determine the best configuration. According to Naterer *et al.* (2008) the internal re-utilization of energy will go a great way in developing the levels of thermal efficiency achievable by a cycle. Studying and optimizing the energy and capital requirements of the five-step cycle through simulation should be a good research starting point. The results of the energy and capital requirements can then be used to compare with the other forms of the copper-chlorine cycle to identify the best form of the cycle. Once the best form of the copper-chlorine cycle has been identified, efforts can be focused on developing the performance of that form.

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CHAPTER 4 : SIMULATION DESIGN AND SELECTION

Overview

In Chapter 4 the simulations used to evaluate the different configurations of the cycle are developed. Sections 4.1-4.3 cover the selection of the steady state process simulator, selection of thermodynamic model and the validation of the chosen thermodynamic model. Sections 4.4- 4.6 discuss different aspects of the design of the core flowsheet. Section 4.7 unifies design of the flowsheets subsections. Section 4.8 discusses the final Aspen Plus™ flowsheets used in this study and Section 4.9 summarizes the chapter.

4.1 Simulation software selection

Computers have increasingly been used to perform design calculations and process analysis procedures due to the speed and quantity of information they can process. With the evolution of design method from hand to computer aided, has arisen an evolution in the software used in the design and process analysis. From the late fifties there has been a shift from expensive software that requires computer specialists to more user-friendly software. Despite changes in software, the basic simulation process has not changed. Early simulation systems required the user to enter not only input conditions but also unit operation programs for all operation blocks and this left a lot of room for errors and slowed down the conceptualization process (Crowe *et al.*, 1971). The usefulness of simulation results depend on how accurately the simulated process is modelled and how well the simulation software can handle complex block interactions which result from recycle streams and complex equipment such as distillation columns. In order to handle complex systems, simulation software must have flexible input submission interface with input error control, a robust calculation execution capacity and capacity for easy retrieval of results without unreasonable demands on computing hardware (Franks, 1972).

The requirements and expectations of designers from simulation software have changed as computing power has become cheaper and thermodynamic data has become more readily available. The modern day simulation software is no longer just expected to provide results but more expectations are in line with how the process model is developed and inbuilt properties such as property databases and result analysis tools (Sundaran, 2005). A detailed comparison of some of the popular advanced process simulators available is tabulated in Table 4.1. For the current work additional considerations were made on top of the functional considerations in Table 4.1. The additional considerations used in the selection of simulation software include:

- Software availability.
- Licensing requirements and cost.
- User friendliness of Interface.
- Depth and accuracy of unit operation calculation models.
- Availability of component data.
- Technical support functionally available within reasonable communication cost.

Table 4.1: Software comparison of advanced process simulators available commercially [Adapted:(Win Sim Inc, 2011)]

Features		Design II for Windows™	HYSYS®	Pro/II	ProMax ®	Aspen Plus ™	Chem CAD
General	1-Click data Export to Microsoft Excel	☺	☺	☺	☺	☺	☺
	Component Library	☺	☺	☺	☺	☺	☺
	Thermodynamic options	☺	☺	☺	☺	☺	☺
	Recycle convergence	☺	☺	☺	☺	☺	☺
	Gas Processing	☺	☺	☺	☺	☺	☺
	Batch simulation		+	☺		+	+
	Dynamic simulation		+	☺		+	+
	Heat Exchanger rating	☺	+	☺	☺	+	+
	Strong Electrolytes		+	☺		+	☺
	Pipeline networks		+	☺		+	+
	Mixed Amines	☺	+	☺	☺	+	
	Claus process	☺	+	☺	☺	+	+
Unit Modules	Rigorous distillation columns	☺	☺	☺	☺	☺	☺
	Batch distillation column	☺	+	☺	☺	☺	☺
	Pipeline	☺	☺	☺	☺	☺	☺
	Heat Exchangers	☺	☺	☺	☺	☺	☺
	Flash	☺	☺	☺	☺	☺	☺
	Reactors	☺	☺	☺	☺	☺	☺
	Pumps and compressors	☺	☺	☺	☺	☺	
	Storage tanks			+		+	+
Interface	Windows based GUI	☺	☺	☺	☺	☺	☺
	Text based UI	☺					
Training	Onsite	☺	☺	☺	☺	☺	☺
	Offsite	☺	☺	☺	☺	☺	☺
	Seminar	☺	☺	☺	☺	☺	☺
Support and Upgrades	Usage support	☺	☺	☺	☺	☺	☺
	Expert process support	☺	☺	☺	☺	☺	☺
	Support by phone	☺	☺	☺	☺	☺	☺
	Support by E-mail	☺	☺	☺	☺	☺	☺

In Table 4.1 the (+) shows optional features and ☺ shows standard features. Table 4.1 shows that there are many possible and properly equipped simulators on the market. From the functional comparisons alone, it is difficult to objectively select software that can be said to be the best; hence the need for the additional considerations. After considering the additional factors Aspen Plus™ was selected by the author from the possible software which included HYSYS®, Pro/II ®, ChemCAD™ and DESIGN II™. Key motivators for the selection were the availability of a current license for the software and the relatively short time required to learn the software.

Aspen Plus™ is being used widely in the Chemical process industry with many international companies having adopted it. Due to the wide range of users, Aspen Technology Inc. has included many inbuilt unit operation models which are sufficient to cover the diverse processes of its users, yet leaving room for customized models called user models (Aspen Technology, 2009). Aspen Technology's experience in supporting a broad spectrum of users has helped the Aspen software to evolve into robust software which can be applied to the simulation of diverse processes (Sinnot, 2005). Close interaction with users has also ensured that the inbuilt models in Aspen Plus™ software has a closer representation of unit operations modelled in chemical process industries. Over time, Aspen property databases have also grown to accommodate diverse users (Aspen Technology, 2009). Having inbuilt properties helps provide some level of consistence in simulation as automated manipulation and retrieval of properties tend to reduce the errors of entry.

Aspen Plus™ offers two simulation approaches which allow the user to manipulate a simulation differently depending on the desired objectives. Typical user objectives in choosing a particular approach may include speeding up the simulation convergence or increasing the level of simulation sequence customization. The simulation approaches are the sequential modular approach and equation oriented approach(Aspen Technology, 2009). Sequential modular flowsheets solve the blocks individually according to a particular sequence. Equation oriented simulations solve block equations simultaneously, thus a good starting point is necessary for use of equation oriented simulation. Sequential modular modelling is used especially when simulating a large number of blocks, and equation oriented simulation is more useful where precise solutions are required (Aspen Technology, 2009). A combination of the two approaches can be used in simulation. When combining the approaches, sequential modular simulation is used to obtain an initial solution and then equation oriented approach is used to optimize the solution.

Aspen Plus™ has many analytical capabilities which enable the user to analyse the model. Some of these analysis tools include sensitivity analysis, optimization and constraint analysis

and regression tools. The sensitivity analysis tool allows the user to carry out parametric studies of the model to understand the influence of particular variables on the cycle (Aspen Technology, 2009). An example sensitivity analysis could be the study of the flow rate of a particular stream on the conversion of either the whole process or just one reactor. Optimization and constraint analysis tools allow one to maximize or minimize certain functions representing aspects of the simulated process while taking into consideration bottlenecks in the cycle (Aspen Technology, 2009). The regression tool allows analysis of results to see trends in the data and fit relationships, etc. (Aspen Technology, 2009). Having such a set of tools inbuilt in the software ensures that a process being simulated can be better understood and made to operate at the best conditions. These tools also make it possible to minimize the capital and operational costs associated with the development and testing of processes.

4.2 Selection of thermodynamic model

The selection of thermodynamic properties for design calculations is a very important exercise which needs to be handled with care. It is important to select thermodynamic properties which enable the accurate description of the system which is being modelled. In chemical engineering design it is common to use property models in the estimation of properties used in design. Selection of inappropriate property methods results in wrong properties which will result in wrong specifications of plant equipment and operating conditions (Aspen Technology, 2009). Wrong specifications of equipment and operating conditions have cost and safety impacts on the designed plant which can cost money and lives. To avoid loss of money and lives, thermodynamic property models used in design should befit the systems in being used in design. Several property models have been developed over time but can generally be grouped into activity coefficient models and equation of state models.

Physical property methods used in Aspen Plus™ for simulation calculations are either based on a property model or on a grouping of these property models (Aspen Technology, 2009). Simple methods, for instance, use the ideal models and more advanced methods can be a combination of equation of state and activity coefficient models. In a combined property method the vapour phase calculations can be done using an equation of state model, and the liquid phase done using an activity coefficient method. As a primer, the equation of state and activity coefficient models shall be discussed in more detail in Sections 4.2.1 and 4.2.2.

4.2.1 Equation of state methods

An equation of state method is an equation that relates the pressure, volume and temperature of pure components and mixtures in estimation of properties. An equation of state is usually written explicitly in terms of pressure. The simplest equation of state is the ideal gas equation. Most equations of state have different terms to represent interactive forces between molecules which can be repulsion or attraction. Most thermodynamic properties, such as fugacity coefficients or enthalpies, can be calculated from equations of state (Smith *et al.*, 2001). Equations of state properties are often calculated with ideal gas properties of the same mixture at the same conditions as a reference. Equations of state have an important role in chemical engineering design and the study of phase equilibria of fluids and fluid mixtures. Equations of state are suitable for vapour mixtures and mixtures of non-polar and slightly polar compounds (Aspen Technology, 2009). They can be used for the calculation of phase equilibria in non-polar mixtures with a reasonable accuracy. Some of the advantages of equations of state include their applicability to wide ranges of temperature and pressure, for mixtures of diverse components. For liquid calculations equation of state models use few binary parameters; hence are limited to liquids with high ideality. Parameters used in equations of state can be extrapolated reasonably with temperature, and property calculations are reasonably consistent at near critical conditions.

Many equations of state have been developed (Soave, 1972;Peng and Robinson, 1976) empirically or theoretically based. Examples are the Van der Waals equation of state which is useful in prediction of vapour–liquid co-existence behaviour. The frequently used Redlich-Kwong equation of state (Soave, 1972) is an improvement of the Van der Waals equation. By including temperature dependence for the attraction term the accuracy of the equation was improved. Peng and Robinson (Peng, 1976) further modified the Redlich-Kwong equation to predict more accurately the vapour pressure, liquid density, and equilibria ratios.

4.2.2 Activity coefficient property methods

Chemical species in the vicinity of each other such as in solutions always display some sort of interaction (Smith, 2001). As mixtures with similarly sized molecules and nature tend to have less intermolecular interactions this scenario justifies idealization. Idealization can also exist between polar molecules if the interactions cancel each other. Generally there are non-ideal interactions in mixtures with dissimilar molecular species. Dissimilarities include size, shape and nature of intermolecular interactions between components (Smith, 2001). The activity coefficient of a mixture γ_i is a thermodynamic factor used to include deviations from ideal behaviour in the calculation of chemical mixture properties. In an ideal mixture the interactions between each pair of chemical species are the same and the enthalpy of mixing

is zero. Assuming ideality the properties of the mixtures can be expressed in terms of concentrations or partial pressures of the substances in the form of ideal mixture laws such as Raoult's law. Deviations from idealization are accommodated by representing concentrations as activities which represent the effective concentration of the species involved. An activity coefficient can then be calculated from the activities (Aspentech, 2009). The vapour and liquid fugacity can be calculated as:

$$f_i^v = y_i \gamma_i f_i^{*v} \quad (4.1)$$

$$f_i^l = x_i \gamma_i f_i^{*l}) \quad (4.2)$$

When γ_i is not equal to one, non-ideal behaviour will be shown by the mixture. In most chemical mixtures, γ_i is greater than one. Fugacity of a substance can be interpreted as the measure of the substance's tendency to vaporize. If a compound vaporizes more than an ideal solution the average inter-molecular separation is increased. Activity coefficients greater than one indicate a higher level of repulsion between dissimilar molecules. If the repulsion between species is strong, different species of the same phase remain separate such as in liquid-liquid separation. It is less common for the activity coefficient, γ_i, to be smaller than one. Activity coefficient less than one indicates the existence of a strong attraction between dissimilar molecules. Such a phenomenon results in the formation of solution complexes. Since the use of an activity coefficient is able to capture and describe non-ideal behaviour, activity coefficient methods are useful for modelling non-ideal systems.

Interaction in Aspen Plus™ is modelled with the help of interaction parameters. Binary parameters are estimated using the Aspen Properties™ tool or regression of experimental data. Experimental data may be available in the form of phase equilibria data. For activity coefficient models, binary parameters are valid within specific range of conditions due to dependencies in temperature and pressure. Values outside of the valid range should be used with caution, especially in liquid-liquid equilibrium applications. The activity coefficient models are more accurate at low to moderate pressures, below 10 atmospheres (Aspentech, 2009). Activity coefficient models have a lower accuracy for systems containing dissolved gases at low pressures. For such systems, such as with light gases, activity coefficient methods should be used with Henry's law for such components. For the purpose of this simulation the ELECNRTL property method will be used as justified by the selection algorithm.

4.2.3 Model selection algorithm

In order to select a property method properly, the system in question needs to be defined in terms of its components before application of any algorithms can be done. The nature of the components and the level of their interaction determine whether an equation of state based or activity coefficient based method will be used or not. The components in the copper-chlorine cycle are listed in Table 4.2.

Table 4.2: Key components and critical properties

Component	Critical Temperature (T_c/°C)	Critical pressure (P_c/bar)
Cu	8006	500
HCl	51.53	82.9
H_2O	375-380	219.9
CuCl	2161	50
$CuCl_2$	1737	50
H_2	-242	20.3
O_2	-118	50.6
$CuOCuCl_2$	1732	50

Table 4.2 shows the components that make up the copper-chlorine cycle. The selection of thermodynamic method was done by applying a thermodynamic method selection algorithm to the state input space in Table 4.2.

There are several methods of selecting property methods listed in literature but in the current work only three of those many algorithms were reviewed. The three algorithms reviewed are the Bob Seader method (Seider *et al.*, 2004), the Eric Carlson method (Seider *et al.*, 2004) and the Aspen method (Aspen Technology, 2009). The Aspen method is in reality composed of a number of alternative algorithms. One set emerges from the use of the built-in property method selection assistant and another algorithm that is presented in the Aspen User Manual (2009). The use of the property method selection assistant will be discussed briefly but not illustrated like the other three methods, Figures 4.1-4.3.

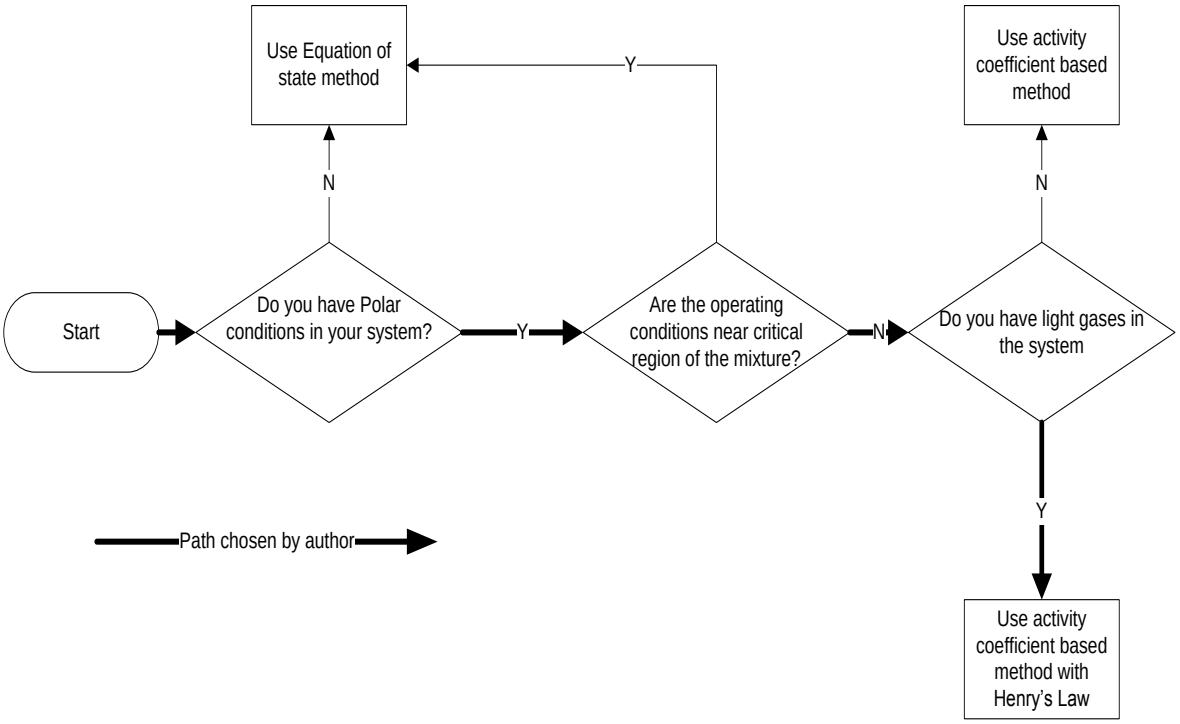

Figure 4.1:The Aspen property selection algorithm

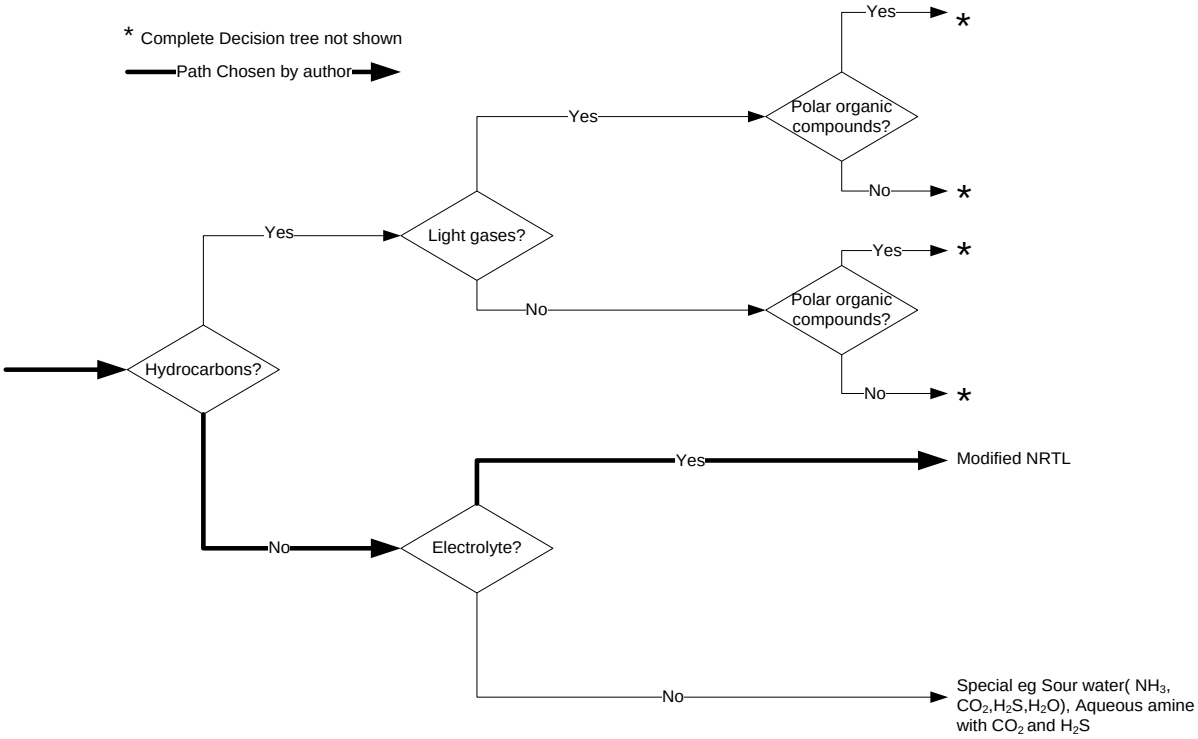

Figure 4.2: The Bob Seader property method selection algorithm

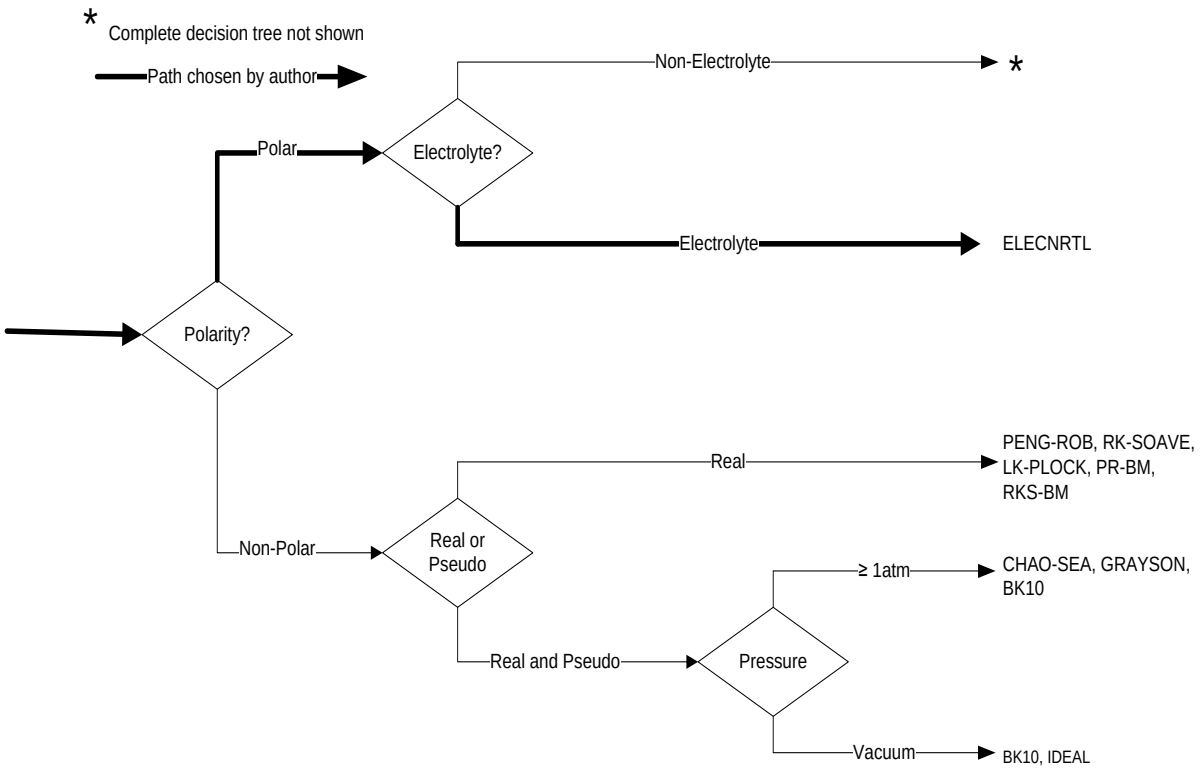

Figure 4.3: The Eric Carlson property method selection algorithm

Figures 4.1-4.3 show an Aspen Technology (2009), Bob Seader and Eric Carlson (Seider *et al.*, 2004) property selection algorithm. On each of the algorithm flow charts, the arrows in bold indicate the results of applying the algorithms to the copper-chlorine thermochemical system cycle. The Aspen flowchart in Figure 4.1, the result is a recommendation to use an activity coefficient based property method. Using the Bob Seader method, a modified NRTL is recommended and the Eric Carlson method recommends ELECNRTL. If the Aspen Plus™ property method selection assistant is used ELECNRTL is also recommended.

The available activity coefficient based methods in Aspen Plus™ include UNIQUAC, Non-Random-Two-Liquid (NRTL), and WILSON among others. According to Aspentech recommendations, if there are many inorganic components which participate in the solution chemistry, the interaction is best described by the Electrolyte NRTL (Aspen Technology, 2009). The Electrolyte NRTL or ELECNRTL is a combination property method as it makes use of the Redlich-Kwong property model for vapour phase calculations. In essence it is modified NRTL (activity coefficient based) which makes it an all-encompassing method which caters for the recommendations of all the algorithms applied. It is also important to consider that the cycle has solids, copper, cuprous chloride and copper oxychloride and the property method used, should have an allowance for calculation of properties. ELECNRTL

fortunately has a provision for calculation of thermodynamic properties of solids via the Barin equations (Aspen Technology, 2009). All these considerations make ELECNRTL the most appropriate property method for the simulation of the copper-chlorine thermochemical.

4.3 Validation of thermodynamics

Thermodynamic data calculated and estimated using thermodynamic property models are useful in energy balances, reaction predictions and product speciation and in the prediction of phase behaviour. As such, in the validation of thermodynamic models, it is important to compare simulation predicted parameters with independent experimental data on those data. In this simulation study, validation was done on a three tier level. The first level of validations was to confirm that all input data were within the model input space. The second level validates the enthalpy prediction by studying the accuracy of prediction of copper (I) chloride enthalpy change with temperature. The final validation step involves validation of phase equilibria data by comparison of experimental data from literature with aspen predictions.

4.3.1 Range of applicability

The starting point of validation of the thermodynamic model was the input range. The ELECNRTL is valid over the temperature and pressure range listed in Table 4.3

Table 4.3: Input range for valid ELECNRTL output calculations

Parameter	Minimum value	Maximum value
T_c (K)	5	2000
P_c (Bar)	0.0005	50
Operating pressure (Bar)	0.5	6

As the comparison of state parameters in Table 4.2 and the boundaries in Table 4.3 show, the input range is well within the required parameter range which suggests that the calculation outputs from the simulation should be acceptably within expected normal range.

4.3.2 Enthalpy prediction

Inaccurate enthalpy predictions can lead to inaccurate energy balances and may influence the free energy calculations which are an essential part of equilibrium speciation predictions. It is therefore important to validate the accuracy of enthalpy predictions of the simulation package before a simulation is done. For the validation of ELECNRTL enthalpy prediction, the CuCl enthalpy change with temperature was studied. Copper (I) chloride has subtle changes in enthalpy when the temperature is varied within the temperature range of the simulation, which makes it a good candidate to use as a validation tool. The changes

expected in the enthalpy temperature diagram of CuCl are due to the allotropic behaviour of copper. Between temperatures 410-430°C, Lewis *et al*(2009) and Chukwu (2008) report that CuCl changes from an alpha crystalline structure to a beta structure and then melts into a liquid. These changes are accompanied by step changes in enthalpy as shown in Figure 4.4.

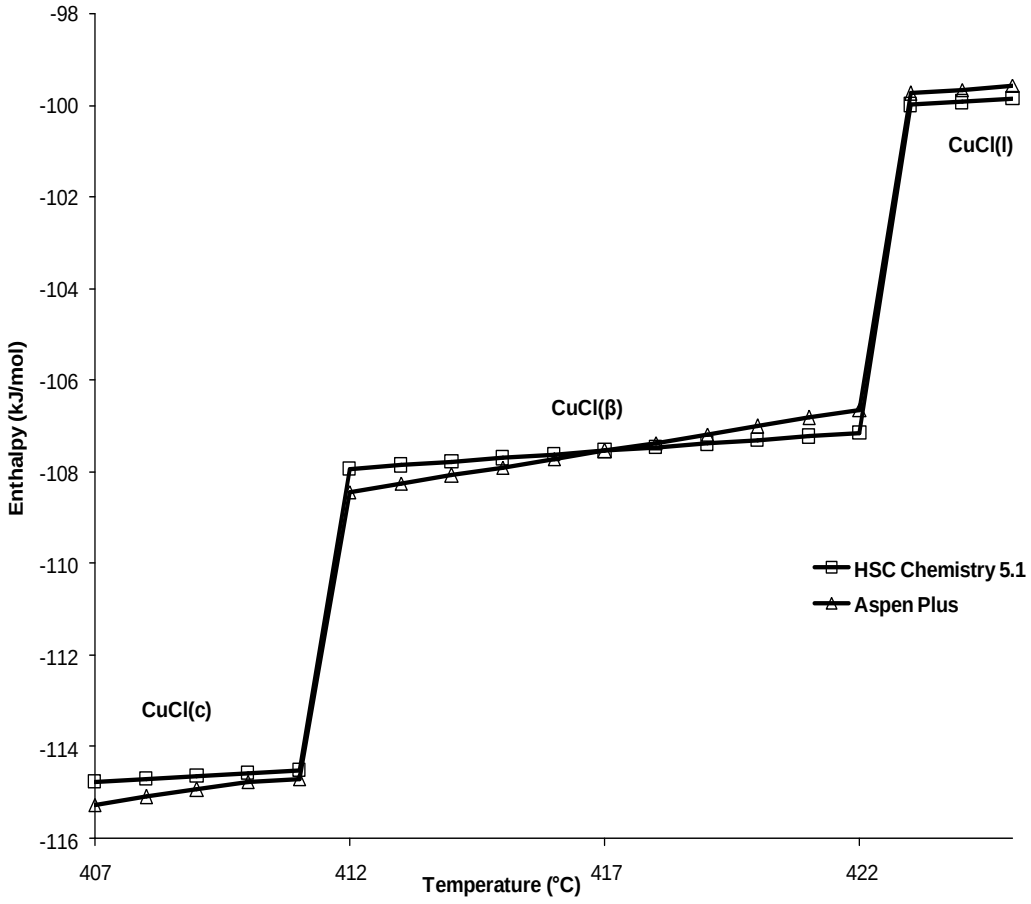

Figure 4.4: CuCl enthalpy change with temperature

A sensitivity plot in Aspen Plus™ initially gave two straight lines with data that are consistent with CuCl (c) and CuCl (l). The CuCl (β) data does not appear to be included in the enthalpy prediction of the Aspen Plus™ ELECNRTL model and so is the enthalpy change that is associated with the solid phase transition. Lewis *et al.* (2009) in their analysis of the system using Aspen Plus™, however, demonstrate that the software can predict correctly the transition temperatures and the transition enthalpies. To validate the claim, enthalpy predictions were done using the relationship, $\Delta H = \Delta G - T\Delta S$, using data from the Aspen Plus™ properties database. A plot of the results obtained was in agreement with data from HSC Chemistry 5.1 software as shown by Figure 4.4.

4.3.3 Phase equilibria data

The phase equilibria relationships of the HCl/H_2O system were used as a test for validation of the thermodynamic prediction of phase behaviour in the simulation. Figures 4.5 and 4.6 are a comparison of two different thermodynamic model predictions from Aspen Plus™. The main point of comparison in the Y-X diagram is the azeotrope since the basic curvature of the data plot is similar.

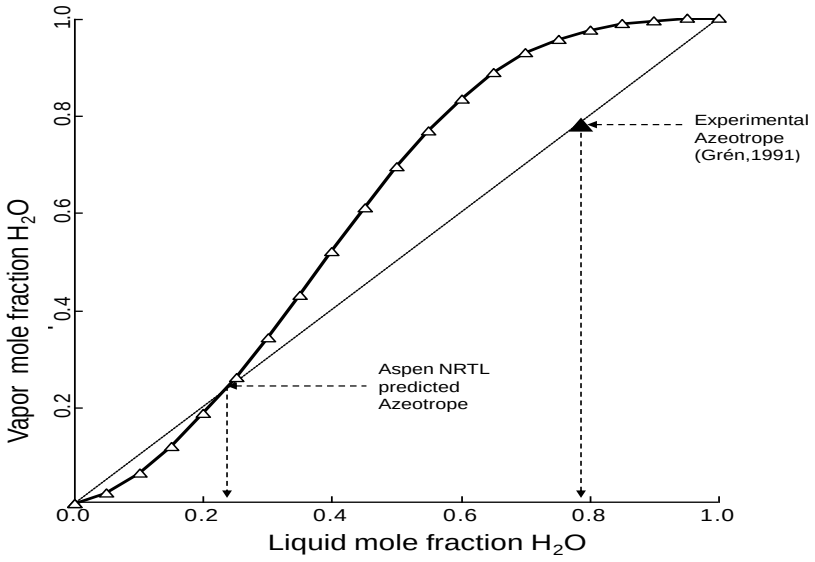

Figure 4.5: NRTL Aspen generated X-Y Diagram for HCL/H_2O system at 1atm

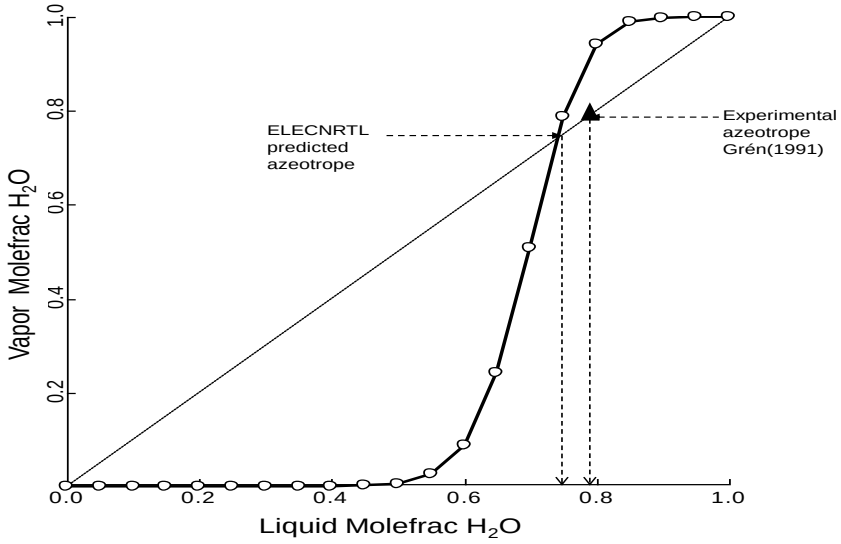

Figure 4.6: ELECNRTL Aspen generated X-Y Diagram for HCL/H_2O system at 1atm

Figures 4.5 and 4.6 show the results of phase predictions for the binary system using NRTL and ELECNRTL. Both methods indicate the existence of an azeotrope in the binary system but differ on the point at which the azeotrope exists. The azeotrope influences the separations of HCl and water in the process; hence the overall process energy, the more accurate the prediction the more accurate the simulation model will represent the real cycle. NRTL predicts existence of an azeotrope at 20% water and ELECNRTL predicts the azeotrope to be at 76% at 1 atmosphere of pressure. Literature (Liu and Gren, 1991;Smith *et al.*, 2001) suggests that the azeotrope exists at 79.8% at the given pressure conditions. Cho (2004) reports an azeotrope for the system at 88% liquid water using HCl Electrolyte method in ProSim/II. Comparison of the values in Liu and Gren (1991) with predicted values shows that the ELECNRTL prediction is a closer estimation than the NRTL. ELECNRTL predicted values are to a 95% confidence level. Given the close comparability of the ELECNRTL to values cited in industrial applications, it is the opinion of the author that ELECNRTL describes the system well.

4.4 Selection of reactor conditions

4.4.1 Reactors overview

The copper-chlorine cycle consists of three, four or five steps (Wang *et al.*, 2009). Two of three or three of four and four of the five reactions are thermal reactions and one is an electrolytic reaction. Hydrogen and oxygen are produced in the copper chlorination and oxychloride decomposition reaction and the rest of the reactions are intermediate reactions which help close the loop. The reactions involved in the five-step cycle are shown in Figure 4.7. As shown in Figure 4.7, each reaction is associated with a reactor which houses the reaction. Due to the reactors being in a closed cycle, the reactors interact with each other. Products from one reactor are feed for other reactors within the cycle, so there is a close relationship between the reactors. By virtue of the close interaction between reactors, feed specifications for some reactors dictate the product specifications of the preceding reactors. The reactor design needs to be designed with an integrated approach to ensure that the process economics and other performance objectives are met (Smith, 2005). A unit by unit approach to the design of reactors is outlined in the Sections 4.4.2-4.4.6. The five-step cycle is used as an example as it covers the steps in the three and four-step cycles as well.

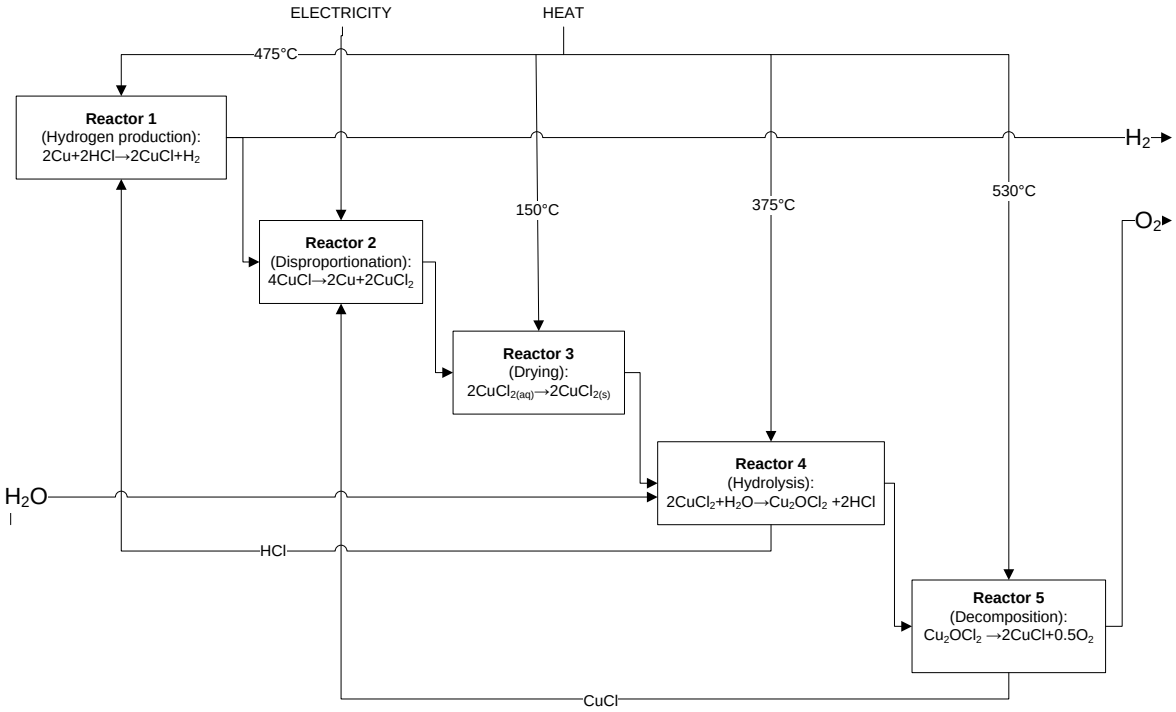

Figure 4.7: Reactors overall block diagram

4.4.2 Step 1: Hydrogen production

In the four and five-step cycles, hydrogen is produced in the hydrogen reactor by reacting copper granules with hydrogen chloride. The hydrogen chloride and copper are contacted counter currently with the gas coming from below and the solids trickling from above. For the simulation, initial reactor conditions were selected to allow the hydrogen production reaction to reach equilibrium. According to Sinnot (2005), the maximum possible conversion is achieved at equilibrium for a reversible reaction. Using equilibrium constants which are calculated at different conditions, the conditions that allow the highest conversion can be found. In the current work, the author used Outokumpu's HSC Chemistry software version 5.1 to calculate equilibrium constants. Where it was not possible to use HSC Chemistry 5.1, to calculate the constants, information was extracted from Zamfirescu *et al.* (2010) to facilitate conversion calculations.

For the hydrogen generation reaction, the starting point was to use stoichiometric ratios of reactants in order to develop generalized expressions for partial pressures at assumed equilibrium conditions. The generalized expressions were then solved using pressure and equilibrium constants to determine the equilibrium conversions. The results for the hydrogen reaction calculations are documented as follows.

Overall reaction: $2Cu_{(s)} + 2HCl_{(g)} \rightarrow H_{2\,(g)} + 2CuCl_{(l)}$ (4.3)

Reactants: Cu solid, HCl gas.

Products: Hydrogen gas (overall process product), CuCl (molten) (Intermediate product).

If the stoichiometric ratios of reactants are fed into the reactor and an unknown amount, *x* moles of hydrogen are produced, the stoichiometric table of the reactor is represented by Table 4.4

Table 4.4: Hydrogen reactor stoichiometric table

Component	Reactor IN (mol.)	Equilibrium (mol.)	Mole fraction at equilibrium	Partial pressure
Cu	2	2-2 *x*	$\frac{(2-2x)}{(4-x)}$	-
HCl	2	2-2 *x*	$\frac{(2-2x)}{(4-x)}$	$\frac{(2-2x)}{(4-x)}P_t$
H_2	-	*x*	$\frac{x}{(4-x)}$	$\frac{x}{(4-x)}P_t$
CuCl	-	2*x*	$\frac{2x}{(4-x)}$	-
Total	4	4-*x*	1	P_t

Using the partial pressure values in Table 4.4 to calculate the equilibrium constant, a generalized expression in *x* was obtained. Generally, the equilibrium constant is calculated according to Equation 4.4

$$\frac{P_{H_2}{}^{c} \cdot P_{CuCl}{}^{d}}{P_{Cu}{}^{a} \cdot P_{HCl}{}^{b}} = K_{eq} \tag{4.4}$$

where a, b, c, d are reaction coefficients. From the balance and general principle the partial pressures for liquids and solids are neglected in the calculation, such that Equation 4.4 becomes Equation 4.5

$$\frac{P_{H_2}{}^{c}}{P_{HCl}{}^{b}} = K_{eq} \tag{4.5}$$

In the hydrogen reaction, b and c are 0.5 and 1, respectively, such that Equation 4.5 becomes Equation 4.6

$$\frac{P_{HCl}{}^{0.5}}{P_{H_2}{}^{1}} = K_{eq} \tag{4.6}$$

Extracting generalized values of partial pressures from the balance,

$$P_{HCl}=\frac{(2-2x)}{(4-x)}P_t \text{ and } P_{H_2}=\frac{x}{(4-x)}P_t$$

Where P_t represents the total system pressure in the reactor system.

When P_{HCl} and P_{H_2} are substituted into Equation 4.6 it yields

$$\frac{\left(\frac{x}{(4-x)}P_t\right)^{0.5}}{\frac{(2-2x)}{(4-x)}P_t}=K_{eq} \tag{4.7}$$

Applying a few algebraic manipulations 4.7 produces

$$8 - 10x + 2x^2 = (K_{eq})^2 \cdot P_t \cdot x^2 \tag{4.8}$$

Equation 4.10 can also be re-written as

$$\left(2-(K_{eq})^2 \cdot P_t\right) x^2 - 10x + 8 = 0 \tag{4.8b}$$

Equation 4.8b is a quadratic equation which can be solved and whose roots can be found using several mathematical tools, available including the simple quadratic formula. The conversion of hydrogen at equilibrium is then equivalent to the real roots of Equation 4.8b that are between the limits of 0 and 1. One mole of hydrogen is the theoretical maximum expected yield of hydrogen from a reaction of 2 moles of Cu with 2 moles of HCl which are the initial stoichiometric inputs. Table 4.5 tabulates some of the results of repeating these calculations at different temperatures and pressures.

Table 4.5: Conversion analysis results for the hydrogen reaction

Temperature (°C)	Copper conversion			
	P_t=1bar	**P_t=4bar**	**P_t=6bar**	**P_t=9bar**
400	0.6636	0.4415	0.3822	0.3280
425	0.7910	0.5794	0.5136	0.4500
450	0.8572	0.6704	0.6050	0.5389
475	0.9038	0.7486	0.6877	0.6229

When plotted, the data in Table 4.5 shows the trends of conversion with the variation of the temperature and pressure. These trends enable the selection of process conditions that maximize conversion. Figures 4.8 and 4.9 are plots conversion trends with the variation of temperature and pressure, respectively.

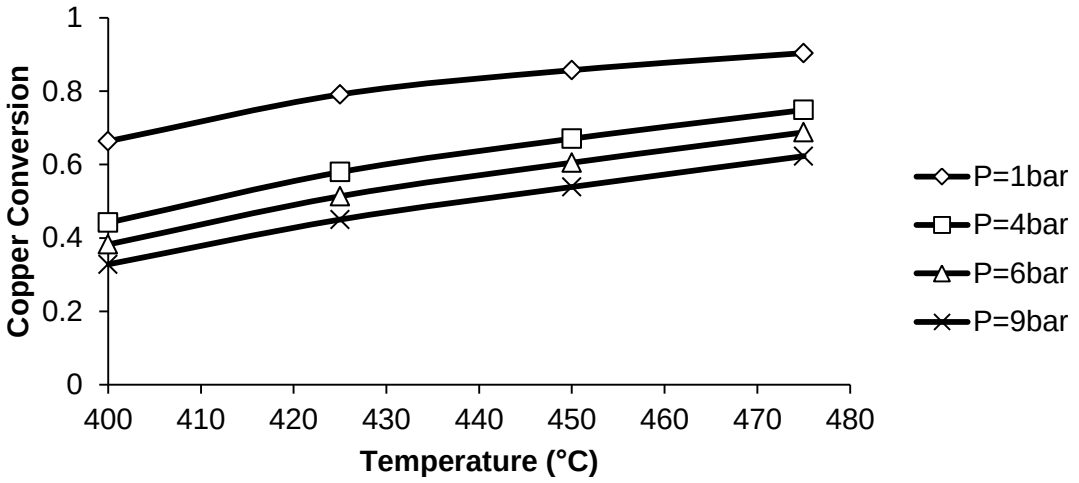

Figure 4.8: Temperature conversion relationship for hydrogen reaction

As Figures 4.8-4.9 show, for the hydrogen reaction the conversion generally increases with increase in temperature and decreases with increasing pressure. In light of this, conditions for the reactor were chosen to have the lowest pressure practically possible and the highest economic temperature. A balance between the conversion and corrosion, operational cost and capital cost of the reactor, were critical considerations in the initial selection.

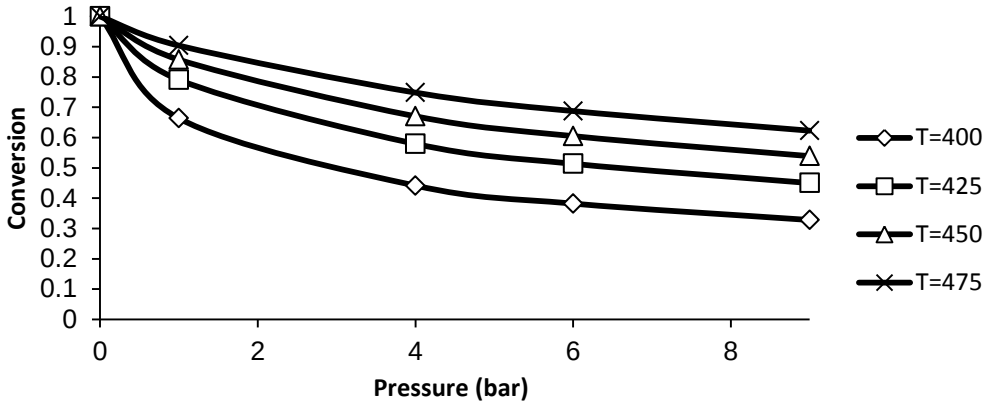

Figure 4.9: Temperature conversion relationship for hydrogen reaction

To avoid complicating the model, the only parametric studies carried out mainly involved analysis of pressure and temperature against conversion relationships. The effect of particle size on the reaction dynamics was extracted from Serban *et al.* (2004) as typically shown by Figure 4.10, which is representative of results of experimental work from Argonne National Laboratory.

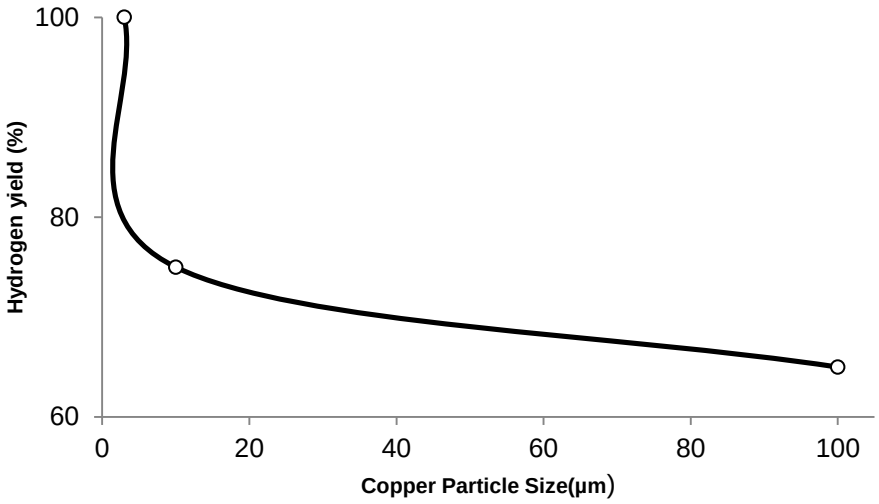

Figure 4.10: Conversion variation with copper particle size [source:(Serban *et al.*, 2004)]

As Figure 4.10 shows, the yield of the hydrogen reaction approaches 100% as the particle size becomes smaller than 3µm. In building the simulation reported in this work, the author assumed the particle size used, was less than 3µm such as would allow full conversion. Explicit inclusion of the study of the effect of particle size was therefore not included in the present work. To summarize: in the hydrogen reactor for the four and five-step cycles, the initial conditions used in the simulations were a temperature of 475°C and 1 bar pressure.

4.4.3 Step 2: Disproportionation reactor

For the four and five-step cycles, disproportionation reaction is an electrochemical reaction where copper (i) chloride is transformed into copper (ii) chloride and elemental copper. For the three-step cycle, the disproportionation reaction includes hydrochloric acid in the reaction and the products are copper(ii) chloride and hydrogen gas. For all the configurations of the copper-chlorine cycle, the disproportionation reactions have the least information in literature. Due to the unavailability of information, literature derived conditions were used in the simulation. A temperature in the range of 25-80°C and a pressure of 1bar are the general reactor conditions recommended by Chukwu (2008) and Wang *et al.* (2009) for the four and five-step cycles. For the three-step cycle, Lewis *et al* (2008) recommend temperature of 100°C and pressure of 24 bar. The reactions are electrolytic and energy intensive so other parameters need to be investigated to optimize the energy used (Wang *et al.*, 2009).

4.4.4 Step 3: Drying

The drying step is found in the five-step cycle only. Drying is a preparatory step for the hydrolysis step where $CuCl_2$ crystals are made from a $CuCl_2$ solution. There are two basic approaches to accomplishing this: use of a spray dryer or use of a crystalliser combined with

an evaporative dryer. Wang *et al*. (2009) have shown that use of a crystalliser requires less energy than using a spray dryer; hence the crystalliser pathway was selected for use in the simulation. Conditions for the crystalliser were selected to optimize product for the hydrolysis reaction. According to work by Wang *et al*. (2009) hydrated $CuCl_2$ crystals are obtained if temperatures between 30-80°C are used in the crystalliser. For temperatures above 42°C, the water molecules in the hydrate are generally between 0-2 and these can be easily driven off in an evaporative dryer (Wang *et al*., 2009). Less energy is used in the evaporative dryer if a filter is used to dewater the slurry. Dewatering efficiencies of up to 98% are reported to be possible using a filter (Richardson *et al.*, 2005;Wills and Napier-Munn, 2006). Due to these findings, for the drying section; if the crystalliser operates at 42°C and 1 bar, a dewatering efficiency of 95% achieved and the dryer operates at 150°C and 1bar.

4.4.5 Step 4: Hydrolysis

In the hydrolysis step, steam reacts with solid copper dichloride to form solid copper oxychloride and HCl gas. Significant experimental work has been done by Ferrandon *et al*. (2010), Daggupati *et al.* (2009) and Serban (2004) to investigate the optimal reactor conditions. From the results of the experimental efforts, all researchers are in agreement that the reaction requires excess steam to suppress side reactions and to achieve complete conversion (Serban, 2005; Daggupati *et al.*, 2009). Using theoretical calculations this observation is difficult to see mainly because thermodynamic data of copper oxychloride are not available in most software databases. The unavailability of these data means that calculation of equilibrium data is difficult or unreliable where it is possible. The implication is that for simulation of the hydrolysis step to be as close to practical as possible, experimental data have to be used as initial reactor estimates. For this simulation the initial reactor conditions used were literature-derived and were a temperature of 375°C and 0.5 bar pressure. An excess amount of steam was used, maintaining a Steam: Cu ratio of 17. According to Wang *et al.* (2009) under these conditions a 100% conversion should be achievable.

4.4.6 Step 5: Decomposition reactor

In the decomposition reactor, found in all three cycle configurations, copper oxychloride is decomposed thermally to form CuCl and oxygen. The initial reaction conditions were calculated using reaction equilibria. Equilibrium constants calculated with HSC Chemistry 5.1 were used to evaluate the conditions that gave the highest conversion of copper oxychloride.

Table 4.6: Stoichiometric table for decomposition reactor

Component	Reactor IN (mol.)	Equilibrium (mol.)	Mole fraction at equilibrium	Partial pressure
Cu_2OCl_2	1	1-2 *x*	$\frac{(1-2x)}{(1+3x)}$	-
O_2	-	*x*	$\frac{x}{(1+3x)}$	$\frac{x}{(1+3x)}P_t$
CuCl	-	4*x*	$\frac{4x}{(1+3x)}$	-
Total	1	1+3*x*	1	P_t

Using the partial pressure values in Table 4.6 to express calculation of the equilibrium constant, a generalized expression in *x* was obtained. Generally, the equilibrium constant is calculated according to Equation 4.9

$$\frac{P_{O_2}^{0.25} \cdot P_{CuCl}^{1}}{P_{Cu_2OCl_2}} = K_{eq} \tag{4.9}$$

Using generalized partial pressures Equation 4.10 is formed

$$\frac{x}{(1+3x)} P_t = K_{eq}^{\ 4} \tag{4.10}$$

Changing it to quadratic form which makes it easier to analyze for root behaviour in MATLAB

$$\left(9K_{eq}^{\ 8} - P_t^{\ 2}\right)x^2 + 6xK_{eq}^{\ 8} + K_{eq}^{\ 8} = 0 \tag{4.11}$$

Using a K_{eq} =6.013 which is derived from Serban's (2004) experimental work for decomposition at 530°C, MATLAB analysis shows a series of complex roots for Equation 4.11 and one real root which is around 0.6995 for all the pressures used in the analysis. Pressures between 1-10 bar were used. As a result, a single pass conversion of 0.7 was used in the simulation as an initial condition. Pressure and temperature values used were extracted from the literature referring to experimental work. Daggupati *et al.* (2010) and Ferrandon *et al.*(2010) cite a temperature of 530°C and atmospheric pressure as side reaction limiting; hence these conditions were used as initial conditions

4.5 Separation and recycle system design

For all reactors used in the copper-chlorine simulation, the reactant conversions are all less than 100%. This makes it necessary to have a system which separates products and un-reacted reactants. In other cases the products need to be separated from each other and have one product redirected to another reactor or recycled and the other be directed to a

purification process. For the copper-chlorine simulation intermediate compounds are used and these are kept in a closed loop. For this to happen there was a separation and recycle system whose key objectives were to bring out purified hydrogen and oxygen and to retain intermediate products. The approach to separation system design will be demonstrated by the hydrogen reactor product separation design. The objectives in the design of the hydrogen reactor product separation system were to

- separate hydrogen, CuCl, and excess H_2O, HCl and Cu;
- purify the hydrogen Stream to 99.97% hydrogen purity as per fuel cell market specifications (Reijerkerk, 2009);
- retain CuCl for use as a feed to the disproportionation reactor; and
- recycle excess HCl and Cu in the product stream for re-use as feed to hydrogen production reactor.

The objectives cater for the need of having a separation system in most processes which is the reason why the hydrogen production reactor product was chosen for demonstration. For most heterogeneous reactors, the separation of solids and liquids from gases is built into the reactor design. In Aspen Plus solid and gas feeds are mixed and a phase separator is necessary to separate the gaseous product and un-reacted reactants. Once the solid and gaseous components are separated the generic process shown in Figure 4.11 is applied to achieve the required hydrogen purity and the CuCl is transferred to the disproportionation reactor. Factors considered in the design of the process are vapour-liquid phase behaviour of components under temperature or pressure changes or both. The differences in the phase behaviour of the different impurities allow separation to be feasible. Changes in temperature or pressure or both change the phase of the mixtures, as illustrated by Figures 4.12 and 4.13. Components with the lower boiling points remain in vapour phase while those with higher boiling points condense as the vapour fraction decreases. For the hydrogen Stream the component boiling points are -252.87°C, -85.1°C and 100°C for H_2, HCl and H_2O, respectively. For the simulation boiling points are good initial estimates for the separation system design, however, detailed design of the physical system would require calculation of the bubble points and dew points.

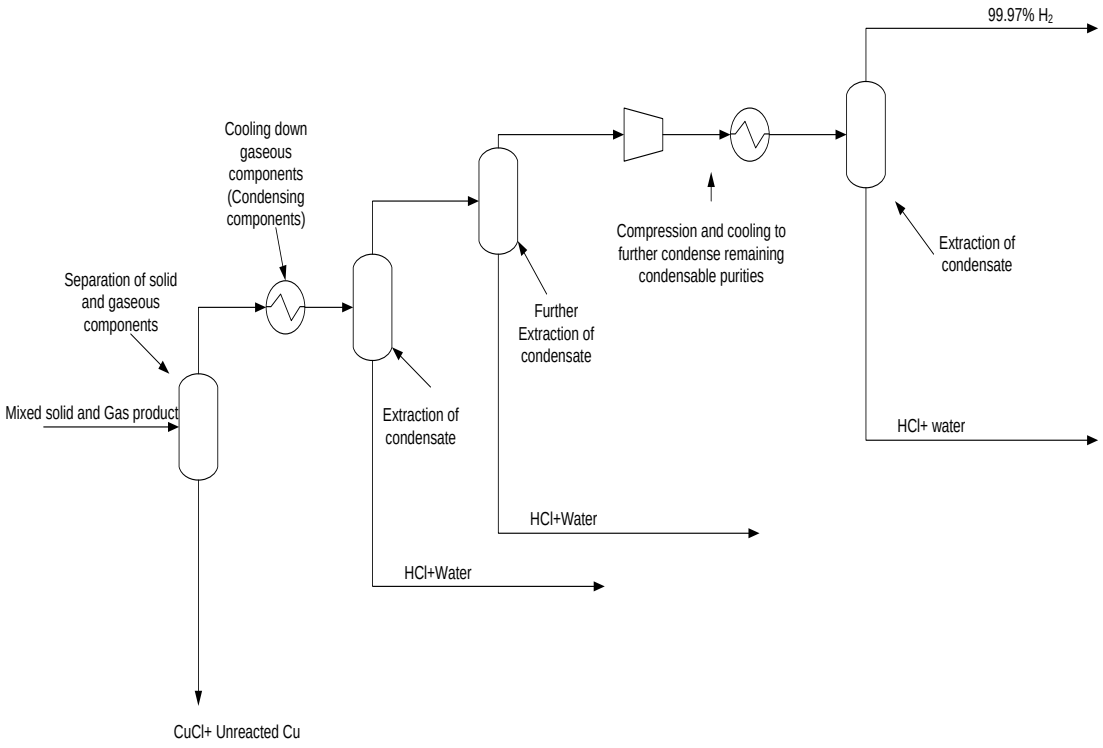

Figure 4.11: Separation process for purification of H_2

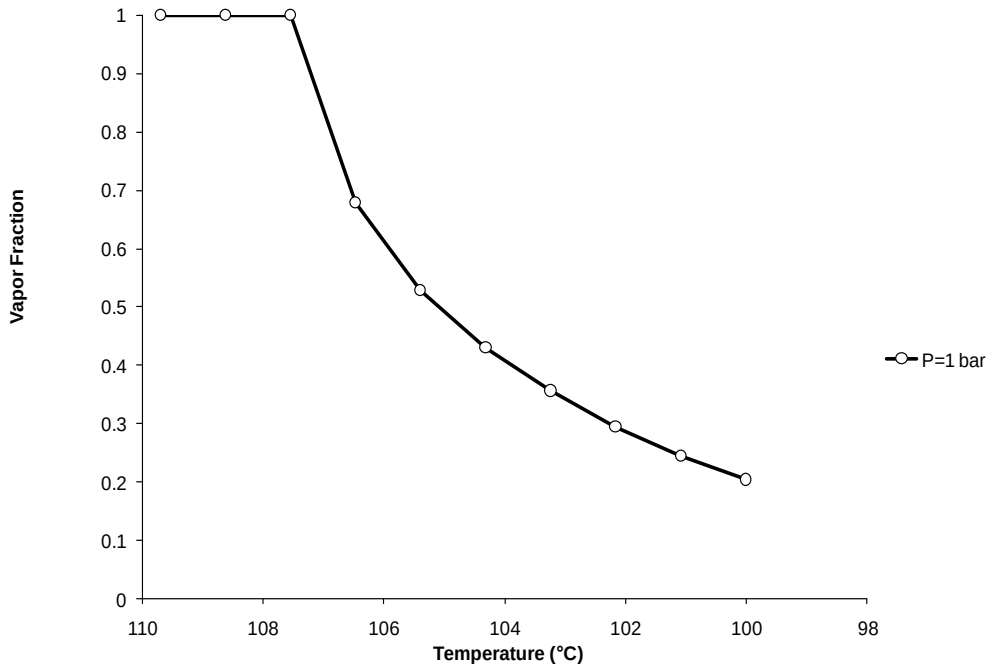

Figure 4.12: Vapour fraction on cooling

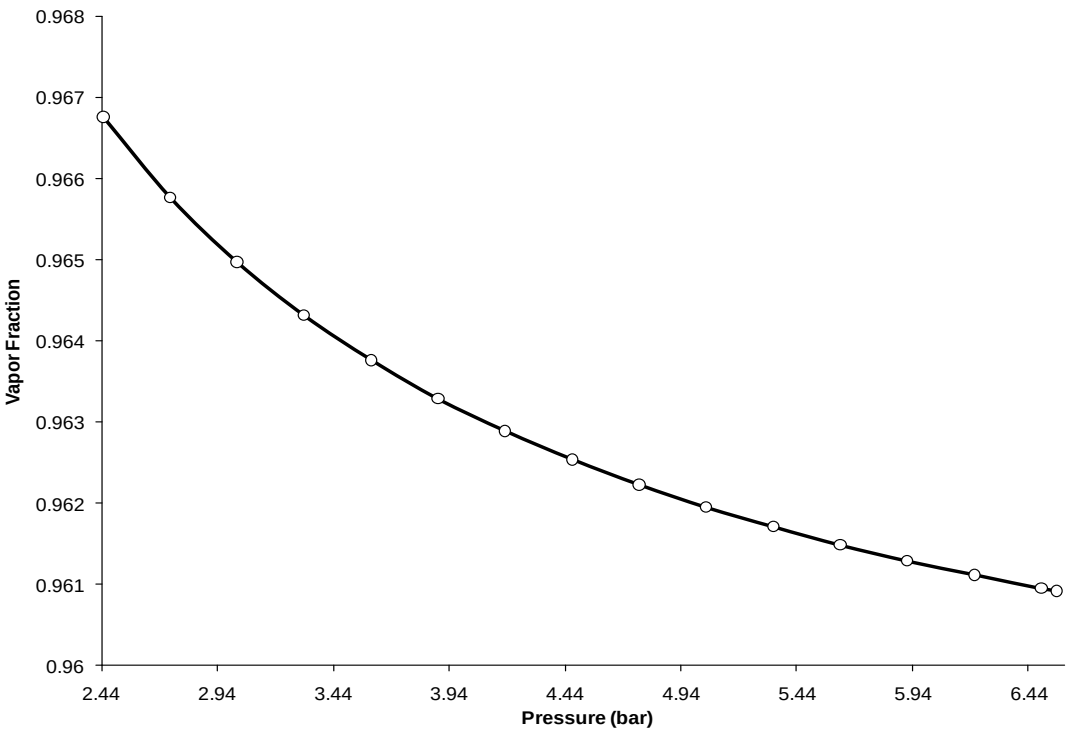

Figure 4.13:Vapour fraction in product Stream after compression and cooling

Figure 4.12 shows that in cooling the gaseous product stream to 100°C, the vapour fraction falls from 1 to 0.2 and an analysis of the cooler product Stream shows that H_2 all remains in vapour phase but most of the H_2O condenses. The condensed H_2O carries some HCl with it, increasing the purity of the hydrogen. After removal of most of the water, Figure 4.13 shows that further purification can be achieved by compression to 6.5 bar which achieves the required hydrogen purity. Such phase manipulations are synonymous with purification technologies such as pressure swing adsorption and other related technologies.

Other phase separations encountered in the copper chloride cycle include solid-solid separations and liquid solid separations. The liquid-solid separations such as dewatering of $CuCl_2$ crystals in the drying stage can be done by filtration or centrifugal separation. The liquid-solid separations mostly use density differences and particle size differences to achieve separation (Richardson *et al.*, 2005). Solid–solid separations can be achieved by use of differences in densities, melting points, solubility and magnetic properties. In the copper-chlorine simulation, high solid conversions eliminate the need to have solid–solid separation. In the case of the hydrogen production section where a significant portion of Cu is not converted to CuCl, the carryover to the disproportionation reactor is allowed. The disproportionation reaction produces copper at the cathode and the carried over copper can be extracted with the anodic copper product.

4.6 Heat recovery system design

A properly designed heat recovery network can reduce the amount of energy required by a process by effectively recovering and reusing some of the heat rejected by one unit in another that requires heat. In order to design an effective recovery system, the design process has to be systematic. Pinch analysis is one of the methods in use in heat exchanger network design (Sinnot, 2005). Pinch analysis builds the heat exchanger network design around the thermodynamic constraint which is known as the process pinch (Smith, 2005). Using the heating and cooling targets established in the design of reactors and the separation system, design of the heat exchanger network is done to avoid transfer of heat across the thermodynamic constraint (Smith, 2005).

Application of pinch analysis to the simulated copper-chlorine cycles was done in the design. Data from the simulation of the five-step cycle was used to demonstrate the application of pinch analysis. The process starts with the extraction of process Stream data. The data required is summarized in Table 4.7.

Table 4.7: Five-step cycle Process Stream Summary

Stream ID	Source temp.	Target temp.	Heat load	Type	MCp	Interval (adjusted) temperatures, °C	
	°C	**°C**	**kW**		**W °C^{-1}**	**T_{source}**	**T_{target}**
42	108.0	475.0	484979.8	cold	1321.47	113.0	480.0
35	80.0	475.0	19076.2	cold	48.29	85.0	480.0
19	450.0	80.0	880294.0	hot	2379.17	445.0	75.0
4	450.0	100.0	742099.7	hot	2120.28	445.0	95.0
8	329.0	20.0	9611.3	hot	31.10	324.0	15.0
17	30.0	375.0	51590.2	cold	149.54	35.0	380.0
24	42.0	150.0	123595.6	cold	1144.40	47.0	155.0
26	150.0	375.0	34491.6	cold	153.295	155.0	380.0
29	530.0	30.0	8480.0	hot	16.96	525.0	25.0
32	375.0	530.0	1221822.4	cold	7882.7	380.0	535.0

After collecting the process stream information in Table 4.7, the next stage of pinch analysis is to find the pinch conditions through application of the problem table method. The problem table method is a numerical method which, when used, can indicate the position of the thermodynamic constraint on system of process streams (Sinnot, 2005). It is an iterative process where heat loads are cascaded to identify the thermodynamic constraint. Table 4.8 summarizes the results of application of the problem table method to the simulated copper-chlorine cycle.

Table 4.8:Problem Table Algorithm results summary for the five-step cycle

T interval	MCp cold	MCp hot	ΔH cold	ΔH hot	ΔH cascade	Hot utility	ΔH net
°C			**kW**	**kW**	**kW**	**kW**	**kW**
535.0					0.0	1063874.9	**1063874.9**
525.0	7882.725	0.000	78827.2	0.0	-78827.2	0.0	985047.7
480.0	7882.725	16.960	354722.6	763.2	-432786.7		631088.2
445.0	9252.490	16.960	323837.1	593.6	-756030.2		307844.7
380.0	9252.490	4516.418	601411.8	293567.2	-1063874.9		**0.0**
324.0	1672.598	4516.418	93665.5	252919.4	-904621.0		159253.9
155.0	1672.598	4547.522	282669.0	768531.3	-418758.7		645116.2
113.0	2663.706	4547.522	111875.6	190995.9	-339638.4		724236.5
95.0	1342.235	4547.522	24160.2	81855.4	-281943.2		781931.7
85.0	1342.235	2427.238	13422.4	24272.4	-271093.2		792781.7
75.0	1293.941	2427.238	12939.4	24272.4	-259760.3		804114.7
47.0	1293.941	48.065	36230.3	1345.8	-294644.8		769230.1
35.0	149.537	48.065	1794.4	576.8	-295862.5		768012.5
15.0	0.000	31.105	0.0	311.0	-295070.8		**768804.1**

The results of the problem table method show the temperature interval in which the heat recovery constraint is located and the utility demands. In Table 4.8, in the ΔH net column, the topmost value (in bold) is the duty of the hot utility requirement and the bottom most value is the cold utility duty (in bold). The interval with a zero ΔH net is the pinch interval (in bold case). The same procedure done for the five-step cycle was repeated for the three and four-step cycles and the results are summarized in Table 4.9

Table 4.9: Summary of pinch results for three, four and five-step cycles

	3 Step cycle	**4 Step cycle**	**5 Step cycle**
Hot Utility (kJ mol^{-1} H_2)	1079.13	1062.22	1,063.87
Cold Utility (kJ mol^{-1} H_2)	802.53	768.92	768.81
Pinch temperature (°C)	535	380	380
Net Heat	276.60	293.30	295.06

After determining the pinch conditions, the heat exchanger network was designed with the aid of Aspen Energy Analyzer™. For more detail, see Appendix 2

4.7 Overall unit integration

The simulation model used in this study was built in sections that correspond to each of the five main reactions of the copper-chlorine cycle. Section 1 has the hydrogen producing reaction and as such was considered as the hydrogen section. Section 2 is where cuprous chloride is electrolytically disproportioned to copper dichloride and elemental copper. This section is the most understated section in the cycle model due to the little information

available on the performance of the electrolytic cell and the mechanism of the process. Section 3 is the drying section, where copper dichloride formed in reaction two is dried in preparation for the hydrolysis reaction which is in Section 4. The hydrolysis reaction where copper oxychloride is produced is Section 4. Section 4 in this study was made simple due to the excessive amount of generalised information available in the literature. The final section is the decomposition section and this is where the oxygen is produced.

4.7.1 Section 1: Hydrogen production section

The hydrogen production section has a reactor which contacts solid copper particles with hydrogen chloride to produce an impure hydrogen product and cuprous chloride. In an industrial setting, the reaction occurs in a fixed bed reactor or a fluidized bed reactor. Fluidized bed reactors are expected to face challenges like entrainment loss because of the size of copper particles used in the reactor and as such the fixed bed is a more likely candidate. In the model, the reactor was modelled using two key units, a stoichiometric reactor and a phase separator. In the industrial setting the reactors normally have a product separation mechanism built in, but in the model a phase separator has to be added to separate the products. If information is available, a plug flow model would have provided more insight into the reaction as conditions and flows are varied, however the kinetic data was not readily available at the time of modelling. Figure 4.14 shows a generic figure of how the hydrogen production section was modelled in Aspen Plus™. The hydrogen purification section was modelled as an auxiliary section.

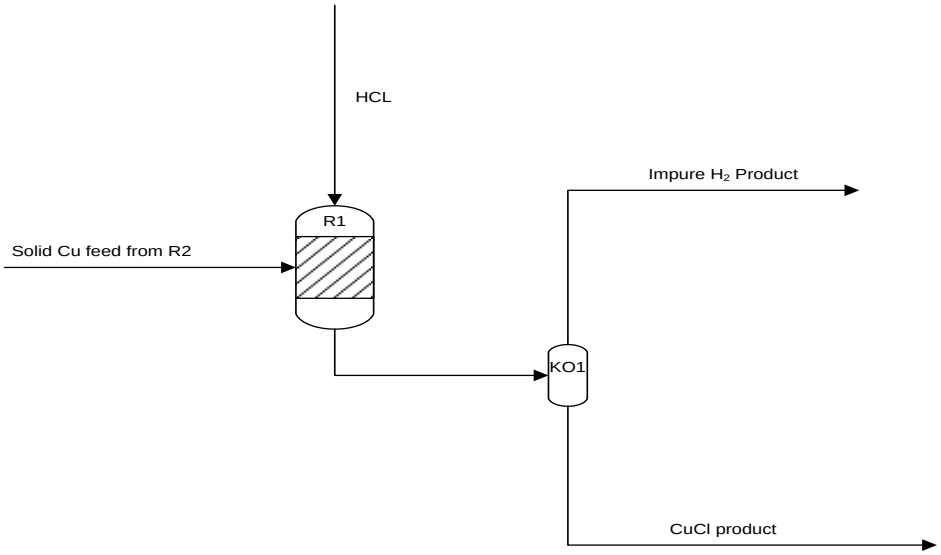

Figure 4.14: Hydrogen reactor section

4.7.2 Section 2: Disproportionation reaction.

The disproportionation reaction involves two steps, a physical dissolution and a chemical disproportionation. To simplify the analysis of results, the disproportionation reaction was modelled in a separate reactor from the dissolution. Figure 4.15 shows the two reactors (framed) that make up the disproportionation reactor in the generic simulation flowsheet. Separating the two steps was also observed to make convergence easier; hence the flowsheet solves faster when the disproportionation reactor is a hierarchy made up of two units inside.

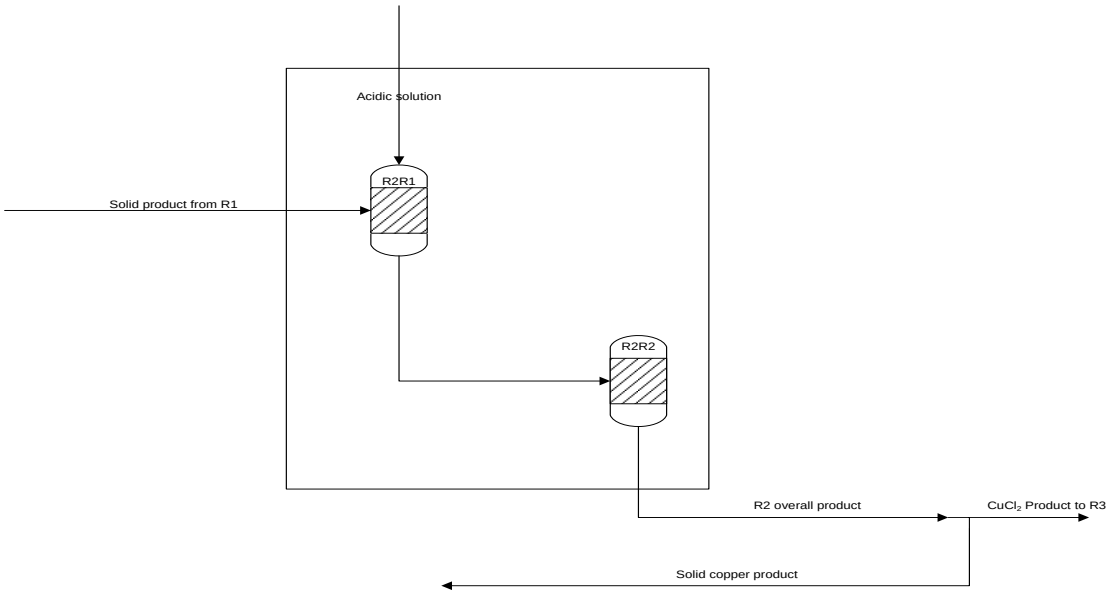

Figure 4.15:The disproportionation reactor hierarchy

4.7.3 Section 3: Drying

Of the two methods available for the drying step (Wang, 2009), use of a crystalliser with an evaporator was selected for this study. In the absence of solid solubility data of $CuCl_2$ in an acidic water solution, the use of the aspen crystalliser model was not feasible; hence the crystalliser was modelled as a reactor. Figure 4.16 shows the set-up of the reactor and dryer. A perfect separator was used in the model to separate $CuCl_2$ crystals in the slurry from the crystalliser. According to a comparison by Wang (2009), de-watering the slurry before drying reduces the heat duty required significantly.

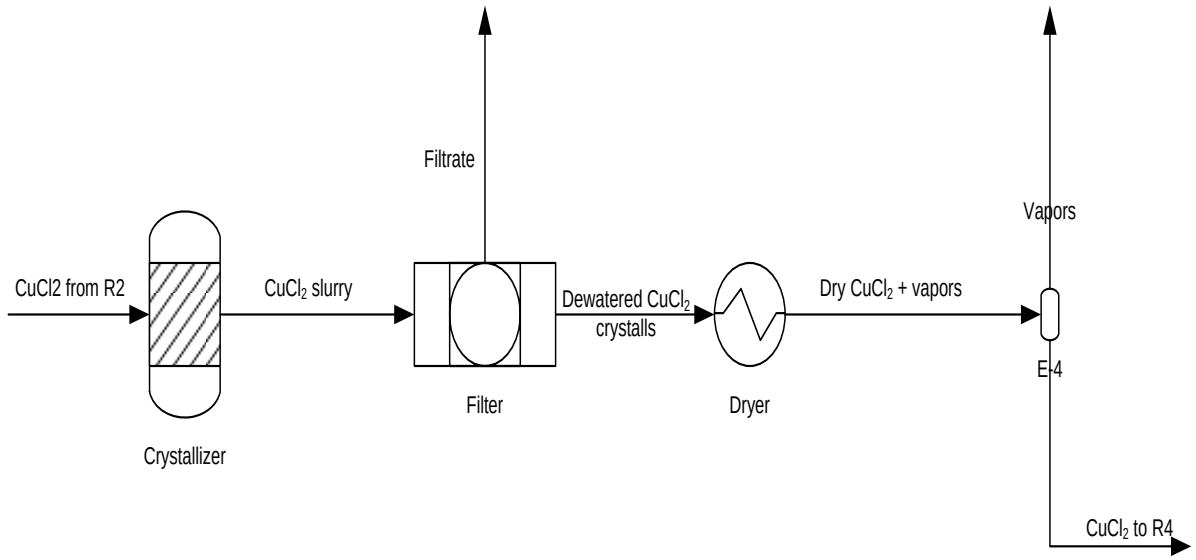

Figure 4.16: Drying circuit

4.7.4 Section 4: Hydrolysis reaction

The hydrolysis reaction has been studied and reported by many researchers, including Lewis (2008), Ferrandon (2009) and Daggupati (2010). The conditions for completion and minimisation of side products have been established even though there are no kinetics in the public domain. Subsequently, the hydrolysis reaction section of the flowsheet was designed to be indicative rather than to provide analytical insights. A stoichiometric reactor with a phase separator was used to model the section to give insight into the energy and material demands as capacities and flows change. Figure 4.17 shows the section generic schematic.

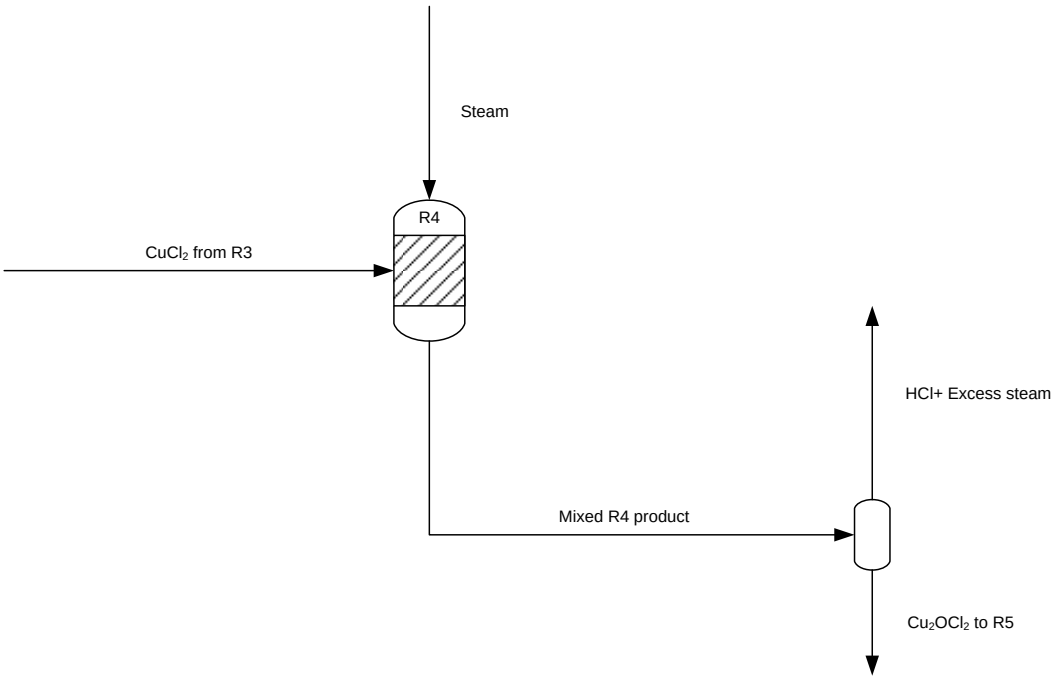

Figure 4.17: Hydrolysis section

4.7.5 Section 5: Decomposition reaction

According to calculations, the decomposition reactor has a maximum conversion of 70% at equilibrium. To counter this and ensure the closed loop of the cycle does not raise too many errors, the rest of the process has to be oversized or the number of recycle loops has to be increased. These strategies come with penalties in terms of the capital and operating expense associated with the process. In order to avoid capturing effects of size and multiple passes, the decomposition reactor is designed as a complex network of reactors with products being removed at each pass. 4.18 is a generic schematic of the hierarchy that represents the decomposition reactor. Such a complex setup comes with convergence challenges but allows several aspects of the reactor to be studied. Some of the aspects include variation of duty with capacity, variation of duty with number of passes, variation of overall conversion with number of passes, etc.

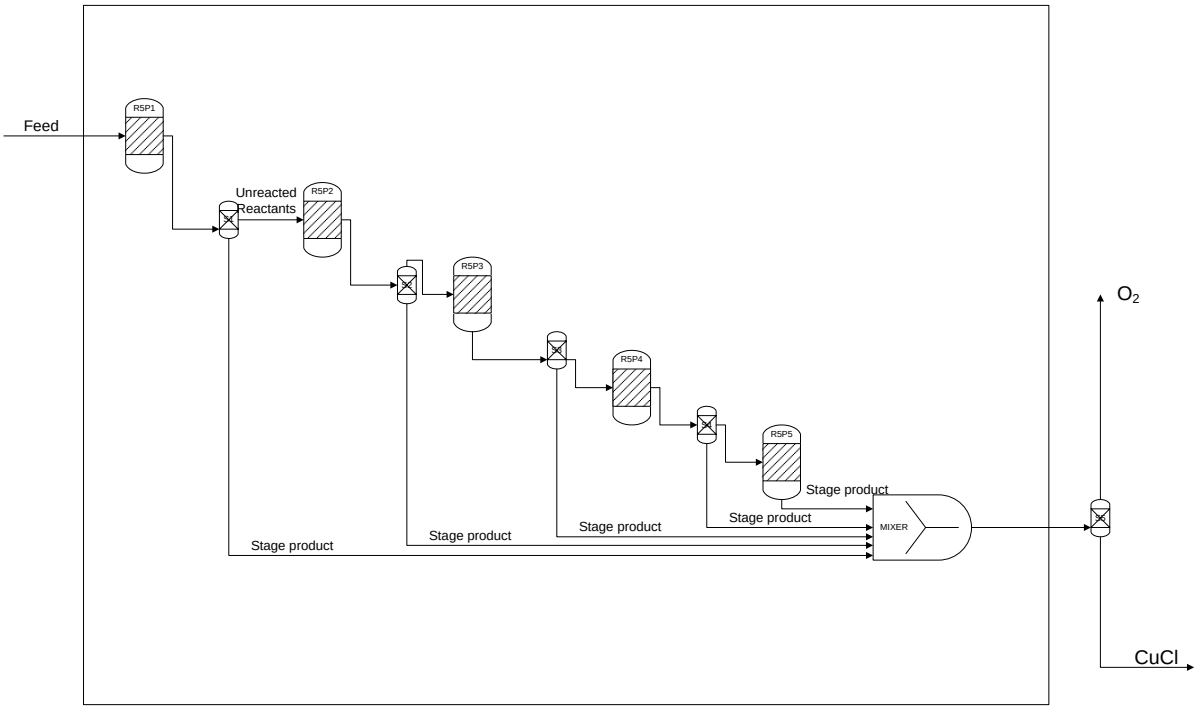

Figure 4.18: Decomposition reactor schematic

4.7.6 Auxiliary equipment.

The reactor sections of the model were joined together to form a closed loop using auxiliary equipment which separated the intermediate compounds and retained them within the cycle. By nature most of the auxiliary equipment is found in the product purification sections where, for hydrogen, compressors and phase separators were used to simulate processes like pressure swing adsorption and other effective methods of purifying the desired products. Other equipment included in the auxiliary equipment are splitters, mixers, heat recovery

systems, process heaters and coolers. More detail of the auxiliary sections is shown in the main flowsheet shown in Chapter 5.

4.8 Final Aspen Plus™ flowsheets

Aspen Plus™ flowsheets were developed by combining either all of the units discussed in Section 4.7 or some of them. The different combinations result in different Aspen Plus™ flowsheets. Sections 4.8.1-4.8.3 discuss the final Aspen Plus™ flowsheets which were then used in the simulation study of the copper-chlorine cycle.

4.8.1 Five-step cycle

The five-step cycle is comprised of five reaction steps as the name of the cycle suggests. The five reaction steps are the hydrogen production reaction, disproportionation reaction (the electrolytic step), drying step, hydrolysis reaction and the decomposition or oxygen production reaction. The simulation flowsheet was the result of joining sections 1 to section 5, discussed in Sections 4.7.1-4.7.5. Figure 4.19 is a picture of the final Aspen Plus™ flowsheet used in the current study.

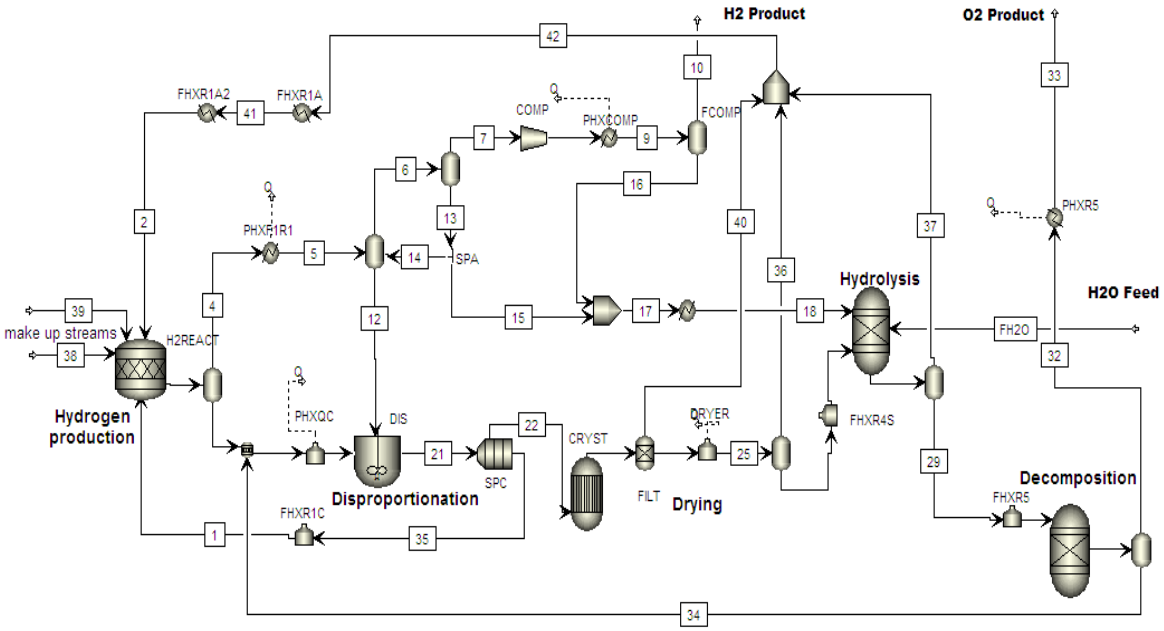

Figure 4.19: Aspen Plus Flowsheet of the five reactions cycle

The flowsheet for the five-step cycle functions as a closed loop, with products from reaction steps serving as reactants for the next reaction step. There is one overall feed to the cycle flowsheet used in the simulation study of the five-step cycle. Water is fed into the flowsheet to produce a hydrogen and an oxygen product stream. Within the closed loop of the cycle,

there are feed and intermediate product Streams that connect different units within the cycle.

The five-step cycle starts with the hydrogen production step where HCl gas in Stream 2 and Copper granules in Stream 1 are fed into the reactor block H2REACT where they react to form copper(i) chloride and hydrogen gas. Stream 3 is sent into a phase separator which separates the gaseous product and molten CuCl. The hydrogen is sent to Stream 4 along with trace amounts of excess HCl and water. Cooling of Stream 4 produces a vapour liquid mixture in Stream 5 which allows extraction of most water and some of the HCl in the phase separator. Stream 6, which consists of mostly hydrogen, is send to a second phase separator which captures some more of the water and HCl leftover from the first separation. Compression of Stream 7 forces the remaining water and HCl to condense and leave Stream 10 with a hydrogen purity of 99.97%. The water collected from the hydrogen product stream is from the separator in Streams 15 and 16 and mixed and heated to provide some of the excess steam required for hydrolysis. Water and excess HCl, which are recovered from the first phase separator F0R1, are directed to the disproportionation reactor to facilitate dissolution of CuCl.

CuCl from the H2REACT is mixed with CuCl from the decomposition reactor, DECOMP in heat recovery in a quenching cell. In the quenching cell, molten CuCl is contacted with water to produce steam and solid CuCl granules. Some of the steam can be used as the feed to the hydrolysis reactor. The CuCl granules are further cooled in PHXQC to the disproportionation reaction temperature of 80°C. In the disproportionation reactor, which is an electrolytic reactor, two steps transformative steps occur to the CuCl. The first is the dissolution of solid CuCl granules in the acidic liquor that serves as the electrolyte and the second is the disproportionation to form $CuCl_{2(aq)}$ and elemental copper. The $CuCl_{2(aq)}$ and copper leave DIS together in Stream 21 and are separated by a centrifuge, SPC. From the centrifuge, copper is sent to Stream 35 where it is heated and sent to Stream 1 which goes back to H2REACT. The aqueous copper dichloride proceeds to Stream 22 which goes to a cooling crystallizer, CRYST which is the first step of the drying process.

In the crystallizer, CRYST, the copper dichloride cools down and forms slurry of copper dichloride and water. The slurry filtered in FILT to reduce the moisture content of the copper dichloride crystals to 5 wt. % moisture. The water is sent through Stream 40 to mixer MX2. The wet solid copper dichloride is sent to an evaporative dryer and the solids are sent to pre-heating for the hydrolysis step. The steam that is produced is also sent to mixer MX2. The solid copper dichloride is contacted with steam in reactor HYDR in vacuum conditions at 375 °C to produce solid copper oxychloride, Cu_2OCl_2 and HCl gas. A phase separator separates

the HCl and Cu2OCl2. HCl is sent to Stream 37 which goes to mixer MX2 and Cu_2OCl_2 to Stream 29 which goes to preheater FHXR5. After being preheated in preheater, the Cu_2OCl_2 is thermally decomposed to produce Oxygen and CuCl molten. Oxygen is separated to Stream 32 which, when cooled, then becomes Stream 33 , the final oxygen outlet Stream. The molten CuCl is sent to Stream 34 which recycles the CuCl to the quenching cells and proceeds to disproportionation. MX2 blends steam and HCl and sends them through Stream 42 to preheaters FHXR1A and FHXR1A2 which heat the gases to H2REACT reaction temperature and the cycle resumes again. A summary of the Streams is shown in Table 4.10

4.8.2 Four-step cycle

The four-step cycle is very similar to the five-step cycle in the main reactions with the exception of one step. Instead of having a drying step before the hydrolysis reaction step, the four-step cycle uses the product from the disproportionation as the hydrolysis feed. Figure 4.20 shows the Aspen Plus™ flowsheet used to study the four-step cycle in the current study.

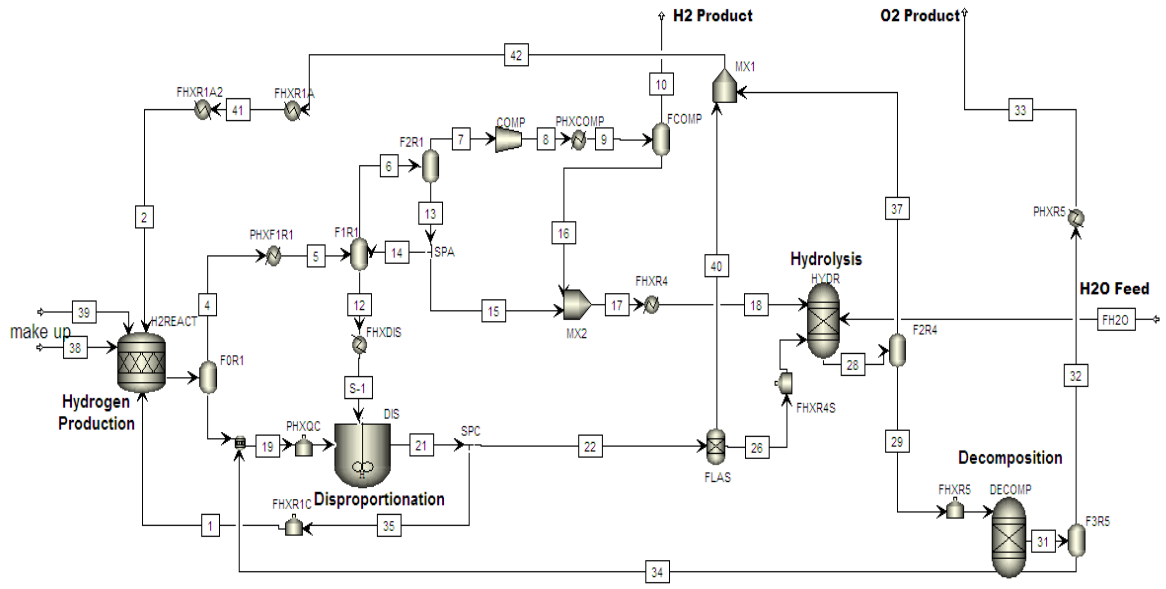

Figure 4.20: Four-step cycle simulation flowsheet

As can be seen from Figure 4.20, the four-step cycle flowsheet is almost exactly the same as the five-step cycle flowsheet. Stream 22 does not go through drying but a part of the Stream is flashed before pre-heating to reduce the heat requirements of the preheater. The concentrated $CuCl_2$ slurry solution is heated to reaction temperature in FHXR4S and fed into the hydrolysis reactor, HYDR. The rest of the flowsheet is exactly the same as the five-step cycle flowsheet. A summary of the Stream table is shown in Table 4.11.

Table 4.10: Stream table for the five-step copper-chlorine cycle simulation

Stream	Units	1	2	3	4	5	6	7	8	9	10	11	19	20	21	22	23
Temperature	°C	475	475	475	450	100	100	30	328.73	20	20	450	450	80	80	80	42
Pressure	bar	1	1	1	1	1	1	1	6.57	6.57	6.57	1	1	1	1	1	1
Mole Flow	kmol s^{-1}	2	35.48	38.38	34.56	34.56	8.56	1.04	1.04	1.04	**1**	3.82	5.82	5.82	39.47	37.47	33.47
Component Mole Flow																	
H_2O	kmol s^{-1}	0	31.84	31.83	31.83	30.12	7.54	0.04	0.04	0.04	0	0.01	0.01	0.01	28.3	28.3	29.84
H_2	kmol s^{-1}	0	0.1	1	1	1	1	1	1	1	**1**	0	0	0	0.1	0.1	0.1
O_2	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	kmol s^{-1}	0	3.54	1.73	1.73	0.02	0.02	0	0	0	0	0	0	0	0	0	1.54
Cu^{++}	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	2	2	0
Cu^{+}	kmol s^{-1}	0	0	1.81	0	0	0	0	0	0	0	1.81	1.81	1.81	0	0	0
H_3O^{+}	kmol s^{-1}	0	0	0	0	1.71	0	0	0	0	0	0	0	0	1.54	1.54	0
OH^{-}	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cl^{-}	kmol s^{-1}	0	0	1.81	0	1.71	0	0	0	0	0	1.81	1.81	1.81	5.54	5.54	0
CuCl	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CuCl (S)	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	2	2	0	0	0
Cu	kmol s^{-1}	2	0	0.19	0	0	0	0	0	0	0	0.19	0.19	0.19	2	0	0
Cu_2OCl_2	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$CuCl_2$	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2

Stream	Units	24	25	26	27	28	29	30	31	32	33	37	38	39	40	FH2O	
Temperature	°C	42	150	150	375	375	375	530	530	530	20	375	50	400	42	120	
Pressure	bar	1	1	1	1	0.5	1	1	1	1	1	1	1	1	1	1	
Mole Flow	kmol s^{-1}	3.67	3.67	2	2	5.01	1	1	2.5	0.5	**0.5**	4	0	0	29.81	**1**	
Component Mole Flow																	
H_2O	kmol s^{-1}	1.42	1.49	0	0	2	0	0	0	0	0	2	0	0	26.88	**1**	
H_2	kmol s^{-1}	0.1	0.1	0	0	0	0	0	0	0	0	0	0	0	0	0	
O_2	kmol s^{-1}	0	0	0	0	0	0	0	0.5	0.5	**0.5**	0	0	0	0	0	
HCL	kmol s^{-1}	0	0.08	0	0	2	0	0	0	0	0	2	0	0	0	0	
Cu^{++}	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Cu^{+}	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
H_3O^{+}	kmol s^{-1}	0.08	0	0	0	0	0	0	0	0	0	0	0	0	1.46	0	
OH^{-}	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Cl^{-}	kmol s^{-1}	0.08	0	0	0	0	0	0	0	0	0	0	0	0	1.46	0	
CuCl	kmol s^{-1}	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	
CuCl (S)	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Cu	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Cu_2OCl_2	kmol s^{-1}	0	0	0	0	1	1	1	0	0	0	0	0	0	0	0	
$CuCl_2$	kmol s^{-1}	2	2	2	2	0	0	0	0	0	0	0	0	0	0	0	

Table 4.11: Stream table for the four-step cycle simulation

Stream	**Units**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**19**	**20**	**21**	**22**
Temperature	C	475	475	475	450	100	100	30	328.73	20	20	450	450	80	80	80
Pressure	bar	1	1	1	1	1	1	1	6.57	6.57	6.57	1	1	1	1	1
Mole Flow	kmol s^{-1}	2	35.48	38.38	34.56	34.56	8.56	1.04	1.04	1.04	**1**	3.82	5.82	5.82	39.47	37.47
Component Mole Flow																
H_2O	kmol s-1	0	31.84	31.83	31.83	30.12	7.54	0.04	0.04	0.04	0	0.01	0.01	0.01	28.3	28.3
H_2	kmol s-1	0	0.1	1	1	1	1	1	1	1	**1**	0	0	0	0.1	0.1
O_2	kmol s-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	kmol s-1	0	3.54	1.73	1.73	0.02	0.02	0	0	0	0	0	0	0	0	0
CU^{++}	kmol s-1	0	0	0	0	0	0	0	0	0	0	0	0	0	2	2
CU^{+}	kmol s-1	0	0	1.81	0	0	0	0	0	0	0	1.81	1.81	1.81	0	0
H_3O^{+}	kmol s-1	0	0	0	0	1.71	0	0	0	0	0	0	0	0	1.54	1.54
OH^{-}	kmol s-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CL^{-}	kmol s-1	0	0	1.81	0	1.71	0	0	0	0	0	1.81	1.81	1.81	5.54	5.54
CUCL	kmol s-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CUCL(S)	kmol s-1	0	0	0	0	0	0	0	0	0	0	0	2	2	0	0
CU	kmol s-1	2	0	0.19	0	0	0	0	0	0	0	0.19	0.19	0.19	2	0
CU_2OCL_2	kmol s-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$CUCL_2$	kmol s-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Stream	**Units**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**37**	**38**	**39**	**40**	**FH2O**		
Temperature	C	150	375	375	375	530	530	530	20	375	50	400	42	120		
Pressure	bar	1	1	0.5	1	1	1	1	1	1	1	1	1	1		
Mole Flow	kmol s^{-1}	2	2	5.01	1	1	2.5	0.5	**0.5**	4	0	0	29.81	**1**		
Component Mole Flow																
H_2O	kmol s^{-1}	0	0	2	0	0	0	0	0	2	0	0	26.88	**1**		
H_2	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0		
O_2	kmol s^{-1}	0	0	0	0	0	0.5	0.5	**0.5**	0	0	0	0	0		
HCL	kmol s^{-1}	0	0	2	0	0	0	0	0	2	0	0	0	0		
CU^{++}	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0		
CU^{+}	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0		
H_3O^{+}	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	1.46	0		
OH^{-}	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0		
CL^{-}	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	1.46	0		
CUCL	kmol s^{-1}	0	0	0	0	0	2	0	0	0	0	0	0	0		
CUCL(S)	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0		
CU	kmol s^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0		
CU_2OCL_2	kmol s^{-1}	0	0	1	1	1	0	0	0	0	0	0	0	0		
$CUCL_2$	kmol s^{-1}	2	2	0	0	0	0	0	0	0	0	0	0	0		

Table 4.12: Stream table for the three-step cycle simulation

Stream	Units	S-4	14	21	S-1	3	4	S-8	6	13	19	S-2	5	S-6	FH20	8	S-3
Temperature	C	100	150	100	71.25	100	100	25	100	44.18	106.39	528.56	100	400	120	400	110
Pressure	BAR	24	1	24	1	1	1	6.5	1	1	1	24	1	1	1	1	1
Mole Flow	KMOL S-1	6.67	2.01	11.66	11.66	1.53	1	1	0.53	6.63	**6.67**	6.67	10.13	10.13	1	6.1	6.1
Component Mole Flow																	
H_2O	KMOL S^{-1}	3.05	0	4.66	4.66	0.53	0	0	0.53	4.63	4.63	4.67	4.13	4.14	1	4.1	4.1
H_2	KMOL S^{-1}	0	0	1	1	1	1	1	0	0	**0**	0	0	0	0	0	0
O_2	KMOL S^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	KMOL S^{-1}	0.39	0	0	0	0	0	0	0	2	1.96	2	0	0	0	2	2
CU^{++}	KMOL S^{-1}	0	0	2	2	0	0	0	0	0	0	0	2	2	0	0	0
CU^{+}	KMOL S^{-1}	0	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H_3O^{+}	KMOL S^{-1}	1.61	0	0.01	0.01	0	0	0	0	0	0.04	0	0	0	0	0	0
OH^{-}	KMOL S^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CL^{-}	KMOL S^{-1}	1.61	0.01	4	4	0	0	0	0	0	0.04	0	4	3.99	0	0	0
CUCL	KMOL S^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CUCL(S)	KMOL S^{-1}	0	1.99	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CU	KMOL S^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CU_2OCL_2	KMOL S^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$CUCL_2$	KMOL S^{-1}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Stream	**Units**	**9**	**S-7**	**11**	**15**	**S-5**	**S-9**										
Temperature	C	400	540	540	150	100	25										
Pressure	Bar	1	1	1	1	1	1										
Mole Flow	KMOL S-1	1.05	1.05	2.55	0.54	2.55	0.54										
Component Mole Flow																	
H_2O	KMOL S^{-1}	0.04	0.04	0.04	0.04	0.04	0										
H_2	KMOL S^{-1}	0	0	0	0	0	0										
O_2	KMOL S^{-1}	0	0	0.5	0.5	0.5	**0.5**										
HCL	KMOL S^{-1}	0	0	0	0	0	0										
CU^{++}	KMOL S^{-1}	0	0	0	0	0	0										
CU^{+}	KMOL S^{-1}	0.01	0.01	0.01	0	0.01	0										
H_3O^{+}	KMOL S^{-1}	0	0	0	0	0	0										
OH^{-}	KMOL S^{-1}	0	0	0	0	0	0										
CL^{-}	KMOL S^{-1}	0.01	0.01	0.01	0	0.01	0										
CUCL	KMOL S^{-1}	0	0	0	0	0	0										
CUCL(S)	KMOL S^{-1}	0	0	1.99	0	1.99	0										
CU	KMOL S^{-1}	0	0	0	0	0	0										
CU_2OCL_2	KMOL S^{-1}	1	1	0	0	0	0										
$CUCL_2$	KMOL S^{-1}	0	0	0	0	0	0										

4.8.3 Three-step cycle

The three-step cycle combines four of the five-step cycle's reaction steps into two reactions to result in three reaction steps. The three reaction steps are an electrolytic hydrogen production reaction, hydrolysis reaction and the oxygen producing decomposition reaction. The resulting flowsheet has much less equipment than the five and the four-step cycles. Figure 4.21 shows the final Aspen plus flowsheet used in the current study.

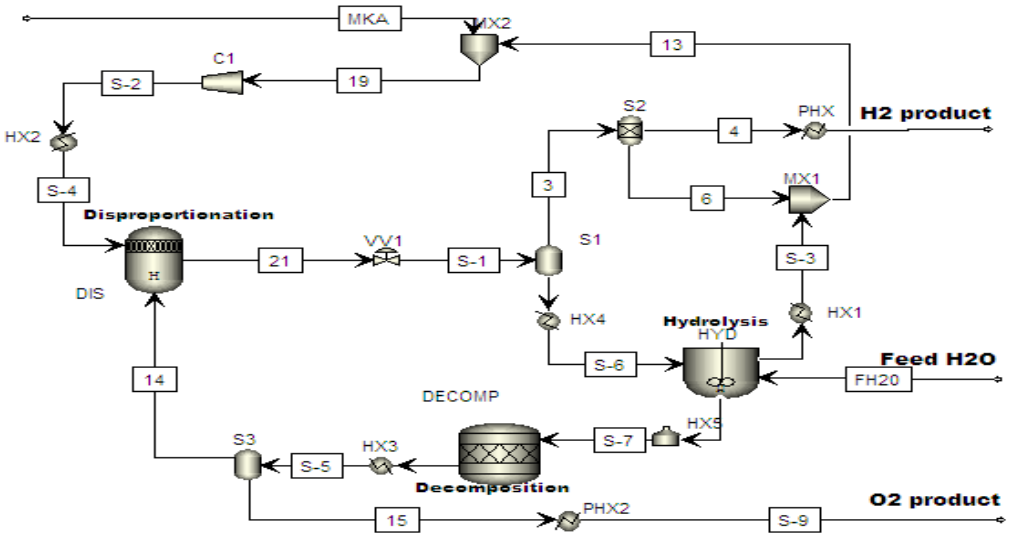

Figure 4.21: Three-step cycle simulation flowsheet

The three-step cycle, like the other flowsheets, operates as a closed cycle. Within the closed cycle, there are three reactive steps: hydrogen production, hydrolysis and decomposition.. In the Aspen Plus flowsheet used to study the three-step cycle, starts with the electrolytic hydrogen production stage in the reactor block DIS. Streams S-4 and 14 feed in HCl and CuCl, respectively. In the reactor a disproportionation of CuCl happens to produce hydrogen gas and $CuCl_{2(aq)}$. The products from DIS are released through Stream 21 where the pressure is reduced from 24 bar to 7 bar before separation. Using separator S1, the products at 7 bar, in Stream S-1, are separated into gas and liquid with the gaseous hydrogen going to Stream 3 and the liquid to Stream 5. The hydrogen in Stream S-8 still contains traces of water which are removed using separator S 2 to give hydrogen of 99.97% purity in Stream 4. Before release, the hydrogen is further cooled to a temperature of 25°C.

The $CuCl_{2(aq)}$ from DIS is separated as S1 bottoms. This is heated up to a temperature of 400°C in HX4 and then fed to the hydrolysis reactor, HYD in Stream S-6. Steam is also fed into reactor HYD through FH2O. The steam and the $CuCl_{2(aq)}$ react to produce Cu_2OCl_2 (s) and HCl(g). The HCl gas is cooled and mixed with Stream 6 and sent to MX2. In MX2 HCl top up is done to cater for trace losses of HCl in the hydrogen product Stream. The HCl from

MX2 is then compressed to 24bar in C1 and then cooled to reaction temperature for the disproportionation reaction. Cu_2OCl_2 (s) is sent to the decomposition reactor, DECOMP. In the decomposition reactor, the Cu_2OCl_2 (s) is thermally decomposed at 540°C to CuCl(l) and $O_{2(g)}$. Heat is recoved from the separated products and then CuCl (l) is sent so the disproportionation and the cycle resumes again. The oxygen is cooled to 25°C in PHX2 to give the final O_2 product. The stream summary is shown in Table 4.12.

4.9 Summary

Chapter 4 covers preparatory aspects of simulation, such as the selection of simulation package, thermodynamic model and simulation conditions for the simulation study of the copper-chlorine cycle. In the selection of simulation conditions, some of the conditions were extracted entirely from literature and other conditions were calculated using primary design calculations. The key output from this chapter was three complete Aspen Plus™ flowsheets which were used in the study of the copper-chlorine cycles. The results obtained from the simulation study are discussed in Chapter 5 of this dissertation.

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CHAPTER 5 : ENERGY AND COST ANALYSIS

Overview

In Chapter 5 simulation results are used to carry out energy and cost analysis of the copper-chlorine cycles. Section 5.2 discusses energy balances in the determination of energy requirements. Section 5.3 discusses the calculation of cycle efficiencies and Section 5.4 discusses the preliminary economics. Section 5.5 is the chapter summary which concludes Chapter 5.

5.1 Introduction

Simulation of the three, four and five reaction cycles was done in Aspen Plus™. Different Aspen Plus™ flowsheets were designed to represent the different copper-chlorine cycle configurations discussed in Chapter 4. In the development of the cycles, it was assumed that most of the reagents and intermediate reagents used in the cycle would allow the cycle to operate continuously in a closed loop with minimal top-up. The results of the different simulations are reported in the Sections 5.2-5.4. The results sections were structured to cover the expected key outcomes which are the energy requirements, cycle efficiencies and the process economics. The initial study was of the five-step simulation and the three and four-step cycles were done at a later stage for comparison. The analysis of the three and four-step cycles in all cases follows the structure of the analysis for the five-step cycle.

5.2 Energy Requirements

It is important to measure the energy requirements of the thermochemical cycle so as to measure how efficiently the cycle converts energy from the primary source to chemical energy in hydrogen. The efficiency of conversion of the cycle influences the overall cost of energy when hydrogen is reconverted at the time when it is required. In Section 5.2 the energy requirements for the three cycles are evaluated. As a check to the results of the simulations, theoretical energy requirements were first calculated in Sections 5.2.1-5.2.3. Once the expected values were determined, the simulation energy requirements were evaluated from the flowsheets developed in Chapter 4 in Section 5.2.4.

5.2.1 : Five-step copper-chlorine cycle simulation

Thermodynamic balances were carried out to determine the energy requirements of each cycle configuration. The overall balances were obtained by carrying out heat balances for each of the reaction steps in the cycle. Tables 5.1-5.4 are a record of the heat balances for the steps considered for the five-step cycle.

Table 5.1:Heat balance for the hydrogen production step

Heat Input	Heat Output
• Heat to remove moisture from Cu $=\Delta H(H2O_{(l,25°C)} \rightarrow H2O_{(l,100°C)} + \Delta H_{vap}(H2O)$	• Heat recovered from hydrogen cooling $=\Delta H(H_{2(l,475°C)} \rightarrow H_{2(l,25°C)})$
• Heat required to raise temperature of reactants to reaction temperature	• Heat recovered from CuCl cooling $=\Delta H(H_{2(l,475°C)} \rightarrow H_{2(l,423°C)}) + \Delta H_{fus}(CuCl(s\beta))$

Heat Input	Heat Output
• $=\int_{25}^{475} C_{p(Cu)}dT + \int_{25}^{475} C_{p(HCl)}dT$	• + $\Delta H(CuCl_{(s\beta,423°C)} \rightarrow CuCl_{(s\beta,412°C)}) + \Delta H_{fus}(CuCl(sc)) + \Delta H(CuCl_{(sc,412°C)} \rightarrow CuCl_{(sc,80°C)})$
	• Heat recovered from vapour from copper drying $=\Delta H(H_2O_{(l,100°C)} \rightarrow H_2O_{(l,25°C)} + \Delta H_{vap}(H_2O))$
	• Heat released by the exothermic reaction

(**Table 5.1** continued)

Heat balance for electrolytic disproportionation step

The disproportionation step is an electrolytic step which requires electrical energy. The overall reaction is as outlined in Equation 5.1.

$$4CuCl_{(aq)} \rightarrow 2CuCl_{2(aq)} + 2Cu_{(s)} \quad (5.1)$$

The reaction, however, occurs as two-step reaction with steps being shown by Equation 5.2 and 5.3

$$4CuCl_{(aq)} + 4Cl^-_{(aq)} \rightarrow 4CuCl^-_{2(aq)} \quad (5.2)$$

$$4CuCl^-_{2(aq)} \rightarrow 2CuCl_{2(aq)} + 4Cl^-_{(aq)} + 2Cu_{(s)} \quad (5.3)$$

The theoretical energy requirement is equivalent to

$$\Delta G = -nFE \quad (5.4)$$

n = number of transferred electrons, *F* is the Faraday's constant and *E* is the cell potential. *E* is dependent on the cell design. Lewis *et al*. (2009) suggest 0.5V as a practical value based on research carried out for the Sulphur Iodine cycle electrolyser. For energy calculations, the electrical energy amount has to be converted to thermal energy based on the thermal to electrical conversion efficiency. The thermal to electrical energy conversion coefficient can be assumed to be 50% based on a similar process (Gorensek & Summers, 2008).

Heat balance for the drying step

In essence, step 3 is not a reactive step but is considered as an independent step as there is a transformation of copper dichloride from an aqueous form to a solid crystalline form. The considerations made in the heat balance are presented in Table 5.2

Table 5.2: Heat balance for the drying step

Heat Input	Heat Output
• Heat required to dry the copper dichloride crystals after crystallization and dewatering $=\Delta H(H_2O_{(l,42°C)} \rightarrow H_2O_{(l,100°C)}) + \Delta H_{vap}(H_2O)$	• Heat expelled from cooling $CuCl_2(aq)$ in crystallizer
	• Heat recovered from water evaporated from $CuCl_2(s)$ crystals

Table 5.3: Heat balance for the hydrolysis step

Heat Input	Heat Output
• Heat required to heat reactants to reaction temperature= $\int_{120}^{530} C_{p(H_2O)} dT + \int_{375}^{530} C_{p(CuCl_2)} dT$	
• Energy to enable the endothermic hydrolysis reaction to proceed.	

Table 5.4:Heat balance for the decomposition step

Heat Input	Heat Output
• Heat required to heat reactants to reaction temperature= $\int_{375}^{530} C_{p(Cu_2OCl_2)} dT$	• Heat recovered from oxygen cooling= $-\int_{25}^{530} C_{p(O_2)} dT$
• Energy to enable the endothermic hydrolysis reaction to proceed.	• Heat recovered from CuCl cooling= $\Delta H(CuCl_{(l,530°C)} \rightarrow CuCl_{(l,423°C)}) + \Delta H_{fus}(CuCl_{(s\beta)}) + \Delta H(CuCl_{(s\beta,423°C)} \rightarrow CuCl_{(s\beta,412°C)}) + \Delta H_{fus}(CuCl(sc)) + \Delta H(CuCl_{(sc,412°C)} \rightarrow CuCl_{(sc,80°C)})$

Consolidating all the considerations in energy balances in Tables 5.1-5.4, the overall balance can be obtained as summarized in Table 5.5

Table 5.5: Overall heat balance of the five-step copper-chlorine cycle

Heat Output		**Heat Input**	
Step Description	*Energy* (kJ mol^{-1} H_2)	*Step Description*	*Energy* (kJ mol^{-1} H_2)
Hydrogen cooling 475-20°C	-13.195	Copper preheating for hydrogen reaction (80-475°C)	21.8
Oxygen cooling 530-40°C	-7.53	Copper drying	29
Hydrogen production reaction heat	-45.742	Decomposition reaction heat	129.1
CuCl product cooling (475-80°C), (530-80°C)	-160.7	Hydrolysis reaction heat	116.6
		Water preheat	53.9
Total output	-227.167	HCl preheating	22.1
Theoretical heat recovery efficiency	72%	$CuCl_2$ preheating for hydrolysis (150-375°C)	32.5
		$CuCl_2$ drying	97.8
		Electrochemical work	192.6
Max recoverable output	-163.56	*Total Input*	695.4
Net heat			**531.84**

Table 5.5 shows that the cycle theoretically has a heat requirement of 531.84 kJ mol^{-1} H_2.. The auxiliary work energy, which includes pumping and separation energy, also not included in the balance, is 28 kJ mol^{-1} H_2. Adding the thermal and auxiliary work, the five-step copper-chlorine cycle theoretically requires 559.84 kJ mol^{-1} H_2

5.2.2 Four-step copper-chlorine simulation

The energy requirements of the four-step simulation were done in a similar manner to the five-step cycle. The summary of the energy requirements calculation considered in the balance are summarized in Table 5.6.

Table 5.6: Four-step cycle energy balance

Heat Output		**Heat Input**	
Step Description	*Energy (kJ mol^{-1} H_2)*	*Step Description*	*Energy (kJ mol^{-1} H_2)*
Hydrogen cooling 475-20°C	-13.195	Copper preheating for hydrogen reaction (80-475°C)	21.8
Oxygen cooling 530-40°C	-7.53	Decomposition reaction heat	129.1
Hydrogen production reaction heat	-45.742	Hydrolysis step	194.2
CuCl product cooling (475-80°C), (530-80°C)	-160.7	Water preheat	53.9
		HCl preheating	42.1
Total output	-227.167	$CuCl_2$ preheating for hydrolysis (150-375°C)	62.5
Theoretical heat recovery efficiency	72%	Electrolysis heat equivalent energy	192.6
Max recoverable output	-163.56	*Total Input*	696.2
Net energy			**532.64**

From Table 5.6 the process energy requirements are 532.64 kJ mol^{-1} H_2. Theoretically, the overall heat requirements would then include the auxiliary work which is 32 kJ mol^{-1} H_2. The theoretical overall energy requirement is thus 564.64 kJ mol^{-1} H_2.

5.2.3 Three-step copper chlorine simulation

The energy balance of the three-step cycle was done in a similar manner to what was done in the four and five-step balance to yield an energy requirement of 580.61 kJ mol^{-1} H_2.

5.2.4 Simulation overall energy requirements

The simulation heat requirement was calculated as the sum of the duties of all the individual blocks in the flowsheet and the net energy requirement for the heat exchanger network. The operating unit block duties were extracted from Aspen Plus™ and heat exchanger network

heat requirements were calculated and optimized with the aid of Aspen Energy Analyzer™ v7.1. Table 5.7 compares the simulation energy requirements to the expected values.

Table 5.7: Comparison of expected and actual energy requirements and efficiencies

Cycle	Energy Requirements (kJ mol^{-1} H_2)		
	Calculated	**Simulated**	**Literature**
Three-step	580.61	809.07	584.73 (Lewis *et al.*, 2009)
Four-step	564.64	625.20	543.70 (Chukwu, 2008)
Five-step	559.84	583.84	562.40 (Wang *et al.*, 2009)

Table 5.7 summarizes compares the expected energy requirements and the actual from simulation and also tabulates the deviation. From Table 5.7, the three and four step cycles show large deviations between the calculated values and the obtained values. In both cases, the expected heat recovery was much more than the actual recovered heat. Some of the low grade heat, which could not be re-used elsewhere in the process, was accounted as recoverable in the theoretical calculations. The highest contributor of this low grade unrecoverable energy was the low temperature electrolytic reaction step for both the three and four step cycles. Significant amounts of electrical energy are used in disproportionation without producing significant heat hence the difficulty of recovery.

Despite the deviations, the results indicate that the energy requirements increase with a decrease of the number of steps in the cycle. Wang *et al.* (2009), in their comparison of the cycles, suggest that the heat requirements increase as steps are combined. Chukwu (2008) reports energy requirements of 584.73 kJ mol^{-1} H_2 and 543.7 kJ mol^{-1} H_2 for his three and four step cycle simulations. Lewis *et al.* (2009) obtained 604 kJ mol^{-1} H_2 for the three step cycle simulation which is relatively close to Chukwu's heat requirements. Wang *et al.* (2009) report a heat requirement of 554.7 kJ mol^{-1} H_2 for the five step cycle which is relatively close to the 583.84 kJ mol^{-1} H_2 obtained in this study's five step simulation. The differences in energy requirements between Chukwu's and Lewis's energy requirements and the current study are attributable to the heat recovery calculation differences. Chukwu did not match heat recovery between streams but rather did a quantitative offset calculation of the heat input and outputs whereas in the current study, energy exchange between streams was matched to avoid heat exchange crossovers.

5.3 Efficiency calculation

Equation 5.5 was used to evaluate cycle efficiencies. Lewis *et al*. (2009), Chukwu (2008) and Law also used Equation 5.5 for efficiency calculations in the evaluation of efficiency in their comparisons of thermochemical systems.

$$\text{Efficiency, } \eta = \frac{\Delta H^f_{H_2O}}{Q_{total} + \frac{W}{0.5}} \tag{5.5}$$

where

$\Delta H^f_{H_2O}$ – Standard enthalpy of formation of water at 25°C.

Q_{total} – The total thermal energy supplied from external sources.

W- Work, which incorporates electrical, chemical and mechanical work, supplied into the cycle.

The work term is converted into thermal equivalent after calculation via division by the work to thermal efficiency which is an average of 50% in thermochemical cycles (Lewis *et al.*, 2009). Three important work components considered in the work calculations are the chemical work, separation work and the electrical work. The electrical work is especially important for the disproportionation step. The heat equivalent chemical work is equal to the reaction free energy of the system and is included in the work term for efficiency calculation if it has a positive value. A negative term indicates theoretically recoverable energy (Lewis *et al.*, 2009). Equation 5.6 and 5.7, respectively, calculate the electrical and ideal separation works.

$$\Delta G = -nFE^0 \tag{5.6}$$

where n-number of electrons being transferred

F- Faraday's constant

E^O- Cell potential as calculated by the Nernst Equation, given reactant and product concentrations

$$\Delta G = RT \sum_{i=1} n_i \ln y_i \tag{5.7}$$

where R- Universal gas constant

T- Absolute temperature

n_i- The amount of material being separated

y_i- The mol fraction of component being separated

Demonstrative calculations were done with five-step cycle data and the procedure repeated for the three and four-step cycles. The applications of efficiency calculations for the copper-chlorine cycle were done in two phases. The first efficiency calculation was done using the theoretical balance energy requirements. The second calculation was done using the heat duties of blocks from the simulation and design of the heat exchanger network. Equation 5.8 is a demonstration of how simulation based efficiency was calculated. A summary of the efficiencies for the three, four and five reaction cycles is given in Table 5.8

Simulation based cycle efficiency

$$\eta_{Simulation} = \frac{\Delta H^{f}_{H_2O}}{Q_{total} + \frac{W}{0.5}} = \frac{241.83}{583.76} \times 100\% = \mathbf{41.42\%} \quad (5.8)$$

Table 5.8: Summary of calculated efficiencies for the simulated copper-chlorine cycles

Description	Current Study	Lewis	Chukwu	Wang*
Five-step cycle				
Overall Energy	583.84	n/a	n/a	562.4
Efficiency	41.42	n/a	n/a	43
Four-step cycle				
Overall Energy	625.2	n/a	543.7	n/a
Efficiency	38.68	n/a	44.5	n/a
Three-step cycle				
Overall Energy	809.07	598.6	584.73	n/a
Efficiency	29.89	40.4	41.65	n/a

* It is not clear how these values were derived by Wang *et al*.(2009), whether by simulation or by theoretical calculations

* n/a- information not available

The cycle efficiency is directly related to the overall energy requirements as the efficiency is the ratio of heat of formation of hydrogen to the energy requirement of the cycle. The relationship between efficiency and overall heat requirement is inverse in nature as the overall heat requirement is in the denominator of the calculation. Table 5.8 summarizes the cycle efficiencies. From Table 5.8 it is evident that the efficiencies of the cycles increase with an increase in the number of reaction steps involved. The decrease in efficiency is caused by the combination of steps where one of the combined steps requires a large input of energy and as such lowers the heat utilization effectiveness of the cycle. An example of such a scenario is in the removal of the drying step in the five-step cycle to form the four-step cycle. The efficiencies for the four-step cycle agree with efficiencies reported by

Chukwu (2008) at around 40%. As expected, the five-steps cycle is also close to the four-step efficiency having a marginally higher efficiency at 41.42%. Lewis (2009) and Chukwu (2008) report 40% and 41.35% respectively, for the three-step cycle and these differ significantly with obtained results for the three-step simulation at 29.89%. The evident trend, however, is that, as the steps increase, the efficiency increases.

5.4 Preliminary process economics

5.4.1. Introduction

According to Goldratt and Cox (1993), the goal of every manufacturing process is not to be efficient or have high utilization but to make money. As a consequence, when designing a process, checking economic viability is important at all the different stages from conceptual design to actual construction and commissioning. One of the most important objectives of the economic viability assessment is to make sure that all the design choices made, ensure a return on the investment on the process (Smith, 2005). Companies tend to use borrowed capital to build processes and the lenders provide this capital expecting a return on their investment (Holland and Wilkinson, 1997). The process of sourcing capital requires sound justification to attract investment and the results of economic viability analysis play an important role in providing justification.

In this simulation study report, the preliminary economics for the three forms of the copper-chlorine cycle simulated were done together. The key objectives of the preliminary economics analysis were to estimate the capital requirements and the hydrogen price required to make the capital investment sustainable.

5.4.2 Assumptions

A few basic assumptions were made to simplify the preliminary economic analysis and the key assumptions are:

i. *Plant is one hundred percent equity funded*: There are two methods of raising capital: debt financing or equity financing. Companies normally have a mixture of debt and equity financing as a source of start-up capital. According to Marsh (1982), equity financing is less risky as there is no obligation to pay back the invested money. A hundred percent equity funded scenario has the least liability if the complete capital requirement can be raised.

ii. *The construction of plant is completed in 24 months and the capital expenditure is spread over the 24 months*: Based on the project life analysis done by Boyce *et al.*

(2004), a typical large centralized hydrogen plant takes approximately 24 months to construct.

iii. *Five year depreciation schedule*:

The South African Revenue Service gives guidelines on maximum allowable deductions for wear and tear of equipment. In Interpretation note number 47 of Act number 58 of 1962 section 11(e), the guidelines specify that an average of 20% of plant cost can be deducted annually as a provision for depreciation of plant (South African Revenue Service, 2009).

iv. *20 year plant operating life*: Based on literature examples, it is common to assume that plant life of a chemical process plant is 20-30 years (Sinnot, 2005;Smith, 2005;Holland and Wilkinson, 1997)

v. *5 year payback period*: Because the priority is to determine the hydrogen price that would make the respective capital investments sustainable, the plants were assumed to be economically viable. According to Black & Veatch(1996), a typical payback period for a typical plant is 17-33% of the plant operating life. As a result of this assumption, the ultimate economic viability for this study is not based on the payback period but on the comparability of the final hydrogen cost to the current global energy costs.

vi. *Taxation rate is defaulted to 28%*: The company tax rate for 2009 to 2010 was set at 28% by the South African Revenue Services (2009). For all economic analyses the set rate will be used for calculations.

vii. *The discounted cash flow rate is set at 14.9%*:

The discount rate is calculated as the sum of the risk free rate and the equity risk premium (Power, 2004).The risk free rate is 9.4% and the equity risk premium rate is 5.5% (First National Bank, 2011).

viii. *Net Present Value analysis is used in the analysis*:

There are many approaches to economic viability analysis. Some methods make maximizing the profit the key objective and others consider the return on investment as the primary objective. According to Smith (2005), the best methods of assessing viability make use of cash flow analysis. There are a number of numerical indicators which capture different aspects of cash flow patterns which are useful in assessment of economic viability including payback period, return on investment, net present value and discounted cash flow rate of return (Douglas, 1988;Smith, 2005). Net present value and Discounted Cash flow rate of return approaches tend to be preferable as they consider the time value of money and as such were used in this analysis. Using the net present value analysis in a spreadsheet, possible hydrogen prices were calculated for the three, four and five-step cycles

5.4.3. Capital cost estimation

There are many considerations that need to be taken into account in assessing the economic viability of a process but some the key considerations include: capital requirements, operational expenses, cost of capital, projected revenues and the patterns of cash flow (Smith, 2005). Expected revenues and cost of capital tend to be market driven factors which are beyond the control of the designer but optimization of operational and capital costs is possible during design. The costs of equipment and the related costs to join the equipment units into a functional process make up the capital requirements of the process. The most important equipment costs are broken down as (Smith, 2005):

- *Battery limits investment*: This is the investment made into acquisition of process equipment and the respective buildings to house the equipment. These costs exclude utility generation, distribution and environmental obligation fees (Smith, 2005).The main cost is the cost of equipment which depends on the size, material of construction and operating conditions of the different individual pieces of equipment (Holland and Wilkinson, 1997). For the current project, these battery costs should be significant, as the plant is a new development.
- *Utility investment*: This is the investment made into utility plant covering generation and distribution of different utilities on site (Smith, 2005).Utilities considered for the current simulation include process water, cooling water, electricity and helium (Assuming high temperature source is a Gas Cooled Nuclear reactor)
- *Offsite investment*: The investment on auxiliary facilities such as offices, medical facilities, staff canteen, roads, waste disposal systems and other associated services that are not core process aspects (Smith, 2005).
- *Engineering fees*: These are development costs normally associated with development of plant and installation of equipment (Smith, 2005).
- *Working capital*: This investment covers costs met before revenue starts coming in, such as raw materials for startup, catalysts, solvents and intermediate products, startup labor and other related costs. Working capital is theoretically recoverable when the plant closes down (Holland and Wilkinson, 1997). For the copper-chlorine cycle to operate as a closed cycle, all intermediate compounds would need to be purchased at startup. These intermediate compounds and raw materials include copper particles, HCl gas, copper chloride, copper dichloride, steam and copper oxychloride.

Primary capital costs are comprised of costs of the equipment in use for a process. Normally there is some basic equipment used for calculation of capital costs of the process. For the simulated copper-chlorine cycle, Table 5.10 lists the basic equipment.

5.4.4 Estimation of purchased equipment cost

The purchased cost of equipment is the basis for many capital estimation methods. The most accurate way of calculating the purchased cost of equipment is to get quotations from equipment suppliers but sometimes this might not be possible. In such cases where it is not possible to get quotes, equipment cost databases can be used to estimate new equipment costs. Where these databases are used, it is often necessary to adjust for capacity and to update the calculation period. Calculation of cost by scaling, shown in Equation 5.9, is one commonly accepted method of evaluating purchase costs of equipment (Peters *et al.*, 2004).

$$PC=PC_B \cdot \left(\frac{CEPCI_{2010}}{CEPCI_{2007}}\right) \cdot \left(\frac{C}{C_B}\right)^m \cdot f_L \qquad (5.9)$$

where:

PC_B- Baseline purchase cost

PC-Equipment purchase cost

C_B -Baseline equipment capacity

C- Equipment capacity

m- Plant capacity exponent

f_L –Lang factor for adjustment of pressure, temperature and location.

$CEPCI_{2007}$- 2007 Chemical Engineering Plant Cost Index (Assuming base year is 2007 which is convenient because a database of 2007 equipment costs is available online from Matches (2011).

$CEPCI_{2010}$- 2010 Chemical Engineering Plant Cost Index

As a demonstrative calculation, the purchased cost of a carbon steel phase separator of diameter 3.92m can be calculated using the purchase cost of a carbon steel with diameter 2m purchased in 2007 at $78400. Using the scaling method in Equation 5.9, C_B= 2m, C=3.92m, PC_B=$78400, from data tables m=0.91 (Smith, 2005). $CEPCI_{2007}$=525.4 and $CEPCI_{2010}$=556.4. Using these data;

$$PC = 78400 \times \left(\frac{556.4}{525.4}\right) \times \left(\frac{3.92}{2.0}\right)^{0.91} = \$152{,}456 \quad (5.10)$$

The calculations done in Equation 5.10 were repeated for all pieces of equipment for the three, four and five-step cycles. Table 5.9 is a summary of the basic equipment that was used in the calculation of purchased equipment cost. Lang factors were used to adjust for pressure, temperature and location. The data and resulting purchase costs are summarized in Appendix C.

Table 5.9: Basic Equipment list

5 Step cycle	4 Step cycle	3 Step cycle
Hydrogen reactor	Hydrogen reactor	Disproportionation reactor
Disproportionation reactor	Disproportionation reactor	Hydrolysis reactor
Crystallizer	Phase separator	Decomposition reactor
Drum Filter	Hydrolysis reactor	HCl cooler
Evaporative dryer	Decomposition reactor	$CuCl_2$ preheater
Phase separator	HCl preheater	CuCl Quenching Cell
Hydrolysis reactor	Cu preheater furnace	Wet cyclone
Decomposition reactor	CuCl Quenching Cell	Compressor
HCl preheater	Wet cyclone	Condenser
Cu preheater furnace	Compressor	Phase separator
CuCl Quenching Cell	Condenser	CuCl heat recovery exchanger
Wet cyclone	Phase separator	Oxygen cooling system
Compressor	CuCl heat recovery exchanger	Hydrogen cooling system
Condenser	Oxygen cooling system	Mixer
Phase separator	Hydrogen cooling system	Mixer
CuCl heat recovery exchanger	Mixer	
Oxygen cooling system	Mixer	
Hydrogen cooling system	Screw conveyor	
Mixer		
Mixer		
Screw conveyor		

5.4.5 Estimation of capital investment requirement

Once the major equipment cost has been calculated, there are several methods that can be used to determine the total investment requirement. Some of the popular methods include scaling factor applied to total investments on similar plants, detailed item estimates, use of Lang factors (Peters *et al.*, 2004). The Lang factor method works by multiplying the basic equipment cost by multiples which factor in the remaining capital components to obtain the

total investment required. The Lang factor method was used in this study and the total investment cost was calculated as,

$$\text{Total Capital Investment (TCI)} = f_{SF} \times \Sigma PC \quad (5.11)$$

In Equation 5.11 f_{SF} is the Lang factor for a Chemical process which processes solids and fluids and ΣPC is the total Purchased equipment cost.

5.4.6 Total product cost calculation

For a new product or process, most costs components of product cost are not accurately known and experience based order of magnitude estimates are commonly used (Sinnot, 2005). The total product cost consists of a variable component and a fixed component. The variable component is made up of raw material costs, utilities, catalysts and solvents and distribution and packaging costs. The fixed production costs include maintenance, operating labour, laboratory costs, supervision, plant overheads, insurance, process royalties and local taxes. Once the direct variable and direct fixed components have been evaluated, the indirect component of product cost is evaluated. The indirect cost is made up of sales expenses, general overheads and research and development costs. Where they are not known exactly, they can be expressed as a fraction of the direct costs.

In the current study many of the costs were not known and product cost was estimated using operating labour, materials and utilities cost and the fixed capital investment. To start off the process, raw materials and intermediates cost were determined from the flowsheet and respective cost information – these formed the core direct variable expenses. Labour estimation was then done to determine the manpower requirements. Labour costs were used to estimate laboratory costs, supervision costs and plant overheads the sum of which can be approximately 1.73 times the labour cost (Holland and Wilkinson, 1997). Maintenance, local taxes and royalties were calculated as fractions of fixed capital investment being typically 18% of fixed capital investment (Sinnot, 2005). According to Sinnot, the indirect costs are typically 30% of the direct costs. The calculations are summarized in Equations 5.12- 5.16

Direct variable costs= cost of materials +cost of utilities+ distribution and packaging (5.12)

Direct Fixed costs= 0.18 FCI + 1.73 labour cost (5.13)

Indirect production costs = 1.3 × (direct fixed costs+ direct variable costs) (5.14)

Total product costs = (indirect costs + direct fixed costs +direct variable costs) (5.15)

= 0.18 ×FCI + 2.73×labour costs + 1.23×materials and utility costs

Final product cost ($/kg) = Total product cost($)/ Annual production capacity (kg) (5.16)

Using Equations 5.12- 5.16 and a spreadsheet, the cost distribution was evaluated summarized in Table 5.10.

Table 5.10: Cost distribution for hydrogen production

Description	Cost ($ kg^{-1} H_2)		
	3 step	4 step	5 step
Direct variable costs			
Materials	0.19	0.19	0.19
Utilities	0.91	0.70	0.43
Direct fixed costs			
Labour	0.01	0.01	0.02
Maintenance, Royalties& Municipal taxes	0.42	0.48	0.66
Indirect costs	2.00	1.80	1.68
Total product cost	**3.53**	**3.19**	**2.98**

Several process economics scenarios were analysed to see a practical product cost range. For a five to ten year payback analysis, the average costs of hydrogen obtained were $3.53, $3.19 and $2.98 per kg for the three, four and five reaction cycles, respectively. Several values are available in the literature for the different cycles all being comparable to the values obtained in the current study. Lewis *et al.* (2009) suggest a hydrogen cost of $3.37 per kg of hydrogen for the three-step cycle which is which is lower but comparable to the $3.50 per kg average obtained in this study for a 5 to 10 year payback period. Orhan *et al.* (2010) report $ 2.20 per kg of hydrogen for the four-step cycle after adjusting for baseline costs and capacity. Wang *et al.* (2009) propose hydrogen cost of between $1.65-2.06 per kg of hydrogen for the five-step cycle and this is again lower but comparable to the cost obtained in this study. Summers (2009) suggests that a realistic cost range for hydrogen production using thermochemical cycles should be $4.15-$7.10 per kg of hydrogen. It is important to note that Summer's evaluation excludes the sale of by-product oxygen. If sales of oxygen are excluded in the current evaluations, costs obtained are $5.78, $5.43 and $5.23 for the three, four and five-step cycles, respectively which are within Summers' range. Comparing the cycle configurations, the five-step cycle provides the lowest average cost at $5.22 per kg of hydrogen for a 5-10 year payback period. These prices are lower than energy from petrol which is $5.82 per kg hydrogen equivalent; hence the three copper-chlorine configurations are economically competitive.

5.4.7 Hydrogen cost sensitivity

Several analyses were done to determine the stability of the hydrogen cost but most attention was given to understanding the effects of cost of capital, taxation, cost of raw materials and energy. Figures 5.1-5.4 are a graphic summary of the sensitivity studies. Effects of cost of capital and taxation, shown in Figures 5.1 and 5.2, were analyzed by varying the percentages of the variable under study. Effects of the energy and raw material, were illustrated in Figures 5.3 and 5.4. Costs were studied using a cost ratio where the cost ratio is the ratio of the cost being used to the baseline cost. As an example, if the baseline energy cost, which was studied using cost of utilities, was $100million, a cost ratio of 0.9 would imply that the cost being used in the sensitivity study is $90million.

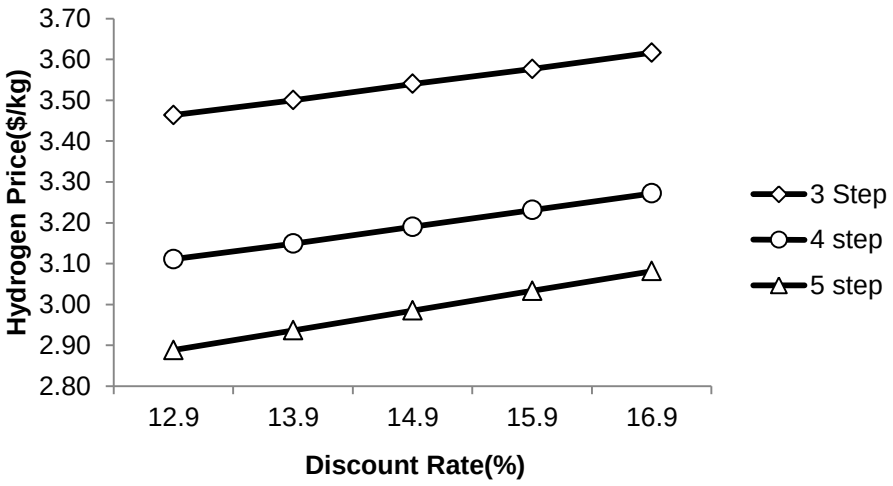

Figure 5.1: Hydrogen price sensitivity to discount rate

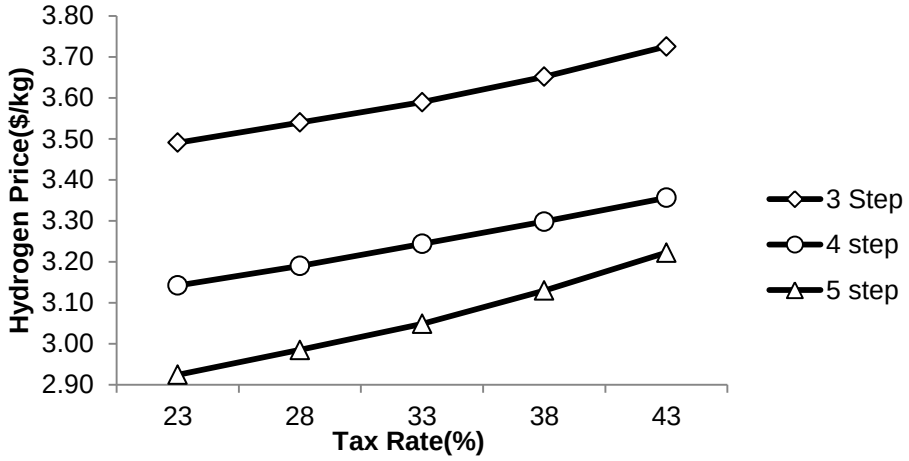

Figure 5.2: Hydrogen price sensitivity to tax rate

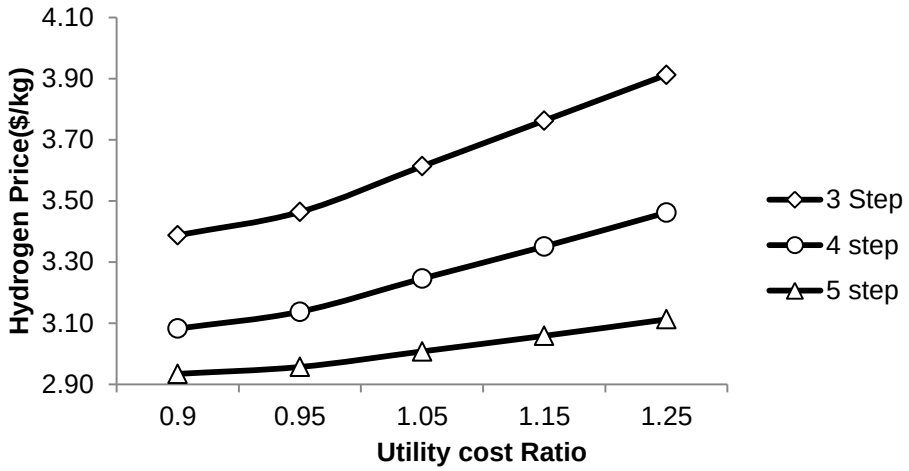

Figure 5.3: Hydrogen price sensitivity to utility costs

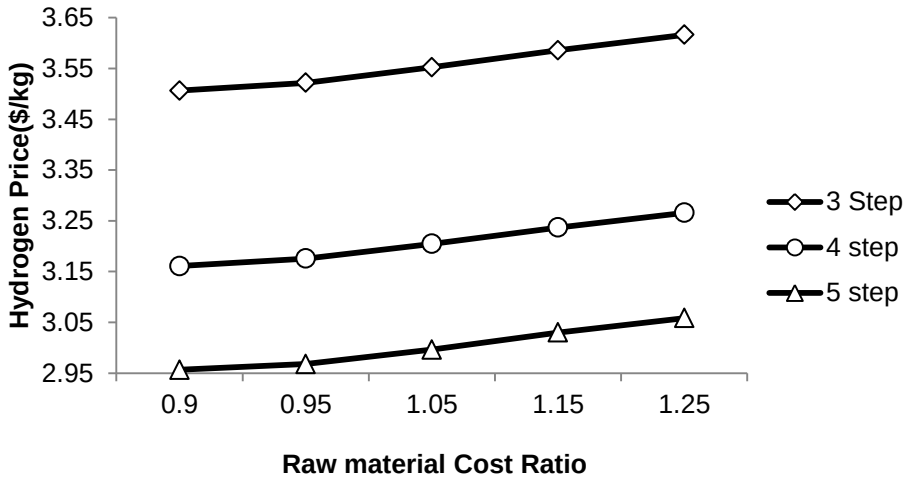

Figure 5.4: Hydrogen price sensitivity to cost of raw materials and intermediates

The sensitivity analyses show that the hydrogen price is most sensitive to the cost of capital, followed by the cost of energy (cost of utilities), taxation and least sensitive to the cost of raw materials. Lewis *et al.* (2009) also report higher sensitivities to cost of capital and cost of energy for their three-step cycle simulation. The low sensitivity to cost of raw materials was as expected as the cycle operates as a closed loop which recycles materials with the exception of water which is consumed as hydrogen and oxygen are taken out of the system. For all the parameters studied, it was observed that the effect of a shorter payback period was strongest on the five-step cycle. For most cost parameters, halving the payback was observed to cause an average of 28% change in the price for the five-step cycle, compared to 17.7% and 21% for the three and four-step cycles.

5.4.8 Economic analysis summary

Table 5.11 summarizes the key economic results, which are the capital requirements, hydrogen price and the respective project Net Present Values. The Net Present values were included to allow comparison of the economic viability of the different plant configurations.

Table 5.11: Summary Economic Analysis Results

Cycle	Current study		Literature		
	CAPEX ($millions)	Price ($/kg)	CAPEX ($millions)	Price ($/kg)	Source
Three-step	273	3.53	190	3.30	(Lewis *et al.*, 2009)
Four-step	300	3.19	320	2.20	(Orhan *et al.*, 2010)
Five-step	370	2.98	360	2.02	(Wang *et al.*, 2009)

The economic evaluation of the three copper-chlorine cycle configurations simulated was done, excluding costs of establishing primary energy source. The results summarized in Table 5.11 were obtained. Five and ten year payback scenarios were analyzed, both giving different cost parameters. As expected the five-step cycle has a higher capital cost than the three and four-step cycles. The higher capital cost of the five-step cycle does not, however, translate to a higher hydrogen cost. Comparative costs of plant for the five-step cycle are not explicitly available in literature as simulation derived. Orhan *et al.* (2010) report a capital of approximately $320 million, after adjusting for capacity and proximity variations, for the four-step cycle which is closely comparable to the capital requirements obtained in this study. For the three-step cycle, Lewis *et al.* (2009) report a capacity adjusted capital requirement of $190million, which is much lower than the $280million obtained in this study.

Figure 5.5 shows the cumulative cash flow summary for the three copper-chlorine configurations. At the prices tabulated in Table 5.11 for the current study, internal rates of return of 26.52%, 26.56% and 26.65% were obtained for the five, four and three-step cycles, respectively. The three-step cycle has a marginally higher internal rate of return implying it is a more attractive process configuration from an investment perspective. Despite having a lower efficiency and marginally higher hydrogen costs, the low capital requirement is a strong influence to select the three-step configuration as the best configuration from an economic standpoint.

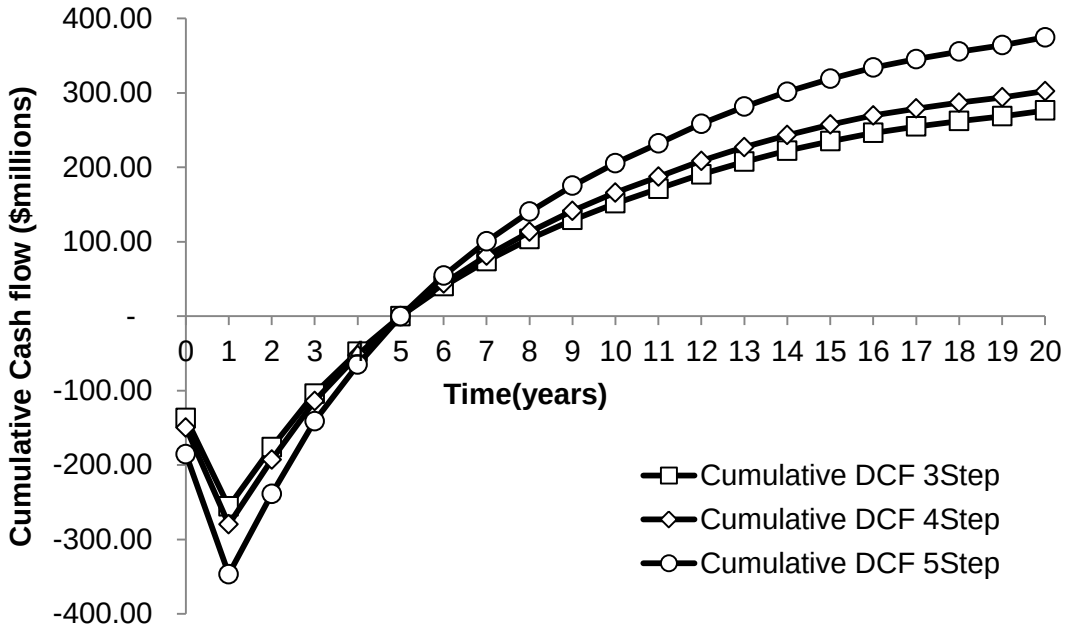

Figure 5.5: Cumulative cash flow analysis for copper-chlorine cycle configurations

5.5 Summary

In Chapter 5 the key results, the overall energy requirements, cycle efficiencies and preliminary economics of the simulation studies are reviewed. The five-step cycle gives the highest cycle efficiency and lowest hydrogen cost though it requires a significantly higher capital investment than the three and four-step cycles. The three-step cycle though, having a much lower efficiency than the five-step cycle, has a higher project internal rate of return which may make it marginally more attractive. If the low efficiency of the three-step cycle can be improved, the three-step configuration should offer the best economic performance and as such is the most promising configuration from the current analysis.

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CHAPTER 6 : CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In this dissertation, hydrogen is discussed as a possible solution to storage of excess energy from alternative and renewable energy sources. From the literature, the copper-chlorine cycle has high potential for commercialisation. The three main cycle configurations of the copper-chlorine cycle were simulated and compared to determine the best configuration. From the simulation study it can be concluded that:

- The five-step cycle has the lowest energy requirement, requiring an energy input of 583.84 kJ mol^{-1} H_2. The four-step cycle requires a slightly higher energy requirement at 625.20 kJ mol^{-1} H_2 due to the increased heat requirement for the hydrolysis step. The three-step cycle has the highest energy requirement, i.e. 809.07 kJ mol^{-1} H_2, resulting from the high electricity requirement for creating high pressure conditions and electrolytic hydrogen production.
- Connected to the energy requirements, the five-step cycle has the highest simulated efficiency at 41.42%, followed by the four-step cycle at 38.68%. The three-step cycle has the lowest cycle efficiency at 29.89% due to high electrical energy requirement and low thermal to electrical energy conversion efficiencies.
- The three-step cycle requires the least capital investment, $275 million, as it has the least equipment requirements. The four-step cycle has a capital requirement of $300 million and the five-step cycle has a capital requirement of $370 million. The five-step cycle has many split steps that require separate equipment hence the higher capital cost in comparison with the more integrated three-step cycle.
- The five-step cycle gives the lowest hydrogen price, $2.98/kg, due to lower energy and operating costs. The four-step cycle offers a slightly higher hydrogen price at $3.19/kg and the three-step cycle has the highest price at $3.53/kg
- Despite having a higher capital cost, the five-step cycle is the best cycle configuration as it converts the most primary energy to chemical energy in hydrogen and offers hydrogen at a reasonably low price at less than $3/kg.

6.2 Recommendations

Aspen Plus™ steady state simulator is a very robust software which allowed the simulation of the copper-chlorine thermochemical cycle for hydrogen production to produce practical results. Limited property data was available for some solid components, such as copper oxychloride, which limited the flexibility of some of the iterative calculations in solving the closed cycle flowsheets. Another challenge with solids was that the inbuilt reactor models

have limited capability when presented with three phases. An example of such a case is where a solid reacts producing a liquid and a gaseous product such as in the decomposition reaction. If a thermodynamic package that has better solid handling capabilities could be found, it would be interesting to simulate the copper-chlorine cycles and compare the results of the other package with those obtained using Aspen Plus™. One such consideration is the OLI package.

In as much as the reliability of the results produced is concerned, some adjustments could be made to the flowsheets to include size correction of solids. For all three cycle configurations, the current study excluded particle size effects on conversion in reactions such as the hydrolysis and decomposition steps. If particle size correction was to be considered, the energy requirements information would probably be different as particle size correction circuits would use energy. The effect of size correction could alter the efficiency performances of the cycle configurations and as such would need to be studied.

Some of the remaining challenges would need to be looked at once the primary energy sources have been specified. The most probable candidates, nuclear and solar still have many challenges which would affect the economic competitiveness of the copper-chlorine cycle.

APPENDICES

Appendix A: Extra thermochemical cycle detail

A.1: Hybrid sulphur cycle

The hybrid sulphur (HyS) cycle was developed by the Westinghouse gas corporation and reported in NASA research documents from the early seventies e.g. in the April 1976 NASACR-134976 contract report (Nuclear Energy Agency, 2004). The HyS cycle was re-popularised in the recent years by work done for US Depart of Energy (US-DOE) reported in publications by Summers and Gorensek. Two publications are notable, an annual report by Summers *et al.* on the process development work on the HyS process,(Summers, 2008) and a report on the Aspen plus simulation and flowsheet optimization work done by Summers and Gorensek (2009). The two documents give a detailed outline of the chemistry, energy consumption and crude preliminary economics of the HyS process, some of their findings are discussed briefly in the following paragraphs.

Chemistry:

The hybrid sulphur process is a simple all fluid, two reaction cycle comprising of the following reactions

$$H_2SO_{4(g)} \rightarrow H_2O_{(g)} + SO_{2(g)} + \frac{1}{2}O_{2(g)} \quad \text{(A.1)}$$

$$SO_{2(g)} + 2\,H_2O_{(g)} \rightarrow H_2SO_{4(g)} + H_{2(g)} \quad \text{(A.2)}$$

Conditions:

The key conditions of the HyS cycle are characterised by the reactions at which the decomposition and the sulphur dioxide depolarised electrolysis (SDE) reaction occur and these are:

Decomposition: *Temperature (T)* = 870°C, *Pressure (P)* = 86 Bar, *Reactor Feed composition* ±80% (wt) H_2SO_4

SDE: *Temperature (T)* = 100°C, *Pressure (P)* = 21 Bar, *Reactor Feed composition* ± 50wt% H_2SO_4

Key technical challenges:

- The decomposition reaction happens at very high temperatures and uses a strong acid which has increased corrosive power at the elevated temperatures and this creates material challenges for the plant construction.
- Membranes currently used in the Membrane Electrode assembly (MEA) have a maximum sulphuric acid tolerance of 50wt% and this necessitates the SDE product to be upgraded before decomposition resulting in higher energy consumption..
- The SDE reaction has to be limited to a conversion maximum of 40% on sulphur dioxide otherwise the cell potential gets high, resulting in higher energy consumption than is desirable. The implication of such a limitation is that there is need to recycle feed and this makes the process complicated from a modelling and operation perspective, besides resulting in higher energy consumption.

Economics:

The estimated capital investment into a HyS cycle plant producing 100million kmol H_2 /yr is not explicitly given in most literature. The basic equipment cost and rule of thumb of eight application suggests a capital investment of approximately US$400 million (Leybros *et al.*, 2010). The hydrogen price for the HyS cycle has a very broad range with Leybros reporting \$8.91/kg H_2 and Summers reporting a baseline price of \$5.94/kg H_2 (Summers, 2009) and suggesting \$1.60 (and \$1.31/kg H_2 including oxygen by-product credits) in an earlier publication (Summers, 2005). Looking at the range, the more realistic cost of H_2 produced by the HyS process may be around \$6/kg H_2 and the price is probably driven by the short expected life spans of such plants due to excessively corrosive operational environments.

A.2: Sulphur-Iodine cycle

Studied extensively by Dr L.C Brown and his colleagues at General Atomics, the sulphur-iodine cycle is a completely thermochemical process. The sulphur-iodine cycle is disputably the best choice of thermochemical cycle for the production of hydrogen from nuclear energy (Brown *et al.*, 2003). According to Brown, from a set of 822 separate references covering 115 unique cycles, the sulphur-iodine thermochemical cycle is the best commercialisation option in spite of the obvious challenges faced in the modelling evaluation of the cycle. It is of interest though, that energy agencies in the developed nations, e.g. US-DOE, Japanese

Atomic Energy Research Institute (JAERI), French CEA, Korean Atomic Energy Research Institute (KAERI) and Chinese Energy agencies are working towards establishing pilot plants. The sulphur-iodine cycle is considered as one of the baseline cycles and has been used widely as a basis of comparison for performance with other cycles, for example work done by Z. L Wang, which compares the Cu-Cl to the S-I as a way of establishing the Cu-Cl as a credible thermocycle (Wang *et al.*, 2009).

Vitart cited the following issues as key concerns with the S-I thermochemical cycle in work published in the Progress in Nuclear Energy issue 50, (X.Vitart *et al.*, 2008): high temperatures of operation, use of corrosive and toxic substances, high material hold-up, especially of iodine, and the difficulty of achieving high efficiencies to the magnitude of 50%. In other publications, notably those by Bagajewicz *et al.* (2009) and Wang *et al.* (2009), there are efficiencies of 81.3 and between 50.4 and 54% (with I_2 gasification - no gasification) respectively, which suggests that it is possible to achieve higher efficiencies than the 50% ceiling given in Vitart's article. To ease the separation challenges in the HI_x section, work has been done to suggest the application of membranes to improve the energy use (Duigou *et al.*, 2005).

Chemistry:

The sulphur-iodine cycle is described by a series of three totally fluid reactions as shown in Figure 2, reactions R3-R5

$$SO_{2(g)} + H_2O_{(g)} + I_2 \rightarrow H_2SO_{4(l)} + 2HI_{(l)} \quad \text{(A.3)}$$

$$H_2SO_{4(g)} \rightarrow H_2O_{(g)} + SO_{2(g)} + \frac{1}{2}O_{2(g)} \quad \text{(A.4)}$$

$$2HI_{(g)} \leftrightarrow H_{2(g)} + I_{2(g)} \quad \text{(A.5)}$$

Conditions:

The peak conditions under which the key reactions take place are:

R3: T= 120°C, P=7bar(Brown *et al.*, 2003)

R4: T=830-900°C, P=35bar(Brown *et al.*, 2003)

R5: T=300-450°C P=22bar(Brown *et al.*, 2003)

Key challenges:

- Use of highly corrosive substances at high temperature presents material challenges especially in the acid decomposition section.
- Existence of an azeotrope in the $HI/I_2/H_2O$ system equilibrium presents separation challenges.
- High material hold-up requirements for iodine increases operational costs.

Economics:

The sulphur-iodine cycle is estimated to have a basic equipment cost of about US$45 million which equates to an turnkey capital cost of US$360 million (using a rule of thumb factor of 8) for a plant producing 100 million kmol H_2/ year (X.Vitart *et al.*, 2008). This results in a hydrogen cost of $2.40/kg H_2 which is slightly higher, but comparable to the $1.42-1.60/kg H_2 given by Brown *et al.* (2003)

A.3: Copper oxide- copper sulphate cycle

Literature suggests that this thermochemical cycle originated from the Westinghouse cycle(Brecher *et al.*, 1976) from which the hybrid sulphur cycle originated. In the mid 1970s, Soliman *et al*(Soliman *et al.*, 1976), proposed that use of metal oxides in the basic Westinghouse cycle would have a catalytic effect on the process. The process has the same basic high temperature requirements as the hybrid sulphur cycle as they both have decomposition of SO_3 in common, however, with respect to materials of construction requirements, the $CuO\text{-}CuSO_4$ process has less stringent requirements as the substances used are not as corrosive as in the hybrid sulphur process (Law *et al.*, 2008). The $CuO\text{-}CuSO_4$ cycle has a maximum attainable efficiency of 60% and an un-optimised flowsheet efficiency of 31%(Law *et al.*, 2008).

Chemistry:

Simplest representation of the cycle is represented as two reactions

$$SO_{2(g)}+H_2O_{(g)}+CuO_{(s)}\rightarrow CuSO_{4(l)}+H_{2(g)} \quad \text{(A.6)}$$

$$CuSO_{4(g)} \rightarrow CuO_{(s)}+ SO_{2(g)}+\frac{1}{2}O_{2(g)} \quad \text{(A.7)}$$

In reality, the chemistry proceeds via the formation of a copper sulphate hydrate which forms in three stages: the formation of a monohydrate, a tri-hydrate and then a penta-hydrate (Law *et al.*, 2008). The amount of water added influences the abundance of each hydrate, with more water being correlated with more penta-hydrate and hence the amount of water used influences the energy efficiency of the cycle (Law *et al.*, 2008).

A four-reaction version dubbed the H-5 was proposed by Foh *et al.* (1981) and the currently available Aspen simulation results (Gonzales *et al.*, 2009) are a based on this reaction scheme:

$$SO_{2(g)}+6H_2O_{(g)}+CuO_{(s)}\rightarrow CuSO_4\cdot 5H_2O_{(s)}+H_{2(g)} \quad \text{(A.8)}$$

$$CuSO_4\cdot 5H_2O_{(s)} \rightarrow CuSO_{4(s)}+5H_2O_{(l)} \quad \text{(A.9)}$$

$$CuSO_{4(g)} \rightarrow CuO_{(s)}+ SO_{3(g)} \quad \text{(A.10)}$$

$$SO_{3(g)} \rightarrow SO_{2(g)}+\frac{1}{2}O_{2(g)} \quad \text{(A.11)}$$

Conditions:

The conditions under which the key reactions take place are:

R6: T=25 °C,P=21.7 bar

R7: T=825°C, P=1.01bar

R8: T=25°C, P=21.7bar

R9: T= 280°C, P=1.01bar

R10: T= 850°C,P=21.7bar

R11: T=850°C, P=5.15-10.3bar

Economics:

Estimated capital cost using cost of basic equipment of $35 million and rule of thumb factor of 8 is $280 million. Using an optimistic price of $5/kg payback period is under a year and if a price comparable to methane-produced hydrogen estimated to be $1,can be realised, then the payback is slightly longer, but is still very short at less than 3years (Law *et al.*, 2008).

A.4: Hybrid chlorine cycle

The hybrid chlorine cycle is also known as the US- Chlorine cycle and originated at the Hallett air products. The cycle uses the reverse Deacon reaction to produce hydrogen (Simpson *et al.*, 2006). In a review by Gooding *et al.* (2009) there are three ways in which this thermochemical cycle can be implemented:

i. Aqueous quench option

ii. Use of a membrane reactor

iii. Use of HCl sequestration

From the results of the Aspen plus simulations reported by Gooding (Gooding, 2009) the membrane reactor and HCl sequestration options had higher efficiencies, with both having a 36% net thermal efficiency.

Chemistry:

The hybrid chlorine cycle is a simple two-step all fluid reaction listed below.

$$Cl_{2(g)}+H_2O_{(g)} \leftrightarrow 2HCl_{(g)}+\frac{1}{2}O_{2(g)} \quad \text{(A.12)}$$

$$2HCl_{(g)} \leftrightarrow H_{2(g)}+Cl_{2(g)} \text{ (Electrolytic)} \quad \text{(A.13)}$$

Conditions:

The conditions under which the key reactions take place are (Gooding, 2009):

A.12: T=850°C, P=21bar

A.13: T=75°C, P=21bar

Economics:

Simpson (2006) made an estimate of the fixed capital requirement and pegged it at $800 million for a 100 million mol/yr plant. Electricity is said to be the biggest cost, requiring $400-460 million annually and resulting in a hydrogen price of around $3/kg.

Appendix B: Heat exchanger network design

B.1 Introduction

The design of the heat exchanger network was done principally using Aspen Energy analyzer. Streams requiring heating or cooling were exported to the Energy analyzer environment, where analysis was done using Pinch technology. Using the analyser possible heat exchanger networks were also designed to obtain the most optimal feasible heat recovery network design. Several designs were developed for the three, four and five-step copper-chlorine cycles and the selected designs were selected to minimize the capital cost of the network and the operation cost. Section A2.2 summarizes some of the designs developed for each of the configurations studied.

B.2 Design summaries

Table B.1: Three-step network design summary

Three-step Cu-Cl							
Design	**Total Cost Index ($/s)**	**Area (m^2)**	**Units**	**Capital cost Index ($mm)**	**Heating (GJ/hr)**	**Cooling (GJ/hr)**	**Operating cost Index ($/s)**
Theoretical target	0.90	205919	2	21.24	76.56	3959.08	0.36
CuCl3.1 Design 3	3.79	84045.97	5	19.52	1211.16	5093.68	3.29
CuCl3.1 Design 4	3.58	106016.8	8	24.78	1073.27	4955.79	2.95
CuCl3.1 Design 2	2.73	294217.2	8	68.14	301.34	4183.86	0.99
CuCl3.1 Design 1	2.48	309978.5	11	71.95	163.45	4045.97	0.64

Table B.2: Four-step cycle heat exchanger network design summary

Four-step Cu-Cl							
Design	**Total Cost Index ($/s)**	**Area (m^2)**	**Units**	**Capital cost Index ($mm)**	**Heating (GJ/hr)**	**Cooling (GJ/hr)**	**Operating cost Index ($/s)**
Targets	29.83	688212.9	5	89.37	10921.79	359.81	27.55
CuCl 4.1 Design 3	31.18	613637.7	17	142.10	11117.44	555.46	27.56
CuCl 4.1 Design 5	31.06	620059	17	143.77	11052.56	490.58	27.39
CuCl4.1 Design 2	30.91	635425.5	17	147.25	10958.61	396.63	27.15
CuCl4.1 Design 4	30.90	634050	21	147.03	10958.61	396.63	27.15
CuCl4.1 Design 1	30.79	598229.8	19	138.61	11008.68	446.69	27.26

Table B.3: Five-step cycle heat exchanger design summary

Five-step Cu-Cl							
Design	**Cost Index ($/s)**	**Area (m^2)**	**Units**	**Capital Index ($mm)**	**Heating (GJ/hr)**	**Cooling (GJ/hr)**	**Operating cost Index ($/s)**
Targets	9.79	506432.2	12	65.91	3829.86	2767.03	8.11
CuCl 5.1 Design 5	19.40	1677226	29	388.51	3748.69	2685.85	9.49
CuCl 5.1 Design 4	13.57	688983.1	26	159.95	3748.33	2685.49	9.49
CuCl 5.1 Design 3	13.31	644975	26	149.83	3748.33	2685.49	9.49
CuCl 5.1 Design 1	13.27	637668.2	28	148.09	3748.69	2685.85	9.49
CuCl 5.1 Design 2	13.04	591374	30	137.26	3775.37	2712.53	9.54

B.3 Design selection

Designs were selected to minimize the capital investment and the operating costs in the heat exchanger networks. To accomplish this balance, designs were compared to other designs and the theoretical optimum requirements. The theoretical requirements were calculated based on the process stream data supplied to Aspen Energy analyser. Smith (2005) and Sinnot (2005) are some authors of books that explain the theory and formulae used in the calculations automated by the Aspen Energy Analyzer. Using the results in the summaries reported in Section A2.2, designs CuCl 3.1 Design 2, CuCl 4.1 Design 2 and CuCl 5.1 Design 3 were selected for the three, four and five-step cycles respectively. .

B.4 Selected design Network diagrams

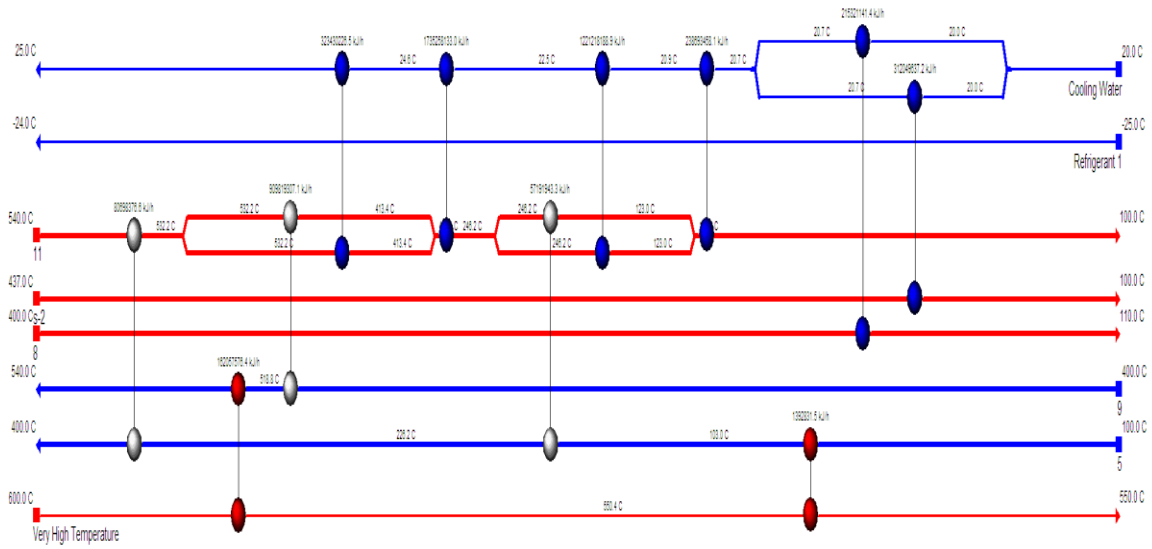

Figure B.1: Heat Exchanger network for the 3-step cycle

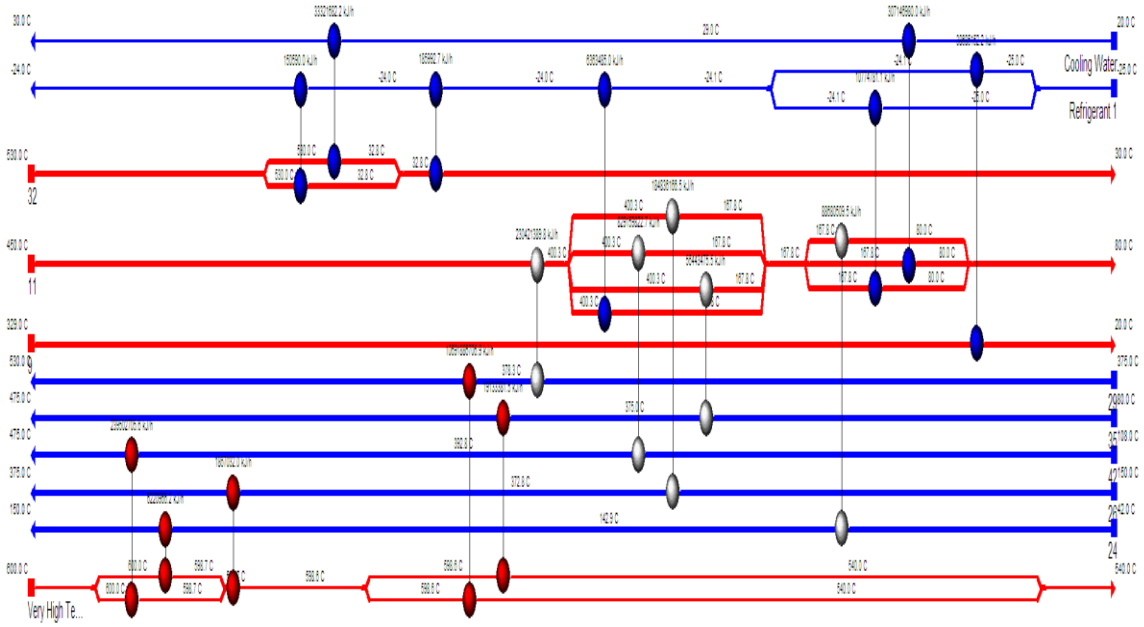

Figure B.2:Heat Exchanger network for the 4-step cycle

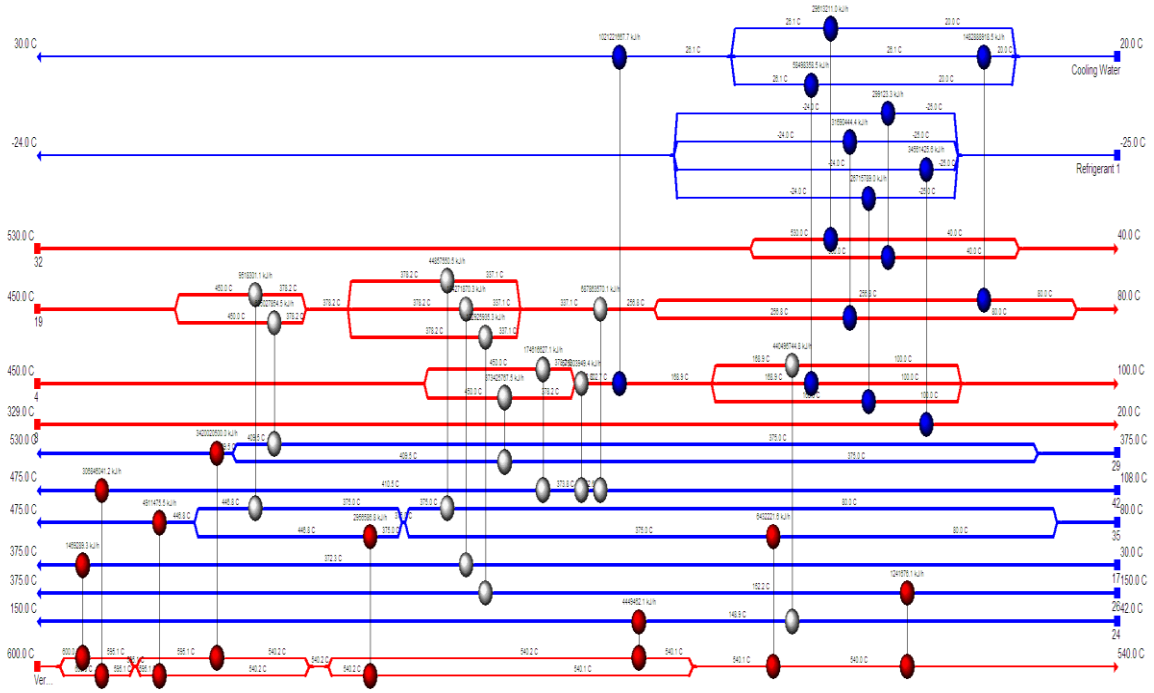

Figure B.3: Heat Exchanger network for the 5-step cycle

Appendix C: Purchased capital cost summary

Using the capacity scaling formula, purchase costs were calculated for respective equipment variable values.

Table C.1: Purchased capital cost summary

Equipment	Capacity, C_2	Capacity , C_B	Base cost, PC_B	Power factor, m	2007 Purchase cost, PC	2010 Purchase cost
Hydrogen reactor	6592	2000	1,804,178	0.56	3,518,458	3,726,056
Disproportionation reactor	2148	2000	1,570,262	0.54	1,631,979	1,728,270
Crystallizer	2823	2000	7,340,382	0.37	8,338,744	8,830,752
Drum Filter	15.7	15	1,338,990	0.49	1,369,253	1,450,043
Evaporative dryer	27.87	20	170,438	0.54	203,886	215,915
Phase separator	4	3	44,118	0.47	50,506	53,486
Hydrolysis reactor	11956	2000	896,917	0.56	2,441,316	2,585,360
Decomposition reactor	6570	1500	4,402,379	0.54	9,774,250	10,350,957
HCl Preheater	12000	1000	1,082,698	0.6	4,808,575	5,092,293
Cu preheater furnace	6000	1000	902,766	0.6	2,645,246	2,801,323
CuCl Quenching Cell	8000	2000	2,122,729	0.44	3,906,619	4,137,120
Wet cyclone	5	2	40,945	0.67	75,652	80,116
Compressor	12253	3000	602,495	0.79	1,831,215	1,939,261
Condenser	187	150	362,102	0.6	413,316	437,702
Phase separator	1.5	2	28,697	0.91	22,088	23,391
CuCl Heat recovery exchanger	9876	1000	1,252,083	0.6	4,947,455	5,239,368
Oxygen cooling system	2870	1000	752,145	0.54	1,329,102	1,407,522
Hydrogen cooling system	3650	1000	934,620	0.51	1,808,859	1,915,587
Mixer	5000	1000	773,059	0.49	1,701,014	1,801,379
Mixer	3000	1000	331,463	0.49	567,839	601,343
Screw conveyor	30	8	7,867	0.69	19,584	20,739

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Appendix D: cash flow projections

Table D.1: Cash flow projections for the five-step cycle (Notes: FCI- Fixed Capital Investment, COM- Cost of manufacturing, DCF- Discounted cash flow)

Five-step cycle cash flow projections							
Total Installed Cost:	$75,668,798	Operating Labour	Chapter 7	Chapter 8	Revenue from Products		
FCI	$370,777,111	C_{ol} =	$1,146,000	Chapter 9	Annual Revenue=	$315,842,129	Chapter 10
Raw Materials	Chapter 11	Utilities	Chapter 12	Chapter 13	Chapter 14	Chapter 15	Chapter 16
C_{rm}=	$22,813,442	C_{ut}=	$39,796,468	Chapter 17	Chapter 18	Chapter 19	Chapter 20
Financial Outlook	Chapter 21	Chapter 22	Chapter 23	Chapter 24	Chapter 25	Chapter 26	Chapter 27
COM=	$146,878,648.79	(without depreciation)		Chapter 28	Chapter 29	Chapter 30	Chapter 31
Year	Depreciation	FCI-deprec.	Revenue	COM	Cash Flow	Discount Cash	Cumulative DCF
0	-	$370,777,111	-	-	($185,388,556)	($185,388,556)	($185,388,556)
1	-	$370,777,111	-	-	($185,388,556)	($161,347,742)	($346,736,297)
2	$74,155,422	$296,621,689	$315,842,129	$146,878,649	$142,417,224	$107,875,410	($238,860,888)
3	$94,918,940	$201,702,748	$315,842,129	$146,878,649	$148,231,009	$97,718,992	($141,141,896)
4	$38,726,928	$162,975,821	$315,842,129	$146,878,649	$132,497,245	$76,019,802	($65,122,094)
5	$31,291,358	$131,684,463	$315,842,129	$146,878,649	$130,415,286	$65,122,094	$0
6	$12,641,708	$119,042,755	$315,842,129	$146,878,649	$125,193,384	$54,407,805	$54,407,805
7	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$46,013,486	$100,421,292
8	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$40,046,550	$140,467,842
9	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$34,853,395	$175,321,237
10	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$30,333,677	$205,654,914
11	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$26,400,067	$232,054,980
12	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$26,400,067	$258,455,047
13	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$22,976,559	$281,431,607
14	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$19,997,006	$301,428,612
15	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$17,403,834	$318,832,447
16	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$15,146,940	$333,979,387
17	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$11,473,208	$345,452,595
18	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$9,985,385	$355,437,980
19	-	$119,042,755	$315,842,129	$146,878,649	$121,653,706	$8,690,501	$364,128,481
20	-	$119,042,755	$315,842,129	$146,878,649	$168,963,480	$10,504,908	$374,633,389
Chapter 32	Taxation rate=	0.28	Discount rate=	0.149	Chapter 33	NPV=	$374,633,389
Chapter 34	Chapter 35	Chapter 36	Chapter 37	Chapter 38	Chapter 39	(Net Present Value)	Chapter 40
Chapter 41	Chapter 42	Chapter 43	Chapter 44	Chapter 45	Chapter 46	Chapter 47	Chapter 48

Table D.2: Cash flow projections for the four-step cycle (Notes: FCI- Fixed Capital Investment, COM- Cost of manufacturing, DCF- Discounted cash flow)

Four-step cycle cash flow projections							
Total Installed Cost:	$61,078,372	Labour			Revenue from Products		
FCI	$299,284,025	C_{ol} =	$946,800		Annual Revenue=	$320,450,462	
Raw Materials		Utilities					
C_{rm}=	$22,813,442	C_{ut}=	$80,934,981				
Financial Outlook							
COM=	$184,066,449.36	(without depreciation)					
Year	Depreciation	FCI-depre**c**.	Revenue	COM	Cash Flow	Discount Cash	Cumulative DCF
0	-	$299,284,025	-	-	($149,642,012)	($149,642,012)	($149,642,012)
1	-	$299,284,025	-	-	($149,642,012)	($130,236,738)	($279,878,751)
2	$59,856,805	$239,427,220	$320,450,462	$184,066,449	$114,956,395	$87,074,919	($192,803,832)
3	$76,616,710	$162,810,509	$320,450,462	$184,066,449	$119,649,168	$78,876,857	($113,926,975)
4	$31,259,618	$131,550,892	$320,450,462	$184,066,449	$106,949,182	$61,361,696	($52,565,279)
5	$25,257,771	$106,293,120	$320,450,462	$184,066,449	$105,268,665	$52,565,279	$0
6	$10,204,140	$96,088,981	$320,450,462	$184,066,449	$101,053,648	$43,916,915	$43,916,915
7	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$37,141,185	$81,058,101
8	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$32,324,791	$113,382,892
9	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$28,132,978	$141,515,870
10	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$24,484,750	$166,000,620
11	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$21,309,617	$187,310,237
12	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$21,309,617	$208,619,854
13	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$18,546,229	$227,166,083
14	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$16,141,191	$243,307,275
15	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$14,048,034	$257,355,309
16	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$12,226,314	$269,581,622
17	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$9,260,949	$278,842,571
18	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$8,060,007	$286,902,579
19	-	$96,088,981	$320,450,462	$184,066,449	$98,196,489	$7,014,802	$293,917,381
20	-	$96,088,981	$320,450,462	$184,066,449	$136,384,013	$8,479,356	$302,396,737
						.	
	Taxation rate=	**0.28**	**Discount =**	**0.149**		**NPV=**	**$302,396,737**
						(Net Present Value)	

Table D.3: Cash flow projections for the three-step cycle(Notes: FCI- Fixed Capital Investment, COM- Cost of manufacturing, DCF- Discounted cash flow)

Three-step cycle cash flow projection							
Total Installed Cost:	$182,266,869	Operating Labour			Revenue from Products		
FCI	$273,400,304	C_{ol} =	$954,000		Annual Revenue=	$336,760,320	
Raw Materials		Utilities					
C_{rm}=	$22,813,442	C_{ut}=	$107,556,532				
Financial Outlook							
COM=	$212,171,542.99	(without depreciation)					
Year	Depreciation	FCI-deprec.	Revenue	COM	Cash Flow	Discount Cash	Cumulative DCF
0	-	$273,400,304	-	-	($136,700,152)	($136,700,152)	($136,700,152)
1	-	$273,400,304	-	-	($136,700,152)	($118,973,152)	($255,673,304)
2	$54,680,061	$218,720,243	$336,760,320	$212,171,543	$105,014,336	$79,544,203	($176,129,101)
3	$69,990,478	$148,729,765	$336,760,320	$212,171,543	$109,301,253	$72,055,155	($104,073,946)
4	$28,556,115	$120,173,650	$336,760,320	$212,171,543	$97,699,632	$56,054,800	($48,019,146)
5	$23,073,341	$97,100,309	$336,760,320	$212,171,543	$96,164,455	$48,019,146	$0
6	$9,321,630	$87,778,680	$336,760,320	$212,171,543	$92,313,976	$40,118,740	$40,118,740
7	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$33,929,012	$74,047,752
8	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$29,529,167	$103,576,919
9	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$25,699,884	$129,276,803
10	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$22,367,175	$151,643,977
11	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$19,466,645	$171,110,622
12	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$19,466,645	$190,577,267
13	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$16,942,250	$207,519,516
14	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$14,745,213	$222,264,729
15	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$12,833,083	$235,097,813
16	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$11,168,915	$246,266,728
17	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$8,460,011	$254,726,739
18	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$7,362,934	$262,089,673
19	-	$87,778,680	$336,760,320	$212,171,543	$89,703,919	$6,408,124	$268,497,796
20	-	$87,778,680	$336,760,320	$212,171,543	$124,588,777	$7,746,015	$276,243,812
	Taxation rate=	0.28	Discount rate=	0.149		NPV=	$276,243,812
						(Net Present Value)	

Appendix E: Aspen Input summaries

E.1 Five-step cycle

```
Input Summary created by Aspen Plus Rel. 23.0 at 15:02:44 Sat Jul 30, 2011

 IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &

      HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &

      VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &

      MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &

      MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &

      PDROP=bar

    Property Method: ELECNRTL

    Flow basis for input: Mass

   Stream report composition

DATABANKS ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  / &  PURE22

PROP-SOURCES ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  / &  PURE22

COMPONENTS

   H2O H2O /

   H2 H2 /

   O2 O2 /

   HCL HCL /

   CU++ CU+2 /

   CU+ CU+ /

   H3O+ H3O+ /

   OH- OH- /

   CL- CL- /

   CUCL CUCL /

   "CUCL(S)" CUCL /

   CU CU /

   CU2OCL2 CU2OCL2 /

   CUCL2 CUCL2 /

   CUCL2-2W "CUCL2*2W"

HENRY-COMPS GLOBAL HCL H2

CHEMISTRY GLOBAL

 DISS CUCL CU+ 1 / CL- 1

   STOIC 1 H2O -2 / H3O+ 1 / OH- 1

   STOIC 2 HCL -1 / H2O -1 / H3O+ 1 / CL- 1

   K-STOIC 1 A=132.89888 B=-13445.9 C=-22.4773 D=0

   SALT CUCL2-2W CU++ 1. / CL- 2. / H2O 2.

FLOWSHEET

   HIERARCHY DIS

   CONNECT $C-1 IN=20 OUT=DIS.FR2

   CONNECT $C-3 IN=12 OUT=DIS.PR2A

   CONNECT $C-2 IN=DIS.PR2 OUT=21

   BLOCK H2REACT IN=38 39 1 2 OUT=3

   BLOCK F0R1 IN=3 OUT=4 11

   BLOCK COMP IN=7 OUT=8

   BLOCK FCOMP IN=9 OUT=10 16

   BLOCK HXQC IN=34 11 OUT=19

   BLOCK SPC IN=21 OUT=22 35

   BLOCK CRYST IN=22 OUT=23

   BLOCK F1R3 IN=25 OUT=36 26

   BLOCK HYDR IN=18 FH2O 27 OUT=28

   BLOCK F2R4 IN=28 OUT=37 29

   BLOCK F3R5 IN=31 OUT=32 34

   BLOCK MX1 IN=37 36 40 OUT=42

   BLOCK F2R1 IN=6 OUT=7 13

   BLOCK F1R1 IN=14 5 OUT=6 12

   BLOCK SPA IN=13 OUT=14 15

   BLOCK MX2 IN=16 15 OUT=17

   BLOCK FHXR4 IN=17 OUT=18

   BLOCK FHXR1A IN=42 OUT=41

   BLOCK FHXR1C IN=35 OUT=1

   BLOCK FHXR4S IN=26 OUT=27

   BLOCK FHXR5 IN=29 OUT=30

   BLOCK PHXR5 IN=32 OUT=33 Q4

   BLOCK PHXCOMP IN=8 OUT=9 Q5

   BLOCK DRYER IN=24 OUT=25 Q3

   BLOCK FILT IN=23 OUT=24 40

   BLOCK PHXQC IN=19 OUT=20 Q1

   BLOCK PHXF1R1 IN=4 OUT=5 Q2

   BLOCK FHXR1A2 IN=41 OUT=2

   BLOCK DECOMP IN=30 OUT=31

PROPERTIES ELECNRTL HENRY-COMPS=GLOBAL CHEMISTRY=GLOBAL  &

      TRUE-COMPS=YES

   PROPERTIES NRTL

STREAM 1

   SUBSTREAM CISOLID TEMP=450 PRES=1

   MOLE-FLOW CU 7200.00025

STREAM 3

   SUBSTREAM MIXED TEMP=450 PRES=1

   MOLE-FLOW H2O 102708.009 / H2 3599.65091 / HCL  &

      5551.30401 / CU+ 7200.00025 / H3O+ 4.75766844 / OH-  &
```

```
      0.00129605078 / CL-
7204.75662

STREAM 4

   SUBSTREAM MIXED
TEMP=450 PRES=1

   MOLE-FLOW H2O 102682.533 /
H2 3599.65007 / HCL  &

      5551.30401

STREAM 6

   SUBSTREAM MIXED
TEMP=100 PRES=1

   MOLE-FLOW H2O 27159.1783 /
H2 3599.8324 / HCL 63.7430221

STREAM 7

   SUBSTREAM MIXED TEMP=30
PRES=1

   MOLE-FLOW H2O 160.097742 /
H2 3599.49776 / HCL  &

      2.772035E-005

STREAM 9

   SUBSTREAM MIXED TEMP=20
PRES=4.82639036

   MOLE-FLOW H2O 160.097714 /
H2 3599.49776 / HCL  &

      3.021510E-014 / H3O+
2.772198E-005 / OH- 1.622467E-
009 / &

      CL- 2.772035E-005

STREAM 10

   SUBSTREAM MIXED TEMP=20
PRES=4.82639036

   MOLE-FLOW H2O 17.8404655 /
H2 3599.48795 / HCL  &

      3.021510E-014

STREAM 11

   SUBSTREAM MIXED
TEMP=450 PRES=1

   MOLE-FLOW H2O 25.4757927 /
H2 0.00084083454 / HCL  &

      8.738182E-018 / CU+
7200.00025 / H3O+ 4.75766845 /
&

      OH- 0.00129605078 / CL-
7204.75662

STREAM 12

   SUBSTREAM MIXED
TEMP=100 PRES=1

   MOLE-FLOW H2O 89941.389 /
H2 0.0649804049 / HCL  &

      2.608012E-010 / H3O+
5534.63983 / OH- 6.192233E-010 /
&

      CL- 5534.63983

STREAM 13

   SUBSTREAM MIXED TEMP=30
PRES=1

   MOLE-FLOW H2O 26935.3375 /
H2 0.334638988 / HCL  &

      1.001385E-013 / H3O+
63.7429943 / OH- 1.148757E-010 /
&

      CL- 63.7429943

STREAM 14

   SUBSTREAM MIXED TEMP=30
PRES=1

   MOLE-FLOW H2O 19905.595 /
H2 0.247309815 / HCL  &

      7.393421E-014 / H3O+
47.0788487 / OH- 8.492881E-011 /
&

      CL- 47.0788487

STREAM 15

   SUBSTREAM MIXED TEMP=30
PRES=1

   MOLE-FLOW H2O 7029.79853 /
H2 0.0873367435 / HCL  &

      2.613494E-014 / H3O+
16.6361534 / OH- 2.998118E-011 /
&

      CL- 16.6361534

STREAM 16

 SUBSTREAM MIXED TEMP=20
PRES=4.82639036

   MOLE-FLOW H2O 142.257248 /
H2 0.00980718385 / HCL  &

      7.403633E-024 / H3O+
2.772198E-005 / OH- 1.622467E-
009 / &

      CL- 2.772035E-005

STREAM 17

   SUBSTREAM MIXED
TEMP=29.8022299 PRES=1

   MOLE-FLOW H2O 7172.05578 /
H2 0.0971439274 / HCL  &

      5.724135E-011 / H3O+
16.6361811 / OH- 3.055679E-011 /
&

      CL- 16.6361811

STREAM 18

   SUBSTREAM MIXED
TEMP=375 PRES=1

   MOLE-FLOW H2O 7188.69196 /
H2 0.0971439274 / HCL  &

      16.6361811

STREAM 19

   SUBSTREAM MIXED TEMP=80
PRES=1

   MOLE-FLOW H2O 25.4784238 /
H2 0.00084083454 / O2  &

      0.257719287 / HCL
4.958571E-008 / CU++
0.719999919 /  &

      CU+ 7200.00025 / H3O+
4.7563894 / OH- 2.532095E-016 /
&

      CL- 7206.19663

   SUBSTREAM CISOLID
TEMP=80 PRES=1

   MOLE-FLOW "CUCL(S)"
7199.28025

STREAM 21

   SUBSTREAM MIXED TEMP=80
PRES=1

   MOLE-FLOW H2O 89973.5491 /
H2 0.0658218659 / O2  &

      0.257699045 / HCL
1.646748E-009 / CU++ 7200.00025
/  &

      H3O+ 5539.41751 / OH-
6.995033E-011 / CL- 19939.418

   SUBSTREAM CISOLID
TEMP=80 PRES=1

   MOLE-FLOW CU 7200.00025

STREAM 22

   SUBSTREAM MIXED TEMP=80
PRES=1

   MOLE-FLOW H2O 89973.5491 /
H2 0.0658218659 / O2  &
```

0.257699045 / HCL 1.646748E-009 / CU++ 7200.00025 / &

H3O+ 5539.41751 / OH- 6.995033E-011 / CL- 19939.418

STREAM 24

SUBSTREAM MIXED TEMP=42 PRES=1

MOLE-FLOW H2O 4501.41316 / H2 0.0658218659 / O2 &

0.257699045 / HCL 8.193913E-007 / CU++ 0.720000025 / &

H3O+ 275.603021 / OH- 1.675491E-012 / CL- 277.043011

SUBSTREAM CISOLID TEMP=42 PRES=1

MOLE-FLOW CUCL2 7199.28025

STREAM 25

SUBSTREAM MIXED TEMP=150 PRES=1

MOLE-FLOW H2O 4777.01554 / H2 0.0658218659 / O2 &

0.257699045 / HCL 275.602379 / CU++ 0.720000025 / &

H3O+ 0.00064268707 / OH- 1.745463E-013 / CL- &

1.44063274

SUBSTREAM CISOLID TEMP=150 PRES=1

MOLE-FLOW CUCL2 7199.28025

STREAM 27

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &

HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &

VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &

MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &

MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &

PDROP=bar

SUBSTREAM MIXED TEMP=375 PRES=1

MOLE-FLOW H2O 0.714245564 / H2 1.558548E-010 / O2 &

1.898207E-008 / HCL 0.00062561406 / CU++ 0.719999919 / &

H3O+ 1.743201E-005 / OH- 3.590967E-007 / CL- &

1.44000691

SUBSTREAM CISOLID TEMP=375 PRES=1

MOLE-FLOW CUCL2 7199.28025

STREAM 28

SUBSTREAM MIXED TEMP=375 PRES=1

MOLE-FLOW H2O 7199.9945 / H2 0.0971439276 / O2 &

1.898207E-008 / HCL 7215.91706 / CU++ 0.719999919 / &

H3O+ 1.743201E-005 / OH- 3.590967E-007 / CL- &

1.44000691

SUBSTREAM CISOLID TEMP=375 PRES=1

MOLE-FLOW CU2OCL2 3599.64012

STREAM 30

SUBSTREAM MIXED TEMP=530 PRES=1

MOLE-FLOW H2O 0.00055104080 / H2 4.888469E-012 / HCL &

1.738780E-008 / CU++ 0.719999919 / H3O+ 3.140834E-005 / &

OH- 1.435281E-005 / CL- 1.44000689

SUBSTREAM CISOLID TEMP=530 PRES=1

MOLE-FLOW CU2OCL2 3599.64012

STREAM 31

SUBSTREAM MIXED TEMP=530 PRES=1

MOLE-FLOW H2O 0.00054895877 / H2 4.877766E-012 / O2 &

1800.01437 / HCL 1.598717E-008 / CU++ 0.720077755 / &

H3O+ 2.907323E-005 / OH- 1.550891E-005 / CL- &

1.44015908 / CUCL 7200.0575

STREAM 32

SUBSTREAM MIXED TEMP=530 PRES=1

MOLE-FLOW H2O 0.00054082793 / O2 1799.56234 / HCL &

1.738780E-008 / CUCL 2.667962E-076

STREAM 34

SUBSTREAM MIXED TEMP=530 PRES=1

MOLE-FLOW H2O 1.021287E-005 / O2 0.257719287 / HCL &

6.958568E-028 / CU++ 0.719999919 / H3O+ 3.140834E-005 / &

OH- 1.435281E-005 / CL- 1.44000689 / CUCL 7199.28025

STREAM 36

SUBSTREAM MIXED TEMP=150 PRES=1

MOLE-FLOW H2O 4776.30192 / H2 0.0658218657 / O2 &

0.257699026 / HCL 275.602379

STREAM 37

SUBSTREAM MIXED TEMP=375 PRES=1

MOLE-FLOW H2O 7200.00025 / H2 0.100363237 / HCL &

7216.64367

STREAM 38

SUBSTREAM MIXED TEMP=50 PRES=1

MOLE-FLOW H2O 5.550837E-010 / H3O+ 2.321023E-018 / OH- &

2.321023E-018

```
   SUBSTREAM CISOLID
TEMP=50 PRES=1

   MOLE-FLOW CU 1E-008

STREAM 39

   SUBSTREAM MIXED
TEMP=400 PRES=1

   MOLE-FLOW H2O 9.626547E-
006 / HCL 9.037345E-005

STREAM 41

   SUBSTREAM MIXED
TEMP=450 PRES=1

   MOLE-FLOW H2O 102712.253 /
H2 0.166185103 / O2  &

      0.257699026 / HCL
12756.0605

STREAM 42

   SUBSTREAM MIXED
TEMP=108.926773 PRES=1

   MOLE-FLOW H2O 91741.5864 /
H2 0.166184476 / O2  &

      0.257719268 / HCL
1792.07604 / H3O+ 10963.9632 /
OH-  &

      6.595398E-011 / CL-
10963.9632

STREAM FH2O

   SUBSTREAM MIXED
TEMP=120 PRES=1

   MOLE-FLOW H2O 3610.22842

BLOCK MX1 MIXER

   PARAM NPHASE=2 T-
EST=176.776338

   BLOCK-OPTION FREE-
WATER=NO

BLOCK MX2 MIXER

   PARAM T-EST=29.9026595

BLOCK SPA FSPLIT

   MOLE-FLOW 14 20000.

BLOCK FILT SEP

   PARAM

   FRAC STREAM=40
SUBSTREAM=MIXED
COMPS=H2O H2 O2 HCL CU++
&

      CU+ H3O+ OH- CL- CUCL
"CUCL(S)" CU CU2OCL2 CUCL2
&

      CUCL2-2W FRACS=0.95 0. 0.
0.95 0. 0. 0. 0. 0. 0.  &

      0. 0. 0. 0. 0.

   FRAC STREAM=40
SUBSTREAM=CISOLID
COMPS="CUCL(S)" CU  &

      CU2OCL2 CUCL2 CUCL2-2W
FRACS=0. 0. 0. 0. 0.

BLOCK DRYER HEATER

   PARAM TEMP=150. PRES=0.

BLOCK FHXR1A HEATER

   PARAM TEMP=408. PRES=0.

   HCURVE 1 NPOINT=20

BLOCK FHXR1A2 HEATER

   PARAM TEMP=475. PRES=0.

   UTILITY UTILITY-ID=U-2

BLOCK FHXR1C HEATER

   PARAM TEMP=475. PRES=0.

   UTILITY UTILITY-ID=U-2

BLOCK FHXR4 HEATER

   PARAM TEMP=375. PRES=1.

BLOCK FHXR4S HEATER

   PARAM TEMP=375. PRES=0.

BLOCK FHXR5 HEATER

   PARAM TEMP=530. PRES=0.

BLOCK PHXCOMP HEATER

   PARAM TEMP=20. PRES=0.

BLOCK PHXF1R1 HEATER

   PARAM TEMP=100. PRES=0.

   HCURVE 1

BLOCK PHXQC HEATER

   PARAM TEMP=80. PRES=0.
MAXIT=100 TOL=0.001

   HCURVE 1 INDEP-VAR=DUTY

   BLOCK-OPTION FLASH-
METHOD=INSIDE-OUT

   UTILITY UTILITY-ID=U-1

BLOCK PHXR5 HEATER

   PARAM TEMP=20. PRES=0.

BLOCK F0R1 FLASH2

   PARAM TEMP=450. PRES=1.

BLOCK F1R1 FLASH2

  PARAM TEMP=100. PRES=1.

BLOCK F1R3 FLASH2

   PARAM TEMP=150. PRES=1.

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL FREE-
WATER=STEAM-TA  &

      SOLU-WATER=3 TRUE-
COMPS=YES

BLOCK F2R1 FLASH2

   PARAM TEMP=30. PRES=0.

BLOCK F2R4 FLASH2

   PARAM TEMP=375. PRES=1.

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL FREE-
WATER=STEAM-TA  &

      SOLU-WATER=3 TRUE-
COMPS=YES

BLOCK F3R5 FLASH2

   PARAM TEMP=530. PRES=1.

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL FREE-
WATER=STEAM-TA  &

      SOLU-WATER=3 TRUE-
COMPS=YES

BLOCK FCOMP FLASH2

   PARAM TEMP=20. PRES=0.

BLOCK CRYST RSTOIC

   PARAM TEMP=42. PRES=1.
SERIES=YES TOL=0.001

   STOIC 1 MIXED H3O+ -1. / CL-
-1. / HCL 1. / H2O 1.

   STOIC 2 MIXED CU++ -1. / CL- -
2. / CISOLID CUCL2 1.

   STOIC 3 MIXED CL- -1. / H2O -
1. / HCL 1. / OH- 1.

   CONV 1 MIXED H3O+ 1.

   CONV 2 MIXED CU++ 0.9999

   CONV 3 MIXED CL- 0.9999
```

```
   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL FREE-
WATER=STEAM-TA  &

      SOLU-WATER=3 TRUE-
COMPS=YES

   BLOCK-OPTION SIM-LEVEL=4
FLASH-METHOD=GIBBS

   UTILITY UTILITY-ID=U-1

BLOCK DECOMP RSTOIC

   PARAM TEMP=530. PRES=1.

   STOIC 1 CISOLID CU2OCL2 -1.
/ MIXED CUCL 2. / O2 0.5

   CONV 1 CISOLID CU2OCL2 1.

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL FREE-
WATER=STEAM-TA  &

      SOLU-WATER=3 TRUE-
COMPS=YES

   UTILITY UTILITY-ID=U-2

BLOCK H2REACT RSTOIC

   PARAM TEMP=475. PRES=1.
SERIES=YES HEAT-OF-
REAC=NO

   STOIC 1 CISOLID CU -2. /
MIXED HCL -2. / CUCL 2. /  &

      H2 1.

   STOIC 2 MIXED O2 -0.5 / H2 -1.
/ H2O 1.

   CONV 1 CISOLID CU 0.9038

   CONV 2 MIXED O2 1.

   UTILITY UTILITY-ID=U-1

BLOCK HXQC RSTOIC

   PARAM TEMP=450. PRES=1.

   STOIC 1 MIXED CUCL -1. /
CISOLID "CUCL(S)" 1.

   CONV 1 MIXED CUCL 1.

   UTILITY UTILITY-ID=U-1

BLOCK HYDR RSTOIC

   PARAM TEMP=375. PRES=0.5

   STOIC 1 CISOLID CUCL2 -2. /
MIXED H2O -1. / CISOLID  &

      CU2OCL2 1. / MIXED HCL 2.

   CONV 1 CISOLID CUCL2 1.

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL FREE-
WATER=STEAM-TA  &

      SOLU-WATER=3 TRUE-
COMPS=YES

   UTILITY UTILITY-ID=U-2

HIERARCHY DIS

DEF-STREAMS MIXCISLD ALL

SOLVE

   PARAM METHOD=SM

   RUN-MODE MODE=SIM

FLOWSHEET

   BLOCK DSPPTN IN=16
OUT=PR2

   BLOCK DPN1 IN=FR2 PR2A
OUT=16

PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL
CHEMISTRY=GLOBAL  &

      FREE-WATER=STEAM-TA
SOLU-WATER=3 TRUE-
COMPS=YES

   PROPERTIES NRTL

STREAM 16

   SUBSTREAM MIXED TEMP=80
PRES=1

   MOLE-FLOW H2O 89966.8674 /
H2 0.0658212395 / O2  &

      0.257719287 / HCL
1.909445E-009 / CU++
0.719999919 /  &

      CU+ 14399.2805 / H3O+
5539.39622 / OH- 6.032288E-011 /
&

      CL- 19940.1167

BLOCK DPN1 RSTOIC

   PARAM TEMP=80. PRES=1.
SERIES=YES

   STOIC 1 CISOLID "CUCL(S)" -1.
/ MIXED CU+ 1. / CL- 1.

   STOIC 2 CISOLID CU -1. /
MIXED H2O -1. / CU+ 1. /  &

      OH- 1. / H2 0.5

   CONV 1 CISOLID "CUCL(S)" 1.

   CONV 2 CISOLID CU 1.

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL
CHEMISTRY=GLOBAL  &

      FREE-WATER=STEAM-TA
SOLU-WATER=3 TRUE-
COMPS=YES

BLOCK DSPPTN RSTOIC

   PARAM TEMP=80. PRES=1.

   STOIC 1 MIXED CU+ -2. / CU++
1. / CISOLID CU 1.

   CONV 1 MIXED CU+ 1.

ENDHIERARCHY DIS

BLOCK COMP COMPR

   PARAM TYPE=ISENTROPIC
PRES=6.56694251

   UTILITY UTILITY-ID=U-3

BLOCK SPC SSPLIT

   FRAC MIXED 35 0.

   FRAC CISOLID 35 1.
```

E.2 Four-step cycle Input summary

```
;Input Summary created by Aspen
Plus Rel. 23.0 at 16:47:03 Fri Jul
29, 2011

IN-UNITS SI MASS-FLOW='kg/hr'
MOLE-FLOW='kmol/hr'  &

      VOLUME-FLOW='cum/hr'
PRESSURE=bar
TEMPERATURE=C DELTA-T=C  &

      PDROP-PER-HT='mbar/m'
PDROP=bar

DEF

   SIM-OPTIONS OLD-
DATABANK=YES

DESCRIPTION "

   Electrolytes Simulation with
Metric Units :
```

```
    C, bar, kg/hr, kmol/hr, Gcal/hr, cum/hr.

    Property Method: ELECNRTL

   Flow basis for input: Mass

    Stream report composition

    ******

DATABANKS ASPENPCD / AQUEOUS / SOLIDS / INORGANIC / & PURE22

PROP-SOURCES ASPENPCD / AQUEOUS / SOLIDS / INORGANIC / &

        PURE22

COMPONENTS

    H2O H2O /

    H2 H2 /

    O2 O2 /

    HCL HCL /

    CU++ CU+2 /

    CU+ CU+ /

    H3O+ H3O+ /

    OH- OH- /

    CL- CL- /

    CUCL CUCL /

    "CUCL(S)" CUCL /

    CU CU /

    CU2OCL2 CU2OCL2 /

    CUCL2 CUCL2 /

    CUCL2-2W "CUCL2*2W"



HENRY-COMPS GLOBAL HCL H2

CHEMISTRY GLOBAL

 DISS CUCL CU+ 1 / CL- 1

    STOIC 1 H2O -2 / H3O+ 1 / OH- 1

    STOIC 2 HCL -1 / H2O -1 / H3O+ 1 / CL- 1

    K-STOIC 1 A=132.89888 B=-13445.9 C=-22.4773 D=0

    SALT CUCL2-2W CU++ 1. / CL- 2. / H2O 2.

FLOWSHEET

    HIERARCHY DIS

    CONNECT $C-1 IN=20 OUT=DIS.FR2

    CONNECT $C-3 IN=S-1 OUT=DIS.PR2A

    CONNECT $C-2 IN=DIS.PR2 OUT=21

    BLOCK H2REACT IN=38 39 1 2 OUT=3

    BLOCK F0R1 IN=3 OUT=4 11

    BLOCK COMP IN=7 OUT=8

    BLOCK FCOMP IN=9 OUT=10 16

    BLOCK HXQC IN=34 11 OUT=19

    BLOCK SPC IN=21 OUT=22 35

    BLOCK HYDR IN=18 FH2O 27 OUT=28

    BLOCK F2R4 IN=28 OUT=37 29

    BLOCK F3R5 IN=31 OUT=32 34

    BLOCK MX1 IN=37 40 OUT=42

    BLOCK F2R1 IN=6 OUT=7 13

    BLOCK F1R1 IN=14 5 OUT=6 12

    BLOCK SPA IN=13 OUT=14 15

    BLOCK MX2 IN=16 15 OUT=17

    BLOCK FHXR4 IN=17 OUT=18

    BLOCK FHXR1A IN=42 OUT=41

    BLOCK FHXR1C IN=35 OUT=1

    BLOCK FHXR4S IN=26 OUT=27

    BLOCK FHXR5 IN=29 OUT=30

    BLOCK PHXR5 IN=32 OUT=33

    BLOCK PHXCOMP IN=8 OUT=9

    BLOCK FILT IN=22 OUT=40 26

    BLOCK PHXQC IN=19 OUT=20

    BLOCK PHXF1R1 IN=4 OUT=5

    BLOCK FHXR1A2 IN=41 OUT=2

    BLOCK DECOMP IN=30 OUT=31

    BLOCK FHXDIS IN=12 OUT=S-1

PROPERTIES ELECNRTL HENRY-COMPS=GLOBAL CHEMISTRY=GLOBAL &

        TRUE-COMPS=YES

    PROPERTIES NRTL

STREAM 1

    SUBSTREAM CISOLID TEMP=475 PRES=1

    MOLE-FLOW CU 7923.5497

STREAM 3

    SUBSTREAM MIXED TEMP=475 PRES=1

    MOLE-FLOW H2O 73589.6039 / H2 3961.68812 / HCL &

        3982.75583 / CU+ 7161.30422 / H3O+ 8.09899765 / OH- &

        0.00132688466 / CL- 7169.40189

    SUBSTREAM CISOLID TEMP=475 PRES=1

    MOLE-FLOW CU 762.245481

STREAM 4

    SUBSTREAM MIXED TEMP=450 PRES=1

    MOLE-FLOW H2O 73568.2168 / H2 3961.68686 / HCL &

        3986.27298

STREAM 6

    SUBSTREAM MIXED TEMP=100 PRES=1

    MOLE-FLOW H2O 27864.7069 / H2 3961.88556 / HCL &

        76.5490796

STREAM 7

    SUBSTREAM MIXED TEMP=30 PRES=1

    MOLE-FLOW H2O 176.082326 / H2 3961.54534 / HCL &

        3.925890E-005

STREAM 9

    SUBSTREAM MIXED TEMP=20 PRES=6.56694251

    MOLE-FLOW H2O 176.082286 / H2 3961.54534 / HCL &
```

3.806203E-014 / H3O+ 3.926038E-005 / OH- 1.478693E-009 / &

CL- 3.925890E-005

STREAM 10

SUBSTREAM MIXED TEMP=20 PRES=6.56694251

MOLE-FLOW H2O 14.4737217 / H2 3961.53018 / HCL &

3.806203E-014

STREAM 11

SUBSTREAM MIXED TEMP=450 PRES=1

MOLE-FLOW H2O 24.9043711 / H2 0.00126260235 / HCL &

8.561478E-018 / CU+ 7161.30422 / H3O+ 4.58180804 / &

OH- 0.00128620277 / CL- 7165.88474

SUBSTREAM CISOLID TEMP=450 PRES=1

MOLE-FLOW CU 762.245481

STREAM 12

SUBSTREAM MIXED TEMP=100 PRES=1

MOLE-FLOW H2O 376071.482 / H2 0.00145328808 / HCL &

3.385486E-011 / H3O+ 2988.23798 / OH- 2.617516E-008 / &

CL- 2988.23798

STREAM 13

SUBSTREAM MIXED TEMP=30 PRES=1

MOLE-FLOW H2O 7363.0228 / H2 0.0168639822 / HCL &

2.409526E-007 / H3O+ 3241.66882 / OH- 1.097477E-016 / &

CL- 3241.66882

STREAM 14

SUBSTREAM MIXED TEMP=30 PRES=1

STREAM 15

SUBSTREAM MIXED TEMP=30 PRES=1

MOLE-FLOW H2O 7722.59988 / H2 0.0951535507 / HCL &

3.648599E-014 / H3O+ 21.409387 / OH- 2.983264E-011 / &

CL- 21.409387

STREAM 16

SUBSTREAM MIXED TEMP=20 PRES=6.56694251

MOLE-FLOW H2O 161.608565 / H2 0.0151640827 / HCL &

1.307153E-023 / H3O+ 3.926038E-005 / OH- 1.478693E-009 / &

CL- 3.925890E-005

STREAM 17

SUBSTREAM MIXED TEMP=29.7960826 PRES=1

MOLE-FLOW H2O 7884.20844 / H2 0.110317633 / HCL &

1.213668E-010 / H3O+ 21.4094262 / OH- 3.041135E-011 / &

CL- 21.4094262

STREAM 18

SUBSTREAM MIXED TEMP=375 PRES=1

MOLE-FLOW H2O 7905.61787 / H2 0.110317633 / HCL &

21.4094262

STREAM 19

SUBSTREAM MIXED TEMP=450 PRES=1

MOLE-FLOW H2O 25.4441946 / H2 0.00126260235 / O2 &

0.122868879 / HCL 0.0768233676 / CU++ 7923.55114 / &

CU+ 7161.30422 / H3O+ 4.87769356 / OH- 0.00554708648 / &

CL- 23013.2786

SUBSTREAM CISOLID TEMP=450 PRES=1

MOLE-FLOW "CUCL(S)" 7923.53768 / CU 762.245481

STREAM 20

SUBSTREAM MIXED TEMP=80. PRES=1.

STREAM 21

SUBSTREAM MIXED TEMP=80 PRES=1

MOLE-FLOW H2O 62482.8017 / H2 381.172648 / O2 &

0.122876647 / HCL 8.59828558 / CU++ 7923.5497 / H3O+ &

3199.01955 / OH- 1.315215E-011 / CL- 19046.1189 / &

CUCL2 7923.53707

SUBSTREAM CISOLID TEMP=80 PRES=1

MOLE-FLOW CU 7923.5497

STREAM 22

SUBSTREAM MIXED TEMP=79.9976568 PRES=1

MOLE-FLOW H2O 62482.8 / H2 381.172648 / O2 0.122876647 / &

HCL 8.59652068 / CU++ 7923.5497 / H3O+ 3199.02131 / &

OH- 1.314930E-011 / CL- 19046.1207 / CUCL2 7923.53707

STREAM 27

SUBSTREAM MIXED TEMP=375 PRES=1

SUBSTREAM CISOLID TEMP=375 PRES=1

STREAM 28

SUBSTREAM MIXED TEMP=375 PRES=0.5

MOLE-FLOW H2O 66281.7381 / H2 346.582253 / HCL &

1668.25768 / CU++ 13617.4396 / H3O+ 0.00071821585 / &

OH- 0.00016535253 / CL- 26571.4907 / CUCL2 219561.763

STREAM 30

SUBSTREAM MIXED TEMP=530 PRES=1

MOLE-FLOW H2O 7.14142645 / H2 6.781980E-008 / O2 &

6.294365E-010 / HCL 0.00034845440 / CU++ 7923.55052 / &

```
      H3O+ 0.481773219 / OH-
0.113325243 / CL- 15847.4695

   SUBSTREAM CISOLID
TEMP=530 PRES=1

   MOLE-FLOW CU2OCL2
3961.76853

STREAM 31

   SUBSTREAM MIXED
TEMP=530 PRES=1

   MOLE-FLOW H2O 7.14142645 /
H2 6.781980E-008 / O2  &

      1980.88427 / HCL
0.00034845440 / CU++
7923.55052 /  &

      H3O+ 0.481773219 / OH-
0.113325243 / CL- 15847.4695 /  &

      CUCL 7923.53707

STREAM 32

   SUBSTREAM MIXED
TEMP=530 PRES=1

   MOLE-FLOW H2O 6.89654652 /
H2 6.781630E-008 / O2  &

      1980.75894 / HCL
0.00034845397 / CUCL
6.779697E-076

STREAM 34

   SUBSTREAM MIXED
TEMP=530 PRES=1

   MOLE-FLOW H2O 0.244871389
/ H2 3.419994E-012 / O2  &

      0.122868879 / HCL
5.556601E-023 / CU++ 0. / H3O+
&

      0.11332525 / OH-
0.113325252 / CL- 0. / CUCL  &

      7923.53768

STREAM 37

   SUBSTREAM MIXED
TEMP=375 PRES=1

   MOLE-FLOW H2O 0.687515977
/ H2 331.850333 / O2  &

      7.136073E-046 / HCL
456.993891 / CUCL2 2.428091E-
079 /  &

      CUCL2-2W 6.213336E-080

STREAM 38

   SUBSTREAM MIXED TEMP=50
PRES=1

   MOLE-FLOW H2O 5.550835E-
010 / H3O+ 2.321022E-018 / OH-
&

      2.321022E-018

   SUBSTREAM CISOLID
TEMP=50 PRES=1

   MOLE-FLOW CU 1E-008

STREAM 39

   SUBSTREAM MIXED
TEMP=400 PRES=1

   MOLE-FLOW H2O 9.626547E-
006 / HCL 9.037345E-005

STREAM 41

   SUBSTREAM MIXED
TEMP=408 PRES=1

   MOLE-FLOW H2O 73597.4585 /
H2 381.281765 / O2  &

      0.122876166 / HCL
11152.1576

STREAM 42

   SUBSTREAM MIXED
TEMP=198.150924 PRES=1

   MOLE-FLOW H2O 73597.4585 /
H2 381.281765 / O2  &

      0.122876166 / HCL
11152.1576

STREAM FH2O

   SUBSTREAM MIXED
TEMP=120 PRES=1

   MOLE-FLOW H2O 3979.678

BLOCK MX1 MIXER

 PARAM NPHASE=2 T-
EST=108.179717

   BLOCK-OPTION FREE-
WATER=NO

BLOCK MX2 MIXER

   PARAM T-EST=29.7963552

BLOCK SPA FSPLIT

   MOLE-FLOW 14 20000.

BLOCK FILT SEP

   PARAM

   FRAC STREAM=40
SUBSTREAM=MIXED
COMPS=H2O H2 O2 HCL CU++
&

      CU+ H3O+ OH- CL- CUCL
"CUCL(S)" CU CU2OCL2 CUCL2
&

      CUCL2-2W FRACS=0.4 0. 0.
0.4 0. 0. 0. 0. 0. 0. 0.  &

      0. 0. 0. 0.

   FRAC STREAM=40
SUBSTREAM=CISOLID
COMPS="CUCL(S)" CU  &

      CU2OCL2 CUCL2 CUCL2-2W
FRACS=0. 0. 0. 0. 0.

BLOCK FHXDIS HEATER

   PARAM TEMP=80. PRES=0.

BLOCK FHXR1A HEATER

   PARAM TEMP=408. PRES=0.

   HCURVE 1 NPOINT=20

BLOCK FHXR1A2 HEATER

   PARAM TEMP=475. PRES=0.

   UTILITY UTILITY-ID=U-2

BLOCK FHXR1C HEATER

   PARAM TEMP=475. PRES=0.

   UTILITY UTILITY-ID=U-2

BLOCK FHXR4 HEATER

   PARAM TEMP=375. PRES=1.

BLOCK FHXR4S HEATER

   PARAM TEMP=375. PRES=0.

BLOCK FHXR5 HEATER

   PARAM TEMP=530. PRES=0.

BLOCK PHXCOMP HEATER

   PARAM TEMP=20. PRES=0.

BLOCK PHXF1R1 HEATER

   PARAM TEMP=100. PRES=0.

   HCURVE 1

BLOCK PHXQC HEATER

   PARAM TEMP=80. PRES=0.
MAXIT=100 TOL=0.001

   HCURVE 1 INDEP-VAR=DUTY

   BLOCK-OPTION FLASH-
METHOD=INSIDE-OUT

   UTILITY UTILITY-ID=U-1

BLOCK PHXR5 HEATER
```

```
   PARAM TEMP=30. PRES=0.
NPHASE=1 PHASE=V

   BLOCK-OPTION FREE-
WATER=NO

BLOCK F0R1 FLASH2

   PARAM TEMP=450. PRES=1.

BLOCK F1R1 FLASH2

   PARAM TEMP=100. PRES=1.

BLOCK F2R1 FLASH2

   PARAM TEMP=30. PRES=0.

BLOCK F2R4 FLASH2

   PARAM TEMP=375. PRES=1.

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL FREE-
WATER=STEAM-TA  &

      SOLU-WATER=3 TRUE-
COMPS=YES

BLOCK F3R5 FLASH2

   PARAM TEMP=530. PRES=1.

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL FREE-
WATER=STEAM-TA  &

      SOLU-WATER=3 TRUE-
COMPS=YES

BLOCK FCOMP FLASH2

   PARAM TEMP=20. PRES=0.

BLOCK DECOMP RSTOIC

   PARAM TEMP=530. PRES=1.

   STOIC 1 CISOLID CU2OCL2 -1.
/ MIXED CUCL 2. / O2 0.5

   CONV 1 CISOLID CU2OCL2 1.

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL FREE-
WATER=STEAM-TA  &

      SOLU-WATER=3 TRUE-
COMPS=YES

   UTILITY UTILITY-ID=U-2

BLOCK H2REACT RSTOIC

   PARAM TEMP=475. PRES=1.
SERIES=YES HEAT-OF-
REAC=NO

   STOIC 1 CISOLID CU -2. /
MIXED HCL -2. / CUCL 2. /  &

      H2 1.

   STOIC 2 MIXED O2 -0.5 / H2 -1.
/ H2O 1.

   CONV 1 CISOLID CU 0.9038

   CONV 2 MIXED O2 1.

   UTILITY UTILITY-ID=U-1

BLOCK HXQC RSTOIC

   PARAM TEMP=450. PRES=1.

   STOIC 1 MIXED CUCL -1. /
CISOLID "CUCL(S)" 1.

   CONV 1 MIXED CUCL 1.

   UTILITY UTILITY-ID=U-1

BLOCK HYDR RSTOIC

   PARAM TEMP=375. PRES=0.5
SERIES=YES

   STOIC 1 MIXED CU++ -1. / CL- -
2. / CISOLID CUCL2 1.

   STOIC 2 CISOLID CUCL2 -2. /
MIXED H2O -1. / CISOLID  &

      CU2OCL2 1. / MIXED HCL 2.

   CONV 1 MIXED CL- 0.99999

   CONV 2 CISOLID CUCL2 1.

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL FREE-
WATER=STEAM-TA  &

      SOLU-WATER=3 TRUE-
COMPS=YES

   UTILITY UTILITY-ID=U-2

HIERARCHY DIS

DEF-STREAMS MIXCISLD ALL

SOLVE

   PARAM METHOD=SM

   RUN-MODE MODE=SIM

FLOWSHEET

   BLOCK DSPPTN IN=16
OUT=PR2

   BLOCK DPN1 IN=FR2 PR2A
OUT=16

PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL
CHEMISTRY=GLOBAL  &

      FREE-WATER=STEAM-TA
SOLU-WATER=3 TRUE-
COMPS=YES

   PROPERTIES NRTL

STREAM 16

   SUBSTREAM MIXED TEMP=80
PRES=1

   MOLE-FLOW H2O 62478.9767 /
H2 381.170366 / O2  &

      0.122868879 / HCL
8.11928555 / CU++ 7923.55114 /
CU+  &

      15847.0874 / H3O+
3199.46184 / OH- 1.845746E-011 /
&

      CL- 34893.6515

BLOCK DPN1 RSTOIC

   PARAM TEMP=80. PRES=1.

   STOIC 1 CISOLID "CUCL(S)" -1.
/ MIXED CU+ 1. / CL- 1.

   CONV 1 CISOLID "CUCL(S)" 1.

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL
CHEMISTRY=GLOBAL  &

      FREE-WATER=STEAM-TA
SOLU-WATER=3 TRUE-
COMPS=YES

BLOCK DSPPTN RSTOIC

   PARAM TEMP=80. PRES=1.

   STOIC 1 MIXED CU+ -2. / CU++
1. / CISOLID CU 1.

   CONV 1 MIXED CU+ 1.

   UTILITY UTILITY-ID=U-3

ENDHIERARCHY DIS

BLOCK COMP COMPR

   PARAM TYPE=ISENTROPIC
PRES=6.56694251

   UTILITY UTILITY-ID=U-3

BLOCK SPC SSPLIT

   FRAC MIXED 35 0.

   FRAC CISOLID 35 1.
```

E.3 Three-step cycle Input summary

```
Input Summary created by Aspen Plus Rel. 23.0 at 15:03:12 Sat Jul 30, 2011

IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
      VOLUME-FLOW='cum/hr' PRESSURE=bar TEMPERATURE=C DELTA-T=C  &
      PDROP-PER-HT='mbar/m' PDROP=bar

DEF-STREAMS MIXCISLD ALL

SIM-OPTIONS
   IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
      HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
      VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
      MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
      MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
      PDROP=bar
   SIM-OPTIONS OLD-DATABANK=YES

DESCRIPTION "
   Electrolytes Simulation with Metric Units :
   C, bar, kg/hr, kmol/hr, Gcal/hr, cum/hr.
   Property Method: ELECNRTL
   Flow basis for input: Mass
   Stream report composition
   ******

DATABANKS ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  / &
      PURE22

PROP-SOURCES ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  / &
      PURE22

COMPONENTS
   H2O H2O /
   H2 H2 /
   O2 O2 /
   HCL HCL /
   CU++ CU+2 /
   CU+ CU+ /
   H3O+ H3O+ /
   OH- OH- /
   CL- CL- /
   CUCL CUCL /
   "CUCL(S)" CUCL /
   CU CU /
   CU2OCL2 CU2OCL2 /
   CUCL2 CUCL2 /
   CUCL2-2W "CUCL2*2W"

HENRY-COMPS GLOBAL HCL H2

CHEMISTRY GLOBAL
    DISS CUCL CU+ 1 / CL- 1
   STOIC 2 HCL -1 / H2O -1 / H3O+ 1 / CL- 1
   SALT CUCL2-2W CU++ 1. / CL- 2. / H2O 2.

FLOWSHEET
   HIERARCHY DIS
   CONNECT $C-1 IN=14 OUT=DIS.FR2
   CONNECT $C-3 IN=S-4 OUT=DIS.12
   CONNECT $C-2 IN=DIS.PR2 OUT=21
   HIERARCHY HYD
   CONNECT $C-4 IN=S-6 OUT=HYD.5
   CONNECT $C-7 IN=FH20 OUT=HYD.TEMP16
   CONNECT $C-5 IN=HYD.11 OUT=8
   CONNECT $C-6 IN=HYD.12 OUT=9
   BLOCK S1 IN=S-1 OUT=3 5
   BLOCK S2 IN=3 OUT=4 6
   BLOCK MX1 IN=6 S-3 OUT=13
   BLOCK DECOMP IN=S-7 OUT=11
   BLOCK S3 IN=S-5 OUT=15 14
   BLOCK VV1 IN=21 OUT=S-1
   BLOCK C1 IN=19 OUT=S-2
   BLOCK HX1 IN=8 OUT=S-3
   BLOCK HX2 IN=S-2 OUT=S-4
   BLOCK HX3 IN=11 OUT=S-5
   BLOCK HX4 IN=5 OUT=S-6
   BLOCK HX5 IN=9 OUT=S-7
   BLOCK MX2 IN=MKA 13 OUT=19
   BLOCK PHX IN=4 OUT=S-8
   BLOCK PHX2 IN=15 OUT=S-9

PROPERTIES ELECNRTL HENRY-COMPS=GLOBAL CHEMISTRY=GLOBAL  &
      TRUE-COMPS=YES
   PROPERTIES NRTL

STREAM 5
   SUBSTREAM MIXED TEMP=100 PRES=1
   MOLE-FLOW H2O 5713.13613 / H2 0.0318425598 / HCL  &
      1.714426E-008 / CU++ 3514.19449 / CU+ 3685.80551 /  &
      H3O+ 572.506045 / CL- 11286.7005

STREAM 8
   SUBSTREAM MIXED TEMP=400 PRES=1
   MOLE-FLOW H2O 8006.99772 / HCL 4045.92666

STREAM 9
   SUBSTREAM MIXED TEMP=400 PRES=1
```

```
   MOLE-FLOW H2O 148.762496 /
H2 0.0886717629 / O2  &

      0.0146799657 / HCL
2.76003053 / CU++ 0.138453757 /
&

      CU+ 277.312146 / H3O+
0.245033224 / CL- 277.834087

   SUBSTREAM CISOLID
TEMP=400 PRES=1

   MOLE-FLOW CU2OCL2
3461.2747

STREAM 11

   SUBSTREAM MIXED
TEMP=540 PRES=1

   MOLE-FLOW H2O 113.068329 /
H2 0.0318425598 / O2  &

      878.531051 / HCL
32.1895642 / CU++ 0.0702838898
/  &

      CU+ 3685.80551 / H3O+
8.51402466 / CL- 3694.4601

   SUBSTREAM CISOLID
TEMP=540 PRES=1

   MOLE-FLOW "CUCL(S)"
3514.1242

STREAM 13

   SUBSTREAM MIXED
TEMP=104.569841 PRES=1
TOL=0.001

   MOLE-FLOW H2O 8921.35554 /
HCL 7159.22613

STREAM 14

   SUBSTREAM MIXED
TEMP=150 PRES=1

   MOLE-FLOW H2O 89.8241557 /
H2 1.446145E-006 / O2  &

      1.24158517 / HCL 4.366772E-
011 / CU++ 0.0702838898 /  &

      CU+ 3685.80551 / H3O+
0.0348528663 / CL- 3685.98093

   SUBSTREAM CISOLID
TEMP=150 PRES=1

   MOLE-FLOW "CUCL(S)"
3514.1242

STREAM 19

   SUBSTREAM MIXED
TEMP=284. PRES=1.

   MOLE-FLOW H2O 16800. / HCL
7200.

STREAM 21

   SUBSTREAM MIXED
TEMP=100 PRES=24

   MOLE-FLOW H2O 4520.69556 /
H2 1757.09724 / HCL  &

      1006.50108 / CU++
3514.19449 / CU+ 3685.80551 /
H3O+  &

      2679.30444 / CL- 13393.4989

STREAM FH20

   SUBSTREAM MIXED
TEMP=120 PRES=1

   MOLE-FLOW H2O 3600

STREAM MKA

   SUBSTREAM MIXED
TEMP=100. PRES=1. TOL=0.001

   MOLE-FLOW H2O 1E-030

STREAM S-2

   SUBSTREAM MIXED
TEMP=684.957448 PRES=24

   MOLE-FLOW H2O 16800. / HCL
7200.

STREAM S-4

   SUBSTREAM MIXED
TEMP=100. PRES=24.

   MOLE-FLOW H2O 16800. / HCL
7200.

STREAM S-6

   SUBSTREAM MIXED
TEMP=400 PRES=1

   MOLE-FLOW H2O 6268.50683 /
H2 0.0318425598 / HCL  &

      555.370698 / CU++
3514.19449 / CU+ 3685.80551 /
H3O+  &

      17.1353466 / CL- 10731.3298

BLOCK MX1 MIXER

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL
CHEMISTRY=GLOBAL  &

      FREE-WATER=STEAM-TA
SOLU-WATER=0 TRUE-
COMPS=YES

BLOCK MX2 MIXER

   PARAM TOL=0.01

BLOCK S2 SEP

   FRAC STREAM=4
SUBSTREAM=MIXED
COMPS=H2O H2 O2 HCL CU++
&

      CU+ H3O+ OH- CL- CUCL
"CUCL(S)" CU CU2OCL2 CUCL2
&

      CUCL2-2W FRACS=0. 1. 0. 0.
0. 0. 0. 0. 0. 0. 0.  &

      0. 0. 0. 0.

   FRAC STREAM=4
SUBSTREAM=CISOLID
COMPS="CUCL(S)" CU  &

      CU2OCL2 CUCL2 CUCL2-2W
FRACS=0. 0. 0. 0. 0.

BLOCK HX1 HEATER

   PARAM TEMP=110. PRES=1.

   UTILITY UTILITY-ID=U-1

BLOCK HX2 HEATER

   PARAM TEMP=100. PRES=24.

   UTILITY UTILITY-ID=U-1

BLOCK HX3 HEATER

   PARAM TEMP=100. PRES=1.

   UTILITY UTILITY-ID=U-1

BLOCK HX4 HEATER

   PARAM TEMP=400. PRES=1.

   UTILITY UTILITY-ID=U-2

BLOCK HX5 HEATER

   PARAM TEMP=540. PRES=1.

   UTILITY UTILITY-ID=U-2

BLOCK PHX HEATER

   PARAM TEMP=25. PRES=6.5

BLOCK PHX2 HEATER

   PARAM TEMP=25. PRES=0.

BLOCK S1 FLASH2

   PARAM TEMP=100. PRES=1.
MAXIT=50

BLOCK S3 FLASH2

   PARAM TEMP=150. PRES=1.

BLOCK DECOMP RSTOIC
```

```
   PARAM TEMP=540. PRES=1.
TOL=0.01

   STOIC 1 CISOLID CU2OCL2 -1.
/ MIXED O2 0.5 / CISOLID  &

      "CUCL(S)" 2.

   CONV 1 CISOLID CU2OCL2 1.

   UTILITY UTILITY-ID=U-2

HIERARCHY DIS

DEF-STREAMS MIXCISLD ALL

SOLVE

   PARAM METHOD=SM

   RUN-MODE MODE=SIM

FLOWSHEET

   BLOCK DSPPTN IN=16
OUT=PR2

   BLOCK DPN1 IN=FR2 12
OUT=16

PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL
CHEMISTRY=GLOBAL  &

      FREE-WATER=STEAM-TA
SOLU-WATER=3 TRUE-
COMPS=YES

   PROPERTIES NRTL

STREAM 16

   SUBSTREAM MIXED
TEMP=100 PRES=24

   MOLE-FLOW H2O 3685.80551 /
HCL 3685.80551 / CU+ 7200 /  &

      H3O+ 3514.19449 / CL-
10714.1945

BLOCK DPN1 RSTOIC

   PARAM TEMP=100. PRES=24.
SERIES=YES

   STOIC 1 CISOLID "CUCL(S)" -2.
/ MIXED CU+ 2. / CL- 2.

   STOIC 2 MIXED H2O -1. / HCL -
1. / H3O+ 1. / CL- 1.

   CONV 1 CISOLID "CUCL(S)" 1.

   CONV 2 MIXED HCL 0.99998

   PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL
CHEMISTRY=GLOBAL  &
;

      FREE-WATER=STEAM-TA
SOLU-WATER=3 TRUE-
COMPS=YES

   UTILITY UTILITY-ID=U-3

BLOCK DSPPTN RSTOIC

   PARAM TEMP=100. PRES=24.

   STOIC 1 MIXED CU+ -2. / H3O+
-2. / CU++ 2. / H2 1. /  &

      H2O 2.

   CONV 1 MIXED H3O+ 1.

   UTILITY UTILITY-ID=U-1

ENDHIERARCHY DIS

HIERARCHY HYD



DEF-STREAMS MIXCISLD ALL

SOLVE

   PARAM METHOD=SM

   RUN-MODE MODE=SIM

FLOWSHEET

   BLOCK HR1 IN=5 OUT=9

   BLOCK HYDR2 IN=9 TEMP16
OUT=10

   BLOCK S3 IN=10 OUT=11 12

PROPERTIES ELECNRTL
HENRY-COMPS=GLOBAL
CHEMISTRY=GLOBAL  &

      FREE-WATER=STEAM-TA
SOLU-WATER=3 TRUE-
COMPS=YES

   PROPERTIES NRTL

BLOCK S3 SEP

   FRAC STREAM=11
SUBSTREAM=MIXED
COMPS=H2O HCL FRACS=0.99
&

      1.

   FRAC STREAM=11
SUBSTREAM=CISOLID
COMPS=CU2OCL2 FRACS=0.

BLOCK HR1 RSTOIC

   PARAM TEMP=400. PRES=1.

   STOIC 1 MIXED CU++ -1. / CL- -
2. / CUCL2 1.

   CONV 1 MIXED CU++ 0.99998

   UTILITY UTILITY-ID=U-2

BLOCK HYDR2 RSTOIC

   PARAM TEMP=400. PRES=1.

   STOIC 1 MIXED CUCL2 -2. /
H2O -1. / CISOLID CU2OCL2 1. / &

      MIXED HCL 2.

   CONV 1 MIXED CUCL2 1.

   UTILITY UTILITY-ID=U-1

ENDHIERARCHY HYD

BLOCK C1 COMPR

   PARAM TYPE=ISENTROPIC
PRES=24. SEFF=0.78

   UTILITY UTILITY-ID=U-3

BLOCK VV1 VALVE

   PARAM P-OUT=1. FLASH-
MAXIT=100

UTILITY U-1 GENERAL

   COST PRICE=6.7E-006 <$/ton>

   PARAM UTILITY-TYPE=WATER
COOLING-VALU=4.187 TIN=20.
TOUT=40.  &

      CALOPT=DUTY

UTILITY U-2 GENERAL

   COST PRICE=2E-006 <$/ton>

   PARAM UTILITY-
TYPE=GENERAL COOLING-
VALU=5.193 TIN=600.  &

      TOUT=540. CALOPT=DUTY

UTILITY U-3 GENERAL

   COST ELEC-PRICE=0.075
<$/kWhr>

   PARAM UTILITY-
TYPE=ELECTRICITY

EO-CONV-OPTI

STREAM-REPOR MOLEFLOW
MOLEFRAC
PROPERTIES=MOLECONC
THERMAL
```

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