Development and Analysis of a High Temperature Electrolyser for the Cu-Cl Cycle for Hydrogen Production

By

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A Thesis Submitted in Partial Fulfilment of the Requirements for the degree of Doctor of Philosophy in Mechanical Engineering

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ABSTRACT

A number of thermochemical cycles have been investigated to produce hydrogen from water. However, most of these cycles operate at over 800°C. The relatively lower temperature (550°C) requirement and use of inexpensive chemicals make the copper-chlorine (Cu-Cl) thermochemical cycle a promising process for hydrogen production. Building a large scale hydrogen production facility based on this cycle presents some challenges that need to be resolved. This thesis addresses the challenges of the Cu-Cl cycle by incorporating high temperature electrolysis to propose and assess four novel configurations of the Cu-Cl cycle. Four novel Cu-Cl cycles using high temperature electrolytic step for hydrogen production are proposed and thermodynamically assessed. In addition, a novel hybrid Cu-Cl cycle for the co-production of hydrogen and copper using copper waste is proposed and assessed thermodynamically. An experimental investigation is made to establish the feasibility of the high temperature electrolytic step. The results suggest that using high temperature electrolysis in the Cu-Cl cycle may be beneficial as it provides a higher energy efficiency than some similar cycles reported in the literature. A detailed electrochemical model is developed to study the J-V characteristics for the proposed electrolyser (a solid oxide electrolyser based on proton conducting electrolyte). The developed model includes all the major losses namely activation, concentration and ohmic losses. Furthermore, energy and exergy analyses are also carried out. The value of energy and exergy efficiencies of the proposed electrolyser are 41.1% and 39.0%, respectively. Simulation results show that at 1073 K, P=100.325 kPa and J=1000 A/m², 1.6 V is required to produce 1 mole of hydrogen which is 0.3 V (approx.) less than the voltage required by the high temperature steam electrolyser (based on proton conducting electrolyte) operating at the same conditions (T=1073 K, P=101.325 kPa and J=1000 A/m²) suggesting that using the proposed electrolyser a new avenue may be open for high temperature electrolysis for hydrogen production, potentially with a low electrical energy requirement. The cost of hydrogen production from the three step Cu-Cl cycle (Scheme 4) is $4.18 per kg of hydrogen. In addition, two nuclear based integrated systems for the production of electricity, fresh water and hydrogen are proposed and assessed. System 1 is more efficient than System 2 in terms of energy and exergy efficiencies and has lower exergy destructions.
ACKNOWLEDGEMENT

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<table>
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<tbody>
<tr>
<td>$B_g$</td>
<td>permeation coefficient ($m^2/s$)</td>
</tr>
<tr>
<td>$\dot{C}$</td>
<td>cost rate ($$/s$)</td>
</tr>
<tr>
<td>$d$</td>
<td>thickness of electrode (m)</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient ($cm^2/s$)</td>
</tr>
<tr>
<td>$E$</td>
<td>potential (V)</td>
</tr>
<tr>
<td>$\dot{E}$</td>
<td>energy rate (kW)</td>
</tr>
<tr>
<td>ex</td>
<td>specific exergy (kJ/kg)</td>
</tr>
<tr>
<td>$\dot{E}_x$</td>
<td>exergy rate (kW)</td>
</tr>
<tr>
<td>$f$</td>
<td>exergoeconomic factor</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant ($C/mol$)</td>
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<tr>
<td>$g$</td>
<td>specific Gibbs free energy (kJ/mol)</td>
</tr>
<tr>
<td>h</td>
<td>specific enthalpy (kJ/kg)</td>
</tr>
<tr>
<td>$H$</td>
<td>enthalpy (kJ)</td>
</tr>
<tr>
<td>J</td>
<td>current density ($A/m^2$)</td>
</tr>
<tr>
<td>$k_b$</td>
<td>Boltzmann constant ($m^2kg/s^2K$)</td>
</tr>
<tr>
<td>$L$</td>
<td>electrolyte thickness (m)</td>
</tr>
<tr>
<td>LHV</td>
<td>lower heating value (kJ/kg)</td>
</tr>
<tr>
<td>$\dot{m}$</td>
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<td>$M$</td>
<td>molecular weight (kg/kmol)</td>
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<tr>
<td>$p$</td>
<td>partial pressure (atm)</td>
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<tr>
<td>$P$</td>
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</tr>
<tr>
<td>q</td>
<td>specific heat (kJ/mol)</td>
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<tr>
<td>$\dot{Q}$</td>
<td>heat transfer rate (kW)</td>
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<tr>
<td>$r$</td>
<td>mean pore radius of electrode (m)</td>
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<tr>
<td>$R$</td>
<td>universal gas constant ($J/molK$)</td>
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<tr>
<td>$T$</td>
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<td>$U$</td>
<td>uncertainty</td>
</tr>
<tr>
<td>$V$</td>
<td>velocity (m/s)</td>
</tr>
<tr>
<td>w</td>
<td>specific work (kJ/mol)</td>
</tr>
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</table>
\( \dot{W} \) work input rate (kW)
\( Z \) height (m)
\( \dot{Z} \) capital cost rate ($/s)

**Greek Letters**
- \( \epsilon \) electrode porosity
- \( \eta \) efficiency
- \( \varepsilon \) effectiveness
- \( \gamma \) specific heat ratio
- \( \mu \) dynamic viscosity (Ns/m²)
- \( \Omega \) dimensionless collision integral
- \( \phi \) electrical resistivity of electrolyte (Ωm)
- \( \rho \) conductivity (S/m)
- \( \sigma \) mean characteristic length (Å)
- \( \tau \) dimensionless temperature
- \( \xi \) electrode tortuosity
- \( \varepsilon/k \) Lennard-Jones potential (K)

**Subscripts**
- \( a \) anode
- \( \text{act} \) activation
- \( c \) cathode
- \( \text{ch} \) chemical
- \( \text{conc} \) concentration
- \( \text{cv} \) control volume
- \( d \) destruction
- \( e \) exit
- \( \text{eff} \) effective
- \( \text{el} \) electric
- \( \text{elec} \) electrolyser
- \( \text{en} \) energy
- \( \text{eq} \) equivalent
ex  exergy
f  filter
g  generator
gen  generation
gt  gas turbine
he  helium
hex  heat exchanger
i  inlet
m  mechanical
max  maximum
mc  mixing chamber
k  Knudsen
ohm  ohmic
ov  overall
p  pump
ph  physical
pp  power plant
pre  precooler
pt  Pelton turbine
r  ratio
rc  reactor core
rec  recuperator
rm  reverse osmosis module
ro  reverse osmosis
Sc  scheme
st  steam turbine
tot  total
tv  throttle valve
ut  utilisation
0  standard, exchange
### Acronyms

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<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>CRF</td>
<td>Capital Recovery Factor</td>
</tr>
<tr>
<td>EES</td>
<td>Engineering Equation Solver</td>
</tr>
<tr>
<td>GFR</td>
<td>Gas-cooled Fast Reactor</td>
</tr>
<tr>
<td>GT</td>
<td>Gas Turbine</td>
</tr>
<tr>
<td>HEX</td>
<td>Heat Exchanger</td>
</tr>
<tr>
<td>LFR</td>
<td>Lead-cooled Fast Reactor</td>
</tr>
<tr>
<td>MHR</td>
<td>Modular Helium Reactor</td>
</tr>
<tr>
<td>MSR</td>
<td>Molten Salt Reactor</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
<tr>
<td>SCWR</td>
<td>Super Critical Water Reactor</td>
</tr>
<tr>
<td>SFR</td>
<td>Sodium-cooled Fast Reactor</td>
</tr>
<tr>
<td>VHTR</td>
<td>Very High Temperature Reactor</td>
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CHAPTER 1: INTRODUCTION

1.1 Energy Demand and Challenges

Worldwide energy demand is continuously increasing over the long term, largely due to rapid growth in developing countries and increases in the global population. In the year 2016, the world’s energy consumption was 101.78 quadrillion kJ and it is been projected that it is going to increase to 112.6 quadrillion kJ by the year 2050. As seen in Table 1, fossil fuels dominated the world’s energy consumption in 2016. Due to the burning of fossil fuels to meet the world’s energy demand, CO₂ emissions were about 5,157 million metric tons in the year 2016 (EIA, 2017).

<table>
<thead>
<tr>
<th>Type of energy</th>
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<tr>
<td>Petroleum and Other Liquids</td>
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<tr>
<td>Natural Gas</td>
<td>30.16</td>
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<tr>
<td>Coal</td>
<td>14.70</td>
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<tr>
<td>Nuclear</td>
<td>8.80</td>
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<tr>
<td>Hydroelectric Power</td>
<td>2.64</td>
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<td>Biomass</td>
<td>2.91</td>
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<td>Other Renewable</td>
<td>3.21</td>
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<tr>
<td>Other</td>
<td>0.44</td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>101.78</strong></td>
</tr>
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</table>

Source: EIA (2017)

With the continuing depletion of readily available fossil fuel reserves and environmental problems associated with their use, many people are seeking other energy sources which are sustainable as well as environmentally benign, for instance, renewable energy sources and nuclear energy. Greenhouse gas emissions from fuel combustion in the transportation and stationary electrical generation sectors, especially carbon dioxide (CO₂) emissions, are a serious global concern. Moreover, although there is debate over the rate of depletion of fossil fuel reserves, these resources are finite and will eventually become much scarcer. It is important to investigate alternative energy resources and systems that are sustainable, more environmentally benign, and practical for implementation within today’s energy infrastructures.
Renewable energy includes energy sources that are derived from natural processes and can be replenished. Presently, the most widely used renewable energy sources are hydraulic, biomass, solar, geothermal, wind and ocean. The conversion of renewable energy sources to useful products (e.g. electricity, heating, cooling, hydrogen, industrial steam, and biofuels) is illustrated conceptually in Figure 1.1, where technology consists of energy conversion devices such as wind turbines, hydroelectric generators, concentrating solar collectors, photovoltaic cells etc.

![Figure 1.1 Transformation of renewable energy sources for useful outputs (modified from NRC, 2017)](image)

Renewable and conventional energy systems are compared in Table 1.2. Renewable energy systems are seen to have attributes that usually make them more attuned with sustainable development than conventional systems.

### Table 1.2 Comparison of renewable and conventional energy systems

<table>
<thead>
<tr>
<th>Factor</th>
<th>Renewable energy resources</th>
<th>Conventional energy resources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Examples</td>
<td>Solar, wind, biomass, ocean, geothermal, hydraulic</td>
<td>Oil, natural gas, coal</td>
</tr>
<tr>
<td>Source</td>
<td>Local environment</td>
<td>Concentrated stores in earth</td>
</tr>
<tr>
<td>Lifetime</td>
<td>Extremely long (almost infinite)</td>
<td>Finite</td>
</tr>
<tr>
<td>Cost at source</td>
<td>Free</td>
<td>Increasingly expensive</td>
</tr>
<tr>
<td>Location and use</td>
<td>Site and society specific</td>
<td>General and invariant use</td>
</tr>
<tr>
<td>Pollution</td>
<td>Very little</td>
<td>Intrinsic and common</td>
</tr>
<tr>
<td>Variability and control</td>
<td>Fluctuating</td>
<td>Steady</td>
</tr>
</tbody>
</table>

Source: Twidell and Weir (2006)

Table 1.3 provides the status of nuclear power of selected countries in the world (as of July 1, 2016). It can be noted from Table 1.3 that 10.7% of the world’s electricity demand is met by nuclear energy, highlighting the importance of nuclear energy.
Table 1.3 Number of nuclear reactors with the share of electricity in the world and selected countries

<table>
<thead>
<tr>
<th>Name of the country</th>
<th>Number of nuclear reactors</th>
<th>Share of electricity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada</td>
<td>19</td>
<td>16.5</td>
</tr>
<tr>
<td>China</td>
<td>34</td>
<td>3.0</td>
</tr>
<tr>
<td>India</td>
<td>20</td>
<td>3.5</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>15</td>
<td>19.0</td>
</tr>
<tr>
<td>World</td>
<td>402</td>
<td>10.7</td>
</tr>
</tbody>
</table>

Source: Schneider and Froggatt (2016)

Table 1.4 lists some existing nuclear power plants in various countries. The nuclear power plant in India is a cogeneration plant used for electricity and pure water while in Japan the High Temperature Nuclear Reactor is used for high temperature process heating.

Table 1.4 Selected major nuclear plants in several countries

<table>
<thead>
<tr>
<th>Country</th>
<th>Plant type</th>
<th>Outputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>India</td>
<td>PHWR</td>
<td>Electricity, pure water</td>
</tr>
<tr>
<td>Russia</td>
<td>ATEC-200</td>
<td>Electricity, domestic heating</td>
</tr>
<tr>
<td>China</td>
<td>NHR-200</td>
<td>Domestic heating</td>
</tr>
<tr>
<td>Japan</td>
<td>HTTR</td>
<td>High temperature process heat</td>
</tr>
</tbody>
</table>

Source: Nuclear News (2015)

According to the Energy Information Administration (EIA, 2017), the share of renewable energy in global energy generation is expected to double in the year 2050 relative to 2016. This highlights the expectation that renewable sources will play a significant role in the production of future energy. In a number of countries (e.g., Germany), strategies and programs are being implemented to support and encourage the use of renewable energy, and hydrogen may be come out as a promising candidate for energy carrier as it may act as link between nuclear and renewable energy resources (Dincer, 2012; Rosen, 2010). There is an increasing level of interest in the development of large-scale non-fossil hydrogen production technologies. A large scale hydrogen infrastructure, based on non-fossil fuel derived hydrogen production technologies such as nuclear or renewable, may be less environmentally damaging than the conventional energy systems of today (Forsberg, 2005; Lewis, 2008; Kruger, 2009).
1.2 **Hydrogen Production Methods**

On earth hydrogen is abundantly available, but only in chemical compound form. To use hydrogen as fuel, it has to be available in element form. There are various methods to produce hydrogen using the different source of energy as shown in Figure 1.2. Hydrocarbon reforming (a conventional method) is the most dominant method (account for 90% of the total hydrogen produced from different methods) for hydrogen production.

![Diagram of Hydrogen Production Methods](image)

Figure 1.2 Routes for hydrogen production using renewable and conventional energy sources (Dincer, 2012)

Renewable energies like solar, wind, ocean thermal etc. can be used to produce hydrogen in a clean and sustainable way. For example, solar energy can be used by photovoltaic cells to produce electricity. The electricity could then be utilised to run the water electrolyser for hydrogen production (see Figure 1.2). Other solar hydrogen production methods such as photoelectrochemical, photocatalytic, artificial photosynthesis etc. are also used. Hydrogen can also be produced from biomass by using various methods such as biological hydrogen production and gasification.

Nuclear energy and thermal energy from industries can also be used to produce hydrogen, and considered as environmentally benign. For example, nuclear energy power plants can be coupled
with a high temperature electrolyser to produce hydrogen (see Figure 1.2). Furthermore, the nuclear reactors could also be utilised to produce hydrogen via thermochemical water splitting, whether by high temperature heat source directly (e.g. Sodium cooled fast reactor, gas turbine modular helium reactor etc.) or by upgrading the heat from low temperature sources (e.g. CANDU reactor).

### 1.3 Thermochemical Cycles for Hydrogen Production

Thermochemical and/or electrochemical process using renewable or nuclear energy sources are some of the ways of producing hydrogen (Forsberg, 2005; Lewis, 2008; Kruger, 2009; Dincer, 2007; Orhan et al., 2008). In the thermochemical cycle, the water is split to produce hydrogen by using series of chemical and physical processes. Usually, all the chemicals used in the cycles are recycled and cause no emissions to the environment. Casper (1978) found that most of the thermochemical cycles have a maximum temperature requirement in the range of 530°C-1100°C.

In general, the thermochemical cycles usually have four basic steps:

- Water-splitting reaction
- Hydrogen production
- Oxygen production
- Recycling and formation of intermediate compounds

Table 1.5 Heat requirement of top rated cycles with maximum temperature

<table>
<thead>
<tr>
<th>Name of cycle</th>
<th>Heat input (kJ/mol H₂)</th>
<th>Heat input (MJ/kg H₂)</th>
<th>Efficiency based on HHV (%)</th>
<th>Maximum temperature required (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid sulfur</td>
<td>560</td>
<td>278</td>
<td>51</td>
<td>850</td>
</tr>
<tr>
<td>Sulfur iodine</td>
<td>635</td>
<td>315</td>
<td>45</td>
<td>850</td>
</tr>
<tr>
<td>Cadmium sulfate</td>
<td>520</td>
<td>258</td>
<td>55</td>
<td>1000</td>
</tr>
<tr>
<td>Barium sulfate</td>
<td>608</td>
<td>302</td>
<td>47</td>
<td>1000</td>
</tr>
<tr>
<td>Hybrid cadmium</td>
<td>539</td>
<td>267</td>
<td>53</td>
<td>1200</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>537</td>
<td>266</td>
<td>53.2</td>
<td>2200</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>572</td>
<td>286</td>
<td>50</td>
<td>2200</td>
</tr>
<tr>
<td>Hybrid copper chloride</td>
<td>583</td>
<td>289</td>
<td>49</td>
<td>550</td>
</tr>
</tbody>
</table>

Over 200 cycles have been reviewed by McQuillan et al. (2010) for the production of hydrogen using thermochemical reactions. Based on their study, they have shortlisted a few cycles as listed...
in Table 1.5. It is to be noted from the table that most of these cycles operate at over 800°C. The relatively lower temperature (550°C) requirement and use of inexpensive chemicals make the hybrid copper-chlorine (Cu-Cl) thermochemical cycle a promising process for hydrogen production. The other cycle that comes next to hybrid Cu-Cl cycle in terms of operating temperature and efficiency is the hybrid sulfur cycle with an operating temperature of 850°C. One may also note from the table that thermochemical cycle based on iron and zinc oxides are the one that has the highest operating temperature (2200°C).

1.4 Hybrid Cu-Cl Cycle

A hybrid Cu-Cl cycle requires the lowest temperature (550°C) among all the thermochemical cycles under investigation. There are various options of hybrid Cu-Cl cycle namely two step, three step, four step, five step. Four step hybrid Cu-Cl cycle has been studied by various institutions especially by Canadian Nuclear Laboratories (CNL) earlier known as Atomic Energy of Canada Limited (AECL) and University of Ontario Institute of Technology (UOIT).

Table 1.6 lists all the chemical steps in the four step hybrid Cu-Cl cycle. The maximum temperature required in the cycle is 550°C (see Table 1.4). The chemical reactions provided in the table form a closed internal loop such that all the chemicals get recycled, without causing harm to the environment.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1: 2CuCl₂(s) + 2H₂O(g) → 2HCl(g) + CuO + CuCl₂(s)</td>
<td>400</td>
</tr>
<tr>
<td>Step 2: CuO + CuCl₂(s) → 2CuCl₁ + 1/2 O₂(g)</td>
<td>550</td>
</tr>
<tr>
<td>Step 3: 2CuCl₁(aq) + 2HCl(aq) → H₂(g) + 2CuCl₂(aq)</td>
<td>25</td>
</tr>
<tr>
<td>Step 4: 2CuCl₂(aq) → 2CuCl₂(s)</td>
<td>&lt; 100</td>
</tr>
</tbody>
</table>

The challenges and advantages of the hybrid copper chlorine cycle are listed in Table 1.7. As seen from the table, one of the key challenges associated with the hybrid copper chlorine cycle is the difficulty in separation of the spent electrolyte from the aqueous solution. In addition, copper crossover in the electrolyser is also one of the problem associated with hybrid copper chlorine cycle.
### Table 1.7 Challenges and advantages of the hybrid Cu-Cl cycle

<table>
<thead>
<tr>
<th>Challenges</th>
<th>Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper crossover in the electrolyser</td>
<td>Cheap material</td>
</tr>
<tr>
<td>Separation of spent electrolyte</td>
<td>Lower temperature requirement (550°C)</td>
</tr>
<tr>
<td>Amount and effect of carryover reagents</td>
<td>Materials of construction identified</td>
</tr>
<tr>
<td>Chemistry and system modeling</td>
<td>Long history of development</td>
</tr>
</tbody>
</table>

Source: Perret (2011)

Figure 1.3 shows the schematic of the four step hybrid Cu-Cl cycle with all the steps. As seen from the figure, the four step hybrid Cu-Cl cycle comprises of four main steps namely; Step 1 (hydrolysis), Step 2 (decomposition), Step 3 (electrolysis), and Step 4 (drying). In Step 1, the high temperature steam reacts with solid \( \text{CuCl}_2 \) to produced hydrogen chloride (HCl) gas and copper oxychloride \( (\text{CuO} \cdot \text{CuCl}_2) \). The copper oxychloride produced in this step is utilised in Step 2. In Step 2, the copper oxychloride is heated to 550°C and decomposed to liquid CuCl and oxygen gas. The liquid CuCl obtained from this step is cooled down and dissolved in water to produced
aqueous CuCl and would be utilised in Step 3. HCl gas produced in Step 1, is also dissolved in water to form aqueous HCl. In Step 3, aqueous HCl and aqueous CuCl are electrolysed to produce hydrogen and aqueous CuCl$_2$. In Step 4, the aqueous CuCl$_2$ produced in Step 3 is dried to produce solid CuCl$_2$. The drying step of the current Cu-Cl cycle is an energy intensive process, and the amount of heat required is much higher compared to the other steps of the cycle. In the drying step, the required energy could increase from 1 to 5 times for slurry feed to the solution, based on the concentration of CuCl$_2$. Thus, in the four step hybrid cycle all the products/reactants (except water) are recycled and hence form a closed cycle. In other words, for the overall cycle, water is the only material input while oxygen, and hydrogen are the only useful material outputs.

Table 1.8 lists all the Generation IV nuclear reactors that have the potential to couple with the hybrid Cu-Cl cycle. As it can be noted from the table, all the listed reactors have an operating temperature of more than 550°C. High temperature reactor requires an operating temperature of 1000°C, while the SFR reactor has the lowest operating temperature among all the listed Generation IV nuclear reactors.

Table 1.8 Type of nuclear reactors that have potential to integrate with the hybrid Cu-Cl cycle

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Typical primary coolant inlet and outlet temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFR</td>
<td>550-800</td>
</tr>
<tr>
<td>GFR</td>
<td>485-850</td>
</tr>
<tr>
<td>VHTR</td>
<td>500-1000</td>
</tr>
<tr>
<td>SCWR</td>
<td>Up to 625</td>
</tr>
<tr>
<td>SFR</td>
<td>520-550</td>
</tr>
<tr>
<td>MSR</td>
<td>700-800</td>
</tr>
</tbody>
</table>

1.5 Motivation
A number of thermochemical cycles have been investigated to produce hydrogen from water. However, most of these cycles operate at over 800°C. The relatively lower temperature (550°C) requirement and use of inexpensive chemicals make the copper-chlorine (Cu-Cl) thermochemical cycle a promising process for hydrogen production. Building a large scale hydrogen production facility based on this cycle presents some challenges that need to be resolved. Firstly, the difficulty in separation of CuCl and CuCl$_2$ from the spent anolyte in the electrolytic step needs to be addressed. Secondly, some copper crossover is observed in the electrolyser membrane resulting in
degradation of the electrolyser performance. One of the possible ways to achieve better kinetics and integration, is the introduction of a high temperature electrolysis step in the Cu-Cl cycle. The high temperature electrolysis step needs to be thoroughly examined in terms of feasibility and practical viability.

1.6 Objectives
The main objective of this thesis is to addresses the challenges of the Cu-Cl cycle by incorporating high temperature electrolysis and to thermodynamically assess four novel configurations of the Cu-Cl cycle for hydrogen production. In addition, a novel hybrid Cu-Cl cycle for the co-production of hydrogen and copper using copper waste is proposed and assessed thermodynamically. Furthermore, two nuclear based integrated systems are proposed and assessed to produce electricity, fresh water and hydrogen. In order to have a comprehensive view, a detailed parametric study is carried out. The developed systems are optimised based on exergy efficiency and exergoeconomic factor.

The specific objectives of this research work, in terms of subobjectives for each main objective, are as follows:

1. To propose high temperature electrolyser for hydrogen production application and to investigate potential integration with Cu-Cl cycle and proposed integrated systems using nuclear energy:
   - To propose and develop high temperature electrolysis for the Cu-Cl cycle for better thermal management.
   - To establish the high temperature electrolytic step via an experimental proof of concept.
   - To integrate this high temperature electrolysis with other steps (hydrolysis, thermolysis, decomposition, etc.) of Cu-Cl cycle.
   - To develop a novel high temperature electrolyser for gas phase electrolysis of hydrogen chloride.
   - To propose and develop four novel configurations of Cu-Cl cycle for hydrogen production.
   - To propose a novel hybrid Cu-Cl cycle for the co-production of hydrogen and copper using copper waste.
   - To develop integrated systems for hydrogen production, electricity and fresh water based on proposed Cu-Cl cycle using nuclear energy.
2. To develop thermodynamic, and electrochemical models of the developed systems and conduct comprehensive energy and exergy analyses, and performance assessments of the systems:
   - To carry out thermodynamic modeling using Engineering Equation Solver by writing mass, energy, entropy and exergy balances.
   - To evaluate the properties and rates of the various streams, and exergy destructions for the components, subsystems, and reactions.
   - To develop electrochemical model which include all the major losses namely activation, concentration and ohmic losses.
   - To perform electrochemical modeling to investigate the relationship between required voltage, current density and thermal energy.
   - To conduct a comprehensive parametric studies to observe the effect of varying operating conditions (i.e. temperature, pressure, etc.) on the energy and exergy efficiencies of the proposed configurations, subsystems and integrated systems.
   - To perform uncertainty analyses by translating the uncertainty values in the temperature to the overall schemes and systems.

3. To evaluate the feasibility of the proposed system in practical applications by conducting exergoeconomic analysis of the subsystem and integrated systems:
   - To estimate component and total system costs of major components.
   - To determine the cost of exergy destruction of major steps of the Cu-Cl cycle.
   - To determine exergoeconomic factors of the major components of the system.

4. To perform multi-objective optimisation of the integrated systems to identify the ideal operating conditions and limitations:
   - To mathematically define the objective functions and constraints for thermodynamic and economic analyses.
   - To optimise the integrated systems for exergy efficiency and exergoeconomic factor using Genetic Algorithm.
CHAPTER 2: LITERATURE REVIEW

In this section, a literature review is provided for studies on Cu-Cl and halogen halides thermochemical cycles including possible system integration for the Cu-Cl cycle. In this chapter recent, advances in the high temperature electrolysis, and Cu-Cl electrolysis are also covered.

2.1 Thermochemical Cycles

As discussed in the introduction, there are more than 200 cycles that can be used for the production of hydrogen. However, in this chapter the literature review pertaining to Cu-Cl cycle and hydrogen halide cycles is provided due to the advantages discussed in introduction.

2.1.1 Cu-Cl Cycle

There are numerous studies reported on the use of Cu-Cl cycle for hydrogen production. One of the first studies is conducted by Dokiya and Kotera (1976) that used the Cu-Cl thermochemical cycle to produce hydrogen. In the electrolysis step, the HCl is reduced at the cathode and cuprous ion to cupric ion at the anode. In the final step CuCl$_2$ reacts with steam at a temperature of more than 600°C and produce oxygen, CuCl and HCl. The hybrid cycle lowered the voltage required in the electrolysis. From preliminary investigation, the cell voltage of the present Cu-Cl cycle was within the range of 0.6-1.0 V. One more advantage of the cycle lies in the ease of thermal reactions. From the preliminary investigation, the authors concluded that it needs further thorough investigation. Specifically, the electrode material, the diaphragm membrane as well as the kinetics of O$_2$ evolution needed to be investigated before reaching any conclusion about the system.

Wang et al. (2010) provided the comparison between the two most promising cycles i.e. Cu-Cl and Sulphur Iodine (SI). They found that the energy requirement for both the cycles was almost the same. However, the Cu-Cl cycle offered a lower operating temperature which is an advantage compared to the SI cycle. They further report that the Cu-Cl cycle has less material issues compared to the SI cycle.

Rosen et al. (2012) examined the issues related to the equipment scale up and process simulation. The simulations were performed on a software called Aspen Plus. The simulation results would be helpful in developing the lab scale cycle demonstration.

Aghahosseini et al. (2013) proposed a model for the integration of hydrolysis and electrolysis processes in the Cu-Cl cycle. They have used an intermediate heat exchanger and introduce a new
separation process (HCl-H$_2$O) consists of rectification and absorption processes. They found that the steam generated by the heat exchanger was sufficient to supply the excess amount of steam required by the hydrolysis step.

Gupta et al. (1997) described a system based on HCl-H$_2$-Cl$_2$ chemistry. In this process, CuCl was oxidized when HCl was passed over the copper surface while H$_2$ was released. Upon the heating to a high temperature, CuCl gets decomposed to copper while releasing Cl$_2$. The formation of this gas was studied as a function of temperature, flowrate and surface area. Temperature was varied between 400 and 600 K which does not show any significant effects on the reaction rate. Surface geometry, on the other hand plays a monotonous role for complete conversion of HCl to H$_2$ while having several thousand gas collisions per molecule.

Zamfirescu et al. (2012) reported the development of new photochemical cell and analysis for the disproportionation of copper in the Cu-Cl water splitting cycle. For the copper disproportionation, cuprous chloride was reacted with hydrochloric acid forming cupric chloride and hydrogen gas. They proposed a cell in which, rather than using external electrical supply, the reaction was done using photonic energy derived from solar radiation. The photochemical cell was made up of a photochemical reactor and an electrochemical reactor, both of which were separated by a proton conducting membrane. In the electrochemical reactor protons were released by the disproportionation of liquid CuCl and the electrons were transferred to the other reactor through an electron conducting medium. The photochemical reactor generates multiple electrons at active sites under the solar radiation and was used as a catalysis for the reduction of water. Hydrogen gas was then collected from the top of the second reactor, and the hydroxyl ions were combined with protons that transfer through the PEM to form water. The feasibility and expected efficiencies of this cell were discussed along with the potential benefits compared with the conventional thermochemical water splitting.

Balashov et al. (2010) investigated the key step in the Cu–Cl thermochemical cycle, which was hydrogen gas evolution. The hydrogen gas evolution occurs by the means of the oxidisation of CuCl that was dissolved in the highly concentrated HCl aqueous solution. Linear sweep voltammetry was used as the method of study for the electrolysis parameters and performance. The electrochemical impedance spectroscopy method was used at ambient temperature. The study found that the best performance of the electrolyser was when pure water was used as the catholyte.
In the study a thermodynamic model was developed for the purpose of speciation of the CuCl–
CuCl₂–HCl aqueous solutions was used to predict effects of the reagent concentration, flow rate,
and the temperature for the electrolysis kinetics. The experimental results found that the
decomposition potential that is needed to initiate the hydrogen evolution reaction was three times
lower than that using water electrolysis at the same conditions. The correspondence of the
hydrogen production rate to Faraday’s law of electrolysis indicated the current efficiency was 98%
and the voltage efficiency was found to be 80% at 0.5 V and 0.1 A/cm².

Gong et al. (2010) investigated hydrogen production by the means of CuCl-HCl electrolysis using
a newly designed electrolyser system. The experiments for the electrolysis reaction were
performed with the following voltage range: 0.35 to 0.9 V. The efficiency of the electrolysis system
was measured based on hydrogen production. The study also assessed the effects of the
temperature and reagent flow rate on the electrolysis. Various types of anion exchange and cation
exchange membranes were tested and their performances were compared relative to the process
efficiency and the tolerance to copper crossover. The various anion and cation exchange
membranes were tested in the electrolyser.

Ferrandon et al. (2009) investigated hydrogen production using hydrolysis of CuCl₂ in the Cu-Cl
cycle. The study noted that a molar ratio as high as 23 is usually required to achieve a conversion
rate of approximately 100% of the CuCl₂ to the desired products at one atm. The study also notes
that the amount of steam needed can be decreased by lowering the pressure of the reaction in
accordance with Le Chatelier’s principle and the equilibrium based model used. The experiment
setup is modified in this study to allow the CuCl₂ hydrolysis in the pressure range of 0.4-1atm.
The experiments resulted in the following findings, the optimal molar ratio for steam-CuCl₂ was
20-23 at 1 atm. As for the experiments where the pressure was 0.4 and 0.7 atm, it was seen that
the steam-CuCl₂ molar ratio could be lowered to 15, without compromising the yield for the
desired products. The reduced pressure decreased the CuCl concentration in solid products.

Dragica et al. (2003) investigated hydrogen production by the means of water electrolysis as well
as the possibilities of energy savings by integrating ion activators. The study also noted that the
conventional technology, which includes aqueous alkalines as electrolytes, could lead to high
costs. This made the conventional technology only viable in countries where electricity is cheap.
Ionic activators were integrated during experimentation to reduce energy consumption. Two types
of activators were used, both ethylenediamine complexes of cobalt are used either separately or with some molybdates. During experimentation, it was found that the activation energy was significantly reduced, with only one ionic activator. However, the optimal results in terms of reducing the activation energy were using the ethylenediamine complexes of cobalt with combinations of molybdate. In conclusion, the experimental results indicated that the activation energy was reduced per mass unit of hydrogen produced in excess of 10% using ionic activators relative to those with non-activated electrolytes.

Orhan et al. (2012) studied a four step copper chlorine (Cu-Cl) cycle. The cycle was studied using Aspen Plus software. The cycle is defined by its four main steps: hydrolysis, oxy-decomposition, electrolysis, and drying. The study notes the factors of the reaction kinetics is factored in all the steps of the reaction. The study found that the hydrolysis reactors with smaller capacities and larger (≥10/1) steam to CuCl ratios are more desirable to improve the reaction efficiency and reduce the number of by-products (CuO and CuCl). It was also found that the larger oxy-decomposition reactors with longer operation time allow for a longer duration of the decomposition of copper oxychloride. The study concluded that 10 or smaller scale hydrolysis reactors could be used to feed on oxy decomposition reactor. Those allows for a large capacity of feeding to allow for continuity of flow in the cycle.

Hall et al. (2015) conducted the electrochemical kinetic investigation of CuCl(aq)/HCl(aq) electrolyser. Since CuCl(aq)/HCl(aq) electrolyser is a crucial component of CuCl thermochemical cycle, reducing the loading improved the economic viability of thermochemical cycle significantly. Electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) were used to study the kinetic properties of aqueous Cu²⁺/Cu⁺ chloride complex reaction with glassy carbon and platinum with a rotating disc-shaped electrode. These reactions were performed using three-electrode cell. The results showed that the standard exchange current density of electrochemical reaction of anode Cu²⁺/Cu⁺ with platinum, 4-12 A/cm², was significantly larger than the values reported for HER cathodic reaction.

Ambike et al. (2005), and Chen and Lin (2005) studied the drying of emulsions, solutions, colloidal mixtures using spray drying. However, Lin and Chen (2006) conducted a study based on droplet evaporation using activation energy to start the evaporation process.
2.1.2 Hydrogen Halides Cycles

Kondo et al. (1983) studied the gas phase electrolysis of Hydrogen Halide (HX) gases (such as HBr or HI) which utilised an electrolyser. They reported that gas phase electrolysis was superior to aqueous electrolysis in the following respects: less theoretical voltage was required (because the gaseous phase HX molecule was at higher energy level compared to aqueous state), in case of aqueous electrolysis it was essential to remove product halogen (X₂) due to solubility of produced halogen into aqueous solution whereas in gas phase electrolysis due to presence of electrolyte X₂ was insoluble, and in several thermochemical cycles where HX were produced mostly in the gaseous phase, the presence of HX in gaseous phase was favorable and efficient.

Park et al. (2011) investigated the electrolytic oxidation of HBr using molten alkali-bromide salts in a porous scaffold of yttria-stabilised zirconia (YSZ), with porous Pt electrodes. Their results exhibited that molten alkali-bromide salts were good ionic conductors and could be used as effective electrolytes. Pt can be used as an effective material for both electrodes, but the possibility of using cheaper material was much more feasible for use at high temperatures.

A complete study on hydrogen production, using hybrid chlorine cycle, with three different processes were developed by Gooding (2009). The main difference between approaches was the HCl isolation during conversion to hydrogen and chlorine gas. The cycle was capable of producing hydrogen at a temperature and pressure of 35°C and 21 bar. Aspen plus software, was utilised in the modeling of the system. Cost estimation, construction materials were identified for a 200 million kg/yr plant. The convincing results indicated that the production of hydrogen with through electrolysis was an economical way with good thermal efficiency. The estimated range of efficiency ranges from 30% to 36% of electrical power value of $0.05 kWh. Hydrogen cost would be $3/kg for the hybrid chlorine cycle. Hydrogen chlorine cycle was relatively simple with no solids involvement except for sorbent in HCl. Experiments indicated that hydrogen chlorine was feasible for mass production of hydrogen by aqueous quench or membrane reactor flow sheets. A good thing was its thermal efficiency, which was comparable to the efficiency of direct water electrolysis.

Simpson et al. (2007) investigated three step hybrid cycle for thermochemical-electrolytic water splitting. The maximum temperature required in the process was 500°C, and it can be linked to low temperature nuclear reactors. The low temperatures allowed less stringent material
requirements. The combined thermochemical reactions are reverse Deacon reaction. The overall savings were almost 15% and it is attributed to lower electric energy requirements in HCl electrolysis. The role of the catalyst in the reaction kinetics and solids’s stability is determined through experiments. It was found that the reverse Deacon cycle is a promising alternative for hydrogen production. The use of silicate and zeolites is investigated for supporting the magnesium based catalyst. The experiments for proof of principles were conducted to demonstrate three of the four requirements. The authors concluded that further study is required for chlorination step and repeatability of steps such as catalyst preparation and hydrolysis. The use of software package such as Aspen is recommended to improve the process analysis efficiency.

2.2 High Temperature Electrolysis

The proton conducting solid oxide electrolyser have certain advantages over the oxygen conducting electrolyser such as better ionic conductivity compared to oxygen ion conductors at a moderate temperature range (773 K to 973 K), and a better chemical compatibility with Nickel (Fabbri et al., 2010; Zuo et al., 2006; Bi et al., 2011). In addition to the above advantages, proton conducting solid oxide electrolyser produced pure and dry hydrogen (Ni et al., 2006).

Salzanao et al. (1985) investigated the ways to reduce the electric energy required for electrolysis. It utilised high temperature thermal energy to assist the electrolysis. It is found to be 40-50% more efficient while operating at 1000°C. The study also investigated the thermal efficiencies, required voltage, steam conversions and recovery of heat. The feasibility of design is discussed while trading off between factors of cell complexity and voltage efficiency, based on this approach the study propose further research and development.

Nieminen et al. (2010) reported the overview of performance characteristics based on the thermodynamic analysis of Proton Exchange Membrane (PEM) and Solid Oxide Steam (SOS). The factors that influenced the energy and exergy efficiencies of the electrolyser were temperature, applied voltage, the summation of overpotentials, and pressure to some extent. Results showed that anodic overpotentials were the major part of the total overpotentials and therefore, it was recommended to further develop catalysts that minimise the overpotentials. In the analysis of PEM electrolyser, the energy and exergy efficiencies were assumed to be equal, mainly due to low operating temperatures. Additionally, an increase in pressure from 1 atm to 5 atm resulted in an increase in the efficiencies by about 2.5% over the range of applicable current densities. The reason
for this was that anodic and cathodic overpotentials tend to go towards the negative values with rising pressures, resulting in the reduction of thermodynamic irreversibility hence, increasing the efficiencies of energy and exergy. Furthermore, in the PEM operation, the hydrogen transport is effective and efficient, accounting for less than 5% of the overpotential distribution. The analysis of the SOS electrolyser showed that the energy and exergy efficiencies change with increasing pressure and current densities. At 1 atm, 3 atm and 5 atm the maximum energy efficiencies were calculated and validated, and the values are reported to approximately 53%, 53.5% and 54% respectively. The maximum energy efficiencies were calculated with a current density of 2100 A/m². With the same current density and at a temperature of 873 K the exergy efficiencies found out to be approximately 62% at 2 atm and 5 atm. Finally, it was observed that electrolytes with an increased ionic conductivity at low temperatures exhibit decreased ohmic overpotentials and increased efficiencies.

Stempien et al. (2015) reported the thermodynamic analysis and optimisation of a combined solid-oxide electrolyser cell and Fisher Tropsch synthesis process, required for the production of sustainable hydrocarbon fuels. The temperature, pressure, reactant composition and molar flux, system efficiency and distribution in the final production effects were described using a comprehensive model. An in-house model for the electrolyser was developed and then validated with the experimental data.

Herring et al. (2006) explored high temperature electrolysis for the purpose of hydrogen production. Steam electrolysis was performed using a sold oxide fuel cell for the production of hydrogen. The experimental setup included a 10-cell planar solid oxide electrolysis stack. The electrolyte used within the stack is scandia stabilised zirconia and was 140μm thick, nickel cermet steam for the hydrogen electrodes, and manganite air for the side electrodes. Ferritic stainless steel were used as the interconnect plates. The experiments were setup to run in the following conditions: the temperature of the steam at the inlet ranges from 800-900°C with a mole fraction of (0.1-0.6), the gas flow rate was within 1000-4000 sccm, and the current density ranged from 0-0.38 A/cm². The hydrogen production rates reached up to 90 normal liters per hour. The electrolysis stack has shown to work independently from the inlet steam flow rate. A Computational Fluid Dynamics (CFD) model was used to predict the internal stack temperatures.
The results showed a net cooling effect for lower operating voltages, and net heating effect for high voltage operations. The CFD and experimental results obtained similar results.

Hauch et al. (2008) explored high temperature electrolysis of water and steam. The study investigated the production of hydrogen gas using sustainable energy in an efficient and cost effective way. The cost competitiveness has to come from the electrolysis cells being cost competitive and efficient. The cells should also have a long service life cycle to be viable, and are fit to perform steam electrolysis in a stable consistent manner. The study noted that high temperature electrolysis was favorable from a thermodynamic perspective, as the process required thermal energy input and the activation barrier that is lowered to increase the hydrogen production. Alkaline and solid oxide electrolysis cells were the two cells explored as they can operate at temperatures above 200°C. The study concluded that the use of solid oxide cells in high temperature steam electrolysis was competitive to fossil fuel based hydrogen production. The study stated that the solid oxide cells was competitive at electricity prices below 0.02–0.03 € per kWh. Further research is needed for solid oxide cells to make an even more competitive range.

Doenitz et al. (1980) studied the production of hydrogen by the means of water vapour electrolysis. The study noted that the conventional water electrolysis plants operated in the following efficiency range: 25-28%. The efficiency was based on the heat necessary for power generation. Thermodynamic advantages of high temperature electrolysis of steam was noted in the study. However, there were challenges that need to be addressed in terms of improvements of the interconnection plates of the electrolysis cells. The cells were measured at a cell voltage of 1.3 V at 0.4 A/cm² current density. New developments are being performed the efficiency of the cells could go up to 40-50% depending on the primary source of energy.

2.3 Main Gaps in the Literature

Individual reactions of the Cu-Cl cycle have been investigated by various researchers in order to determine the reaction kinetics, cell potential, and theoretical heat requirements. Cycle analyses is performed mainly based on stoichiometry without considering the reaction behaviour of individual steps. It has been found in the literature that the electrolysis step of Cu-Cl is performed mainly in the aqueous phase at a temperature less than 100°C. However, no effort has been made to carry out the electrolytic step of Cu-Cl cycle in other phases such as molten or gaseous at higher temperature, while for hydrogen halide cycles the electrolytic step is carried out both in aqueous
and gaseous phases and well-studied using different types of membranes except high temperature solid proton conducting membrane.

Hot HCl gas is cooled and mixed with water to obtain the aqueous solution. Similarly, high temperature liquid CuCl is cooled and mixed with water to obtain low temperature aqueous solution. Cooling down of liquid CuCl results in loss of large amount of thermal energy. This energy may be recovered in the closed cycle but it is practically difficult and makes the whole process complicated. Likewise extracting heat from the hot HCl gas has practical material issues. The solubility of solid CuCl (melting point ~430°C) is very poor and thus requires a large amount of water and stirring work. Unlike the liquid and gaseous phases, the solid phase results in a difficult (to move) and costly batch process.

The conversion of CuCl to CuCl$_2$ in electrolysis step is extremely low and needs to be separated from the spent anolyte so that the CuCl would go back to electrolyser and the CuCl$_2$ to the hydrolyser. Also, some copper crossover is also observed in the electrolyser membrane resulting in electrolyser performance degradation by creating a physical blockage for chemical mass transfer on the cathode. Lastly, from integration point of view electrolysis step needs to be addressed to achieve a continuous, high yield and efficient process.
CHAPTER 3: SYSTEM DEVELOPMENT

In this chapter, various schemes of Cu-Cl cycle are presented by considering all the main chemical reactions using a high temperature electrolysis as the main influencing reaction. Furthermore, a novel hybrid Cu-Cl cycle for the co-production of hydrogen and copper using copper waste is proposed. In addition, two nuclear based integrated systems are proposed. The main goal of these systems is to produce multiple useful outputs such as electricity, hydrogen, and fresh water without causing harm to the environment.

3.1 Schemes of Cu-Cl Cycle for Hydrogen Production

As discussed in the introduction, the main objective of this thesis is to carry out the electrolytic step at higher temperature for better thermal management and integration. Since all the reactions of the Cu-Cl cycle are at a higher temperature except the electrolytic step (See Table 1.5) which is at very low temperature, this causes a temperature mismatch between the electrolytic step and the other steps. In the literature, the electrolytic step for the Cu-Cl cycle is in the aqueous phase, making the electrolytic step impossible at an elevated temperature. The electrolytic step is carried out at a higher temperature by changing the phase of the electrolytic step from aqueous to molten and gaseous. Once, the electrolytic step is carried out at a higher temperature, there should be the subsequent reactions that will close the Cu-Cl cycle so that all the materials used will be recycled except water. Hence, various reactions from the literature are studied and coupled to the electrolytic step so that a closed loop cycle is formed resulting into various schemes for Cu-Cl cycle for hydrogen production. Several schemes are considered at initial stage, however only four have been selected. The others schemes have been discarded due to issues such as either the state of the subsequent reactions are not well studied or well reported by various researchers. For example, Cu-Cl vapour electrolysis can be used to develop the schemes but due to very low operating pressure (sub-atomic pressure), this scheme has been discarded.

Four novel different schemes of Cu-Cl cycle for hydrogen production using high temperature electrolysis as a main influencing reaction are presented. In the proposed schemes i.e. Schemes 1-4, all the products/reactants (except water) are recycled and thus form a closed cycle. In other words, for the overall cycle, water is the only material inputs while oxygen, and hydrogen are the only useful material outputs.
3.1.1 Scheme 1

Figure 3.1 shows the proposed novel four step Cu-Cl cycle for hydrogen production i.e. Scheme 1 in which water is the only material input while hydrogen is the useful output. As shown in the figure, the cycle is comprised of the following four main steps:

Step 1 (Hydrolysis Step):

$$\text{Cl}_2(g) + \text{H}_2\text{O}(g) \overset{903 \text{ K}}{\rightarrow} 2\text{HCl}(g) + \frac{1}{2}\text{O}_2(g) \quad (3.1)$$

In this step, high temperature steam reacts with chlorine gas to produced hydrogen chloride (HCl) gas and oxygen. The hydrogen chloride gas produced in this step is utilised in Step 2. Dokiya and Kotera (1976) suggests that Step 1 should be carried out at above 900 K. Gupta et al. (1991) shows experimentally that at 900 K an equilibrium conversion of about 90.0% can be achieved.

Step 2 (Hydrogen Production Step):

$$2\text{Cu}(s) + 2\text{HCl}(g) \overset{723 \text{ K}}{\rightarrow} 2\text{CuCl}(l) + \text{H}_2(g) \quad (3.2)$$

This step has been well studied by various researchers (Zamfirescu et al., 2010; Serban et al., 2004). Copper powder is allowed to react with heated HCl gas to produce liquid CuCl and hydrogen gas. The liquid CuCl obtained from this step is utilised in Step 3.

Step 3 (Electrolytic Step):

$$4\text{CuCl}(l) \overset{773 \text{ K}}{\rightarrow} 2\text{Cu}(s) + 2\text{CuCl}_2(l) \quad (3.3)$$

In this step, the liquid CuCl obtained from Step 2 is electrolysed to produce liquid CuCl$_2$ and copper. This copper is pure, as it is obtained through an electrolytic step and utilised in Step 2. The CuCl$_2$ produced in this step is used in Step 4.

Step 4 (Decomposition Step):

$$2\text{CuCl}_2(l) \overset{833 \text{ K}}{\rightarrow} \text{Cl}_2(g) + 2\text{CuCl}(l) \quad (3.4)$$

The CuCl$_2$ obtained from Step 3 is heated to 833 K and decomposed into liquid CuCl and chlorine gas. The chlorine gas obtained from this step is input to Step 1 while obtained liquid CuCl is input to Step 3. Gupta et al. (1997) show that, for a temperature above 750 K, solid CuCl$_2$ can decompose
to solid CuCl and chlorine gas. However, in this case we suggest that this reaction be carried out at 833 K (i.e., above the melting point of CuCl, which is 771 K).

Figure 3.1 Schematic of the first option of the Cu-Cl cycle for hydrogen production (Scheme 1)

3.1.2 Scheme 2

In order to overcome the higher electricity requirement in Scheme 1, another option of Cu-Cl cycle is proposed. Figure 3.2 shows the second option of Cu-Cl cycle having high temperature electrolysis step. As shown in the figure, the cycle is comprised of the following three main steps:

Step 1 (Hydrolysis Step):
Dokiya and Kotera (1976) suggests that Step 1 should be carried out at above 900 K. Gupta et al. (1991) shows experimentally that at 900 K an equilibrium conversion of about 90.0% can be achieved. Note that this step is the same step as in Scheme 1. The hydrogen chloride gas produced in this step is utilised in Step 2 to produce hydrogen as follows:

\[
\text{Cl}_2(g) + \text{H}_2\text{O}(g) \xrightarrow{903 \text{ K}} 2\text{HCl}(g) + \frac{1}{2}\text{O}_2(g) \tag{3.5}
\]

Step 2 (Electrolytic and Hydrogen Production Step):

\[
2\text{CuCl}_2(l) + 2\text{HCl}(g) \xrightarrow{773 \text{ K}} 2\text{CuCl}_2(l) + \text{H}_2(g) \tag{3.6}
\]

Figure 3.2 Schematic of the second option of the Cu-Cl cycle for hydrogen production (Scheme 2)
In this step, the liquid CuCl reacts with HCl gas and gets electrolysed to produce liquid CuCl$_2$ and hydrogen. The above step in aqueous state is well studied in literature. However, to the authors’ knowledge in molten state this step is not yet reported. The CuCl$_2$ produced in this step is used in Step 3.

Step 3 (Decomposition Step):

$$2\text{CuCl}_2(\ell) \xrightarrow{833 \text{ K}} \text{Cl}_2(\text{g}) + 2\text{CuCl}(\ell)$$  \hspace{1cm} (3.7)

The CuCl$_2$ obtained from Step 2 is heated to 833 K and decomposed into liquid CuCl and chlorine gas. The chlorine gas obtained from this step is input to Step 1 while obtained liquid CuCl is input to Step 2. Gupta et al. (1997) shows that for a temperature above 750 K, solid CuCl$_2$ can decompose to solid CuCl and chlorine gas.

3.1.3 Scheme 3

Figure 3.3 shows the third option of the Cu-Cl cycle for hydrogen production using high temperature electrolytic step. In this scheme, the electricity requirement is further reduced (see Figure 3.3) by considering the gaseous phase electrolysis. The other benefit of this scheme is its lower operating temperature compared to Schemes 1 and 2. As shown in the figure, the cycle is comprised of the following four main steps:

Step 1 (Hydrolysis Step):

$$2\text{CuCl}_2(\ell) + \text{H}_2\text{O}(\text{g}) \xrightarrow{673 \text{ K}} 2\text{HCl}(\text{g}) + \text{Cu}_2\text{OCl}_2(\text{s})$$  \hspace{1cm} (3.8)

In this step, high temperature steam reacts with liquid CuCl$_2$ to produced hydrogen chloride (HCl) gas and copper oxychloride. The hydrogen chloride gas produced in this step is utilised in Step 4 to produce hydrogen while copper oxychloride is utilised in Step 2. Ferrandon et al. (2008) shows experimentally the feasibility of the hydrolysis reaction to produce hydrogen chloride gas and copper oxychloride.

Step 2 (Decomposition Step):

$$\text{Cu}_2\text{OCl}_2(\text{s}) \xrightarrow{773 \text{ K}} 2\text{CuCl}(\ell) + \frac{1}{2}\text{O}_2(\text{g})$$  \hspace{1cm} (3.9)
The copper oxychloride obtained from Step 1 is heated to 773 K and decomposed into liquid CuCl and oxygen gas. The obtained liquid CuCl is cooled down to 673 K before utilising in Step 3. Serban et al. (2004) shows experimentally the feasibility of the decomposition step to produce liquid CuCl and oxygen gas.

Step 3 (Chlorination Step):

\[
2\text{CuCl}_\text{(s)} + \text{Cl}_2(\text{g}) \xrightarrow{673 \text{K}} 2\text{CuCl}_2(\text{s})
\]  

(3.10)

The cooled CuCl obtained from Step 2 reacts with chlorine gas to produce solid CuCl\(_2\) which would be utilised in Step 1.

Figure 3.3 Schematic of the third option of the Cu-Cl cycle for hydrogen production (Scheme 3)
Step 4 (Electrolytic and Hydrogen Production Step):

\[
2\text{HCl}_\text{(g)} \xrightarrow{773 \text{ K}} \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)}
\]  

(3.11)

The HCl gas obtained from Step 1 is electrolysed to produce hydrogen and chlorine gases. Obtained chlorine gas would be utilised in Step 3. This step is discuss in detail in the coming section (Section 3.2). As seen from Figures. 3.1-3.3, the electricity requirement for this electrolytic step is the least among all the three schemes (Schemes 1-3).

### 3.1.4 Scheme 4

Balta et al. (2010) suggests a four step Cu-Cl cycle for hydrogen production in which they propose that the hydrolysis, and decomposition steps can be combined to a single step. Based on their results the fourth option of the Cu-Cl cycle is developed. Figure 3.4 shows the fourth option of the Cu-Cl cycle for hydrogen production using high temperature electrolytic step. As shown in the figure, the cycle is comprised of the following three main steps:

Step 1 (Combined Step):

\[
2\text{CuCl}_2\text{(l)} + \text{H}_2\text{O}_\text{(g)} \xrightarrow{773 \text{ K}} 2\text{HCl}_\text{(g)} + 2\text{CuCl}_\text{(l)} + \frac{1}{2}\text{O}_2\text{(g)}
\]  

(3.12)

In this step, the liquid CuCl$_2$ reacts with high temperature steam to produce hydrogen chloride gas, oxygen gas, and liquid CuCl. This step is the combination of Step 1 and Step 2 of the Scheme 3 based on the suggestion provided by Balta et al. (2010). Obtained liquid CuCl is cooled down before using in Step 2 while obtained HCl gas is electrolysed to produce hydrogen and chlorine gases in Step 3.

Step 2 (Chlorination Step):

\[
2\text{CuCl}_\text{(s)} + \text{Cl}_2\text{(g)} \xrightarrow{673 \text{ K}} 2\text{CuCl}_2\text{(s)}
\]  

(3.13)

The cooled CuCl obtained from Step 1 reacts with chlorine gas to produce solid CuCl$_2$ which would be utilised in Step 1.

Step 3 (Electrolytic and Hydrogen Production Step):

\[
2\text{HCl}_\text{(g)} \xrightarrow{773 \text{ K}} \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)}
\]  

(3.14)
The HCl gas obtained from Step 1 is electrolysed to produce hydrogen and chlorine gases. Obtained chlorine gas would be utilised in Step 2.

Step 2 (Chlorination Step):

\[ 2\text{CuCl}_\text{(s)} + \text{Cl}_2\text{(g)} \xrightarrow{673 \text{ K}} 2\text{CuCl}_2\text{(s)} \]  

(3.13)

The cooled CuCl obtained from Step 1 reacts with chlorine gas to produce solid CuCl₂ which would be utilised in Step 1.

Step 3 (Electrolytic and Hydrogen Production Step):

\[ 2\text{HCl}_\text{(g)} \xrightarrow{773 \text{ K}} \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \]  

(3.14)
The HCl gas obtained from Step 1 is electrolysed to produce hydrogen and chlorine gases. Obtained chlorine gas would be utilised in Step 2.

3.1.5 **Comparison of the Proposed Schemes**

Figure 3.5 provides the comparison of the proposed schemes (Schemes 1-4) with their advantages and disadvantages.

![Scheme 1](image1.png)  
**Scheme 1**  
- Step 1: Hydrolysis  
- Step 2: H₂ Production  
- Step 3: Electrolytic  
- Step 4: Decomposition  
  - No need for membrane  
  - One process is batch  

![Scheme 2](image2.png)  
**Scheme 2**  
- Step 1: Hydrolysis  
- Step 2: H₂ Production & Electrolytic  
- Step 3: Decomposition  
  - All processes are continuous  
  - Membrane

![Scheme 3](image3.png)  
**Scheme 3**  
- Step 1: Hydrolysis  
- Step 2: Decomposition  
- Step 3: Chlorination  
- Step 4: H₂ Production & Electrolytic  
  - Low voltage requirement  
  - One process is batch  

![Scheme 4](image4.png)  
**Scheme 4**  
- Step 1: Hydrolysis & Decomposition  
- Step 2: Chlorination  
- Step 3: H₂ Production & Electrolytic  
  - Fewer steps: reduce losses, cost  
  - One process is batch

Figure 3.5 Comparison of the proposed schemes

Each scheme has certain advantages and disadvantages, suggesting one has to choose the proposed cycle based on the application. For example, Scheme 1 comprises of four steps while Scheme 2 has only three steps, which makes Scheme 2 much simpler in comparison relative to Scheme 1. However, in Scheme 1 there is no need for the membrane during electrolysis which is an advantage over Scheme 2 as in this scheme membrane is required. Similarly, on comparing Schemes 3 and 4, one can note that Scheme 4 has one step less than compared to Scheme 3, which would result in lower costs and reduce the amount of losses. By comparing all the schemes, one can find that Scheme 1 does not require a membrane while the other schemes do. In Scheme 2 all the processes
are continuous i.e. no movement of solid is there, which is an advantage over other schemes as Schemes 1, 3 and 4 have the involvement of solid which make their one or more processes as batch processes. It is to be noted from the figure that Scheme 2 comes directly from the Scheme 1 after combining the hydrogen production and electrolytic step of Scheme 1. Similarly, Scheme 4 comes from Scheme 3 after combining the hydrolysis and decomposition steps of Scheme 3.

3.2 Electrolysis of HCl Gas
The electrochemical step of Schemes 3 and 4 is presented here in detail with its working mechanism. To the authors’ knowledge, this constitutes the first report of gas phase electrolysis of hydrogen chloride utilising a high temperature proton conducting solid electrolyte.

Figure 3.6 Schematic of the proposed high temperature electrolyser for the gas phase electrolysis of HCl for hydrogen production

Figure 3.6 shows the working mechanism of the proposed high temperature electrolyser for the gas phase electrolysis of HCl for hydrogen production. HCl gas is fed to the porous anode where it is electrochemically split to form chlorine gas and hydrogen ions (H⁺) at the anode-electrolyte interface, according to

\[ 2\text{HCl} \rightarrow \text{Cl}_2 + 2\text{H}^+ + 2\text{e}^- \]  

(3.15)
The produced chlorine gas can be collected from the anode flow channel. The hydrogen ions pass through the electrolyte to the cathode and are reduced to form hydrogen gas in the following reaction:

\[ 2H^+ + 2e^- \rightarrow H_2 \]  
(3.16)

Thus, the net reaction can be expressed as

\[ 2\text{HCl} \rightarrow \text{H}_2 + \text{Cl}_2 \]  
(3.17)

3.3 **Four Step Cu-Cl Cycle for Co-Production of Hydrogen and Copper**

Copper is one of the most widely used metals in the world, with applications including energy technologies, electronic devices, electricity transport, and coin production. With advances in electrical and electronic technology and decreases in prices, the use of such equipment has increased (Huang et al. 2009; Ni and Zeng, 2009). This has led to increases in copper waste, especially in the industrial world (Wildmer et al., 2006), posing a worldwide challenge for safe disposal (Wong et al., 2006; Goosey and Kellner, 2003). There are numerous methods available to recycle copper from copper waste, like pyrometallurgy, hydrometallurgy (Hagelüken et al., 2005; Lin et al., 2011, Yang et al., 2011; Oh et al., 2003). Each process has drawbacks, however. For instance, the energy consumption is very high and the temperature requirement is high (more than 1273 K) in pyrometallurgy (Pagnanelli et al., 2016) while the Cu is recovered in the form of Cu-based compounds such as Cu2O and CuCl in hydrometallurgy (Xiu and Zhang, 2014; Zhang and Zhang, 2013; Hou et al., 2017). Hence, efficient recovery of copper from copper waste is one of the most challenging issues in the disposal of copper waste. In the present study, a novel hybrid thermochemical Cu-Cl cycle is developed for the co-production of hydrogen and copper using copper waste.

Figure 3.7 shows the proposed novel four step Cu-Cl cycle for co-production of hydrogen and copper from copper waste. As shown in the figure, the cycle is comprised of the following four main steps:

Step 1 (Hydrolysis Step):

\[ \text{Cl}_2(g) + \text{H}_2\text{O}(g) \xrightarrow{903 \text{ K}} 2\text{HCl}(g) + \frac{1}{2}\text{O}_2(g) \]  
(3.18)
In this step, high temperature steam reacts with chlorine gas to produce hydrogen chloride (HCl) gas and oxygen. The hydrogen chloride gas produced in this step is utilised in Step 2. Dokiya and Kotera (1976) suggest that Step 1 should be carried out at above 900 K. Gupta et al. (1997) show experimentally that at 900 K an equilibrium conversion of about 90.0% can be achieved.

Step 2 (Hydrogen Production Step):

\[ 2\text{Cu (waste)} + 2\text{HCl}_\text{(g)} \xrightarrow{723\text{ K}} 2\text{CuCl}_\text{(l)} + \text{H}_2\text{(g)} \]  

(3.19)

The copper waste obtained from industry is crushed into a fine powder before being utilised in this step. In order to produce pure hydrogen, it is advisable to use pure copper waste. That powder is heated to 723 K and allowed to react with heated HCl gas to produce liquid CuCl and hydrogen gas. The liquid CuCl obtained from this step is utilised in Step 3.

Step 3 (Electrolytic Step and Copper Production Step):

\[ 4\text{CuCl}_\text{(l)} \xrightarrow{773\text{ K}} 2\text{Cu}_\text{(s)} + 2\text{CuCl}_2\text{(l)} \]  

(3.20)

In this step, the liquid CuCl obtained from Step 2 is electrolysed to produce liquid CuCl₂ and copper. This copper is pure, as it is obtained through an electrolytic step. The CuCl₂ produced in this step is used in Step 4.

Step 4 (Decomposition Step):

\[ 2\text{CuCl}_2\text{(l)} \xrightarrow{833\text{ K}} \text{Cl}_2\text{(g)} + 2\text{CuCl}_\text{(l)} \]  

(3.21)

The CuCl₂ obtained from Step 3 is heated to 833 K and decomposed into liquid CuCl and chlorine gas. The chlorine gas obtained from this step is input to Step 1 while obtained liquid CuCl is input to Step 3.

In the proposed cycle, all the products/reactants (except water and copper waste) are recycled and thus form a closed cycle. In other words, for the overall cycle, copper waste and water are the only material inputs while oxygen, hydrogen and pure copper are the only useful material outputs. One has to note that most of the reactions of this scheme are similar to that of Scheme 1 except Step 2. In Scheme 1, the produced electrolytic copper is used for hydrogen production while in this scheme, the copper waste from the industry is utilised to produce hydrogen.
3.4 **Reverse Osmosis System**

There are mainly three methods of seawater desalination employed commonly, based on the type of energy used, such electricity, thermal and both electricity and thermal. The thermal based desalination techniques, namely multistage flash, thermal vapour compression etc., require extensive amount energy input and different reactor coupling while the ones, using electricity, e.g., reverse osmosis (RO), require less amount of energy, resulting in a lower cost of desalination (IAEA, 1992). The reverse osmosis plants are then easily coupled with any type of nuclear plants since they only require electricity.

Figure 3.8 is the schematic of the reverse osmosis system for seawater desalination. The salient feature of the proposed system is that an energy recovery Pelton turbine is utilised to capture the energy released with relatively high pressure brine rejected from the RO module.

![Diagram of Cu-Cl cycle for co-production of copper and hydrogen](image)

**Figure 3.7** Schematic of the proposed hybrid Cu-Cl cycle for co-production of copper and hydrogen
3.5 Integrated Systems

Integrated systems are important for the production of the useful outputs in which several systems are integrated based on their energy requirements. In our case, proposed Cu-Cl cycle and reverse osmosis system requires both thermal and electrical energy. Hence their coupling with the energy source that can provide electricity, and heat is essential. Nuclear power reactors are suitable for processes that require energy in the form of electrical power and heat.

3.5.1 System 1

Figure 3.8 shows a schematic of a Sodium-cooled Fast Reactor (SFR) power plant used for desalination, hydrogen and electricity generation. A SFR power plant is chosen because, of the proposed Generation IV nuclear reactor designs (as most of the reactors operate at temperature more than 550°C), the most experience is with SFR reactors which in part makes them good candidates for coupling with desalination and Cu-Cl cycle. As these reactors are usually large, they have enough potential to drive seawater desalination using reverse osmosis and producing
hydrogen utilising Cu-Cl cycle. The other salient feature of the SFR power plant is its ability to manage uranium resources and high level wastes (IAEA, 2013).

As shown in the figure, the thermodynamic and economic properties of subsystems are evaluated by considering following state points:

- 1-16 SFR plant
- 17-30 RO desalination system
- 31-34 Cu-Cl cycle for hydrogen production

The salient feature of the system consider is that, while in a typical power plant condenser cooling water is discharged as waste heat, in this plant it is possible to use the heated seawater as a feed to an RO desalination plant, thereby improving the performance of the desalination plant.

3.5.2 System 2

Another Generation IV reactors that is gaining lot of attention is the Gas Turbine-Modular Helium Reactor (GT-MHR) because of its high proliferation resistance, economics, good safety, and environmental benign nature due to reduced waste heat and better utilisation of fuel (Baldwin et al., 2008).

Figure 3.9 shows the schematic of a Gas Turbine Modular Helium Reactor (GT-MHR) power plant used for desalination, hydrogen and electricity generation. As shown in the figure, the thermodynamic and economic properties are evaluate by considering the following state points:

- 1-18 GT-MHR plant
- 19-32 RO desalination system
- 33-39 Cu-Cl cycle for hydrogen production

The novelty of the proposed system is that helium exiting the gas turbine is utilised to provide heat to the Cu-Cl cycle. The other salient feature is that helium before entering the precoolers is further cooled down in heat exchanger 1 by the DuraTherm-T oil. In addition, to utilise the waste heat exiting from the gas turbine a bottoming Rankine cycle is used for electricity generation.
Figure 3.9 Schematic of a Sodium-cooled Fast Reactor (SFR) power plant used for desalination, hydrogen and electricity generation
Figure 3.10 Schematic of a Gas Turbine Modular Helium Reactor (GT-MHR) power plant used for desalination, hydrogen and electricity generation
CHAPTER 4: ANALYSIS AND MODELING

In this chapter, detailed description of the thermodynamic, electrochemical, and economic analyses are presented.

4.1 Thermodynamic Analysis

The mass, energy, entropy and exergy balances are required in the first step for the exergy analysis in order to determine the heat input/output, entropy generation rate, exergy destructions, and energy and exergy efficiencies of any thermodynamic system. So, the detailed thermodynamic analyses are conducted by writing the mass, energy, entropy and exergy balance equations for each system and its components as presented in the following sections.

4.1.1 Mass Balance Equation

According to conservation of mass principle one can write the mass balance for the control volume as follows:

$$\sum m_i - \sum m_e = \frac{dm_{cv}}{dt}$$ (4.1)

where $\dot{m}$ and $m$ represent the mass flow rate and mass, respectively and the subscripts $i$ and $e$ refers to the inlet and exit of the control volume, respectively while $cv$ represent the control volume.

4.1.2 Energy Balance Equation

The energy balance equation for a control volume comprises of all the inputs and outputs of a selected control volume. According to first law of thermodynamics the detailed energy balance equation for the control volume can be written as follows:

$$\dot{Q} - \dot{W} + \sum m_i (h_i + \frac{v_i^2}{2} + gZ_i) - \sum m_e (h_e + \frac{v_e^2}{2} + gZ_e) = \frac{dE_{cv}}{dt}$$ (4.2)

where $\dot{Q}$, $\dot{W}$, $E$ and $t$ are the heat transfer rate, work rate, energy and time, respectively while symbols $h$, $V$, $g$ and $Z$ stand for specific enthalpy, velocity, acceleration of gravity and elevation, respectively.

For a chemical reaction, the heat transfer is determined as follows:

$$Q = H_P - H_R$$ (4.3)
4.1.3 Entropy Balance Equation

The entropy that is generated within the process is called entropy generation denoted by $S_{\text{gen}}$. In Bejan (2002), the entropy generation rate over a control volume is given as

$$\dot{S}_{\text{gen}} = \frac{dS_{\text{cv}}}{dt} + \sum_l \dot{m}_e s_e - \sum_l \dot{m}_i s_i - \sum_k \frac{Q_k}{T_k}$$

(4.4)

4.1.4 Exergy Balance Equation

Exergy analysis involves the concept of both first and second laws of thermodynamics. The detailed provide by exergy analysis is valuable for understanding the details of the overall system. It would be useful in providing the guidelines and strategies for more efficient and effective use of energy and utilise it for various thermodynamic processes such as power generation, refrigeration etc. Basically the exergy consist of four substance, physical and chemical exergy are the most commonly and widely used as the other two kinetic and exergy terms are assumed to be neglected as there are very little change in velocity and elevation. The physical exergy is defined as the maximum work that is obtained when the system interacts with environment which is in mechanical and thermal equilibrium. The chemical exergy is considered when the system is not in chemical equilibrium with the environment like in the case of combustion chamber and the processes where chemical change take place. According to second law of thermodynamics the exergy balance for a control volume can be written as

$$\dot{E}_x Q + \sum_l \dot{m}_i e_{xi} = \sum_e \dot{m}_e e_{xe} + \dot{E}_x W + \dot{E}_x d$$

(4.5)

where i and e denotes the inlet and exit of the control volume, respectively while the exergy destruction is denoted by $\dot{E}_x d$ and the other terms are as follows:

$$\dot{E}_x Q = \dot{Q}_i \left(1 - \frac{T_0}{T_i}\right)$$

(4.6)

$$\dot{E}_x W = W$$

(4.7)

$$e_{x} = e_{x_{\text{ph}}} + e_{x_{\text{ch}}}$$

(4.8)

The physical exergy, $e_{x_{\text{ph}}}$ can be calculated as follows:

$$e_{x_{\text{ph}}} = h - h_0 - T_0(s - s_0)$$

(4.9)
4.2 Electrochemical Model

In this section, a complete electrochemical model including all major losses (activation, concentration and ohmic) for the proposed electrolyser of Scheme 3 is developed and the performance is assessed by evaluating the energy, exergy and voltage efficiencies (see subsection). As with other electrochemical models (Ni et al., 2006a, 2008) for steam electrolysers, the following reasonable assumptions and simplifications are used (Ni et al., 2007a, 2007b; Nishida et al., 2004):

1. A one dimensional electrochemical model is adequate.
2. Operation is at steady state.
3. No temperature variation exists in the porous electrode layer.
4. All electrochemical reactions take place at the electrode-electrolyte interface.

As with a proton conducting high temperature steam electrolyser, the required potential ($E_{\text{tot}}$) applied to the proposed electrolyser can be written as

$$E_{\text{tot}} = E + E_{\text{conc},a} + E_{\text{conc},c} + E_{\text{act},a} + E_{\text{act},c} + E_{\text{ohm}}$$ (4.10)

where $E$ is the equilibrium potential; $E_{\text{conc},a}$ and $E_{\text{conc},c}$ are the anode and cathode concentration overpotentials, respectively; $E_{\text{act},a}$ and $E_{\text{act},c}$ are the activation overpotentials at anode and cathode, respectively; and $E_{\text{ohm}}$ is the ohmic overpotential.

The equilibrium potential can be expressed as follows:

$$E = E_0 + \frac{RT}{2F} \ln \left( \frac{p_{H_2}p_{Cl_2}}{p_{HCl}} \right)$$ (4.11)

where $p_{H_2}$, $p_{Cl_2}$ and $p_{HCl}$ are the partial pressures of hydrogen, chlorine, and hydrogen chloride, respectively, and $E_0$ is the standard potential, which can be calculated as

$$E_0 = \frac{\Delta g}{2F}$$ (4.12)

In modern cells, the contact resistance between the solid-solid interface and the electrodes is negligible compared to the electrolyte resistance (Menon et al., 2015). So, the ohmic overpotential can be expressed as

$$E_{\text{ohm}} = JL\phi$$ (4.13)
where $L$ is the thickness of electrolyte and $\phi$ is its electrical resistivity. The electrical resistivity can be written as

$$\phi = \frac{1}{\rho_{el}}$$  \hspace{1cm} (4.14)

where $\rho_{el}$ is the electrical conductivity of electrolyte, expressible as (Menon et al., 2015)

$$\rho_{el} = \rho_0 T^{-1} \exp \left( \frac{E_{el}}{RT} \right)$$  \hspace{1cm} (4.15)

Here, $E_{el}$ is the activation energy of ion transport and $\rho_0$ is the pre-exponential factor.

The concentration overpotentials ($E_{conc,a}$ and $E_{conc,c}$) are due to the resistance of the porous electrode to the transport of gaseous species (Ni et al., 2006b, 2008). For the proposed electrolyser, the concentration overpotential at cathode is evaluated using the procedure in (Ni et al., 2008):

$$E_{conc,c} = \frac{RT}{2F} \ln \left( \frac{\sqrt{\left( \frac{p_0^0}{p_{H_2}} \right)^2 + \frac{J_{RT} \mu_{H_2} d_c}{F B_g}}}{p_0^0} \right)$$  \hspace{1cm} (4.16)

where $p_0^0$ is the partial pressure of hydrogen at the surface of the relevant electrode (cathode), $d_c$ is the thickness of the cathode, $\mu_{H_2}$ is the dynamic viscosity of hydrogen, and $B_g$ is the permeation coefficient, which can be determined using the Kozeny-Carman relationship as follows (Nam and Jeon, 2006; Zhua et al., 2005):

$$B_g = \frac{\epsilon^2}{72 \xi (1-\epsilon)^2} (2r)^2$$  \hspace{1cm} (4.17)

Mass transfer at the anode side is complex as it involves both diffusion (driven by concentration gradient) and permeation (driven by pressure gradient) phenomena. In a solid oxide electrolyser, however, due to presence of porous electrodes, the total pressure change within the pores is negligible (Chan and Xia, 2002; Hernández-Pacheco et al., 2004). This causes the concentration overpotential to be governed mainly by diffusion and expressible as

$$E_{conc,a} = \frac{RT}{2F} \ln \left( \frac{\left( p_0^0 - \frac{J_{RT} d_a}{2F D_{HCl}} \right) p_0^{0, HCl}}{p_0^{0, Cl_2} \left( \frac{J_{RT} d_a}{2F D_{HCl}} \right)^2} \right)$$  \hspace{1cm} (4.18)
where \( p_{\text{Cl}_2}^0 \) and \( p_{\text{HCl}}^0 \) are the partial pressures of chlorine and hydrogen chloride respectively at the surface of the relevant electrode (anode), \( d_a \) is the thickness of the anode, and \( D_{\text{HCl}}^{\text{eff}} \) is the effective diffusion coefficient of hydrogen chloride, which can be calculated using Bosanquet formula as (Veldsink et al., 1995)

\[
\frac{1}{D_{\text{HCl}}^{\text{eff}}} = \frac{\xi}{\epsilon} \left( \frac{1}{D_{\text{HCl-Cl}_2}} + \frac{1}{D_{\text{HCl}}^{\text{eff}}} \right)
\]  

(4.19)

The molecular diffusion coefficient \( D_{\text{HCl-Cl}_2} \) for a HCl-Cl\(_2\) binary system can be evaluated using the Chapman-Enskog theory of an ideal gas as (Hernández-Pacheco et al., 2004; Reid et al., 1987)

\[
D_{\text{HCl-Cl}_2} = \frac{0.0026T^{3/2}}{P_{\text{M}_{\text{HCl-Cl}_2}}^{0.5} \sigma_{\text{HCl-Cl}_2}^2 \Omega_D}
\]  

(4.20)

\[
M_{\text{HCl-Cl}_2} = \frac{2}{M_{\text{HCl}}^{-1} + M_{\text{Cl}_2}^{-1}}
\]  

(4.21)

where \( M_{\text{HCl}} \) and \( M_{\text{Cl}_2} \) are the molecular weights of HCl and Cl\(_2\), respectively.

The characteristic length of a HCl and Cl\(_2\) binary system can be evaluated as (Reid et al., 1987)

\[
\sigma_{\text{HCl-Cl}_2} = \frac{\sigma_{\text{HCl}} + \sigma_{\text{Cl}_2}}{2}
\]  

(4.22)

The dimensionless diffusion collision integral \( (\Omega_D) \) can found as follows (Reid et al., 1987):

\[
\Omega_D = \frac{1.06}{\tau^{0.156}} + \frac{0.193}{\exp(0.476\tau)} + \frac{1.036}{\exp(1.53\tau)} + \frac{1.765}{3.894\tau}
\]  

(4.23)

where \( \tau \) is the dimensionless temperature, expressible as

\[
\tau = \frac{k_b T}{\epsilon_{\text{HClCl}_2}}
\]  

(4.24)

where \( k_b \) is the Boltzmann constant.

The Lennard-Jones potential for a HCl-Cl\(_2\) binary system can be evaluated as

\[
\epsilon_{\text{HClCl}_2} = \sqrt{\epsilon_{\text{HCl}} \epsilon_{\text{Cl}_2}}
\]  

(4.25)

where \( \epsilon_{\text{HCl}} \) and \( \epsilon_{\text{Cl}_2} \) are the Lennard-Jones potentials for HCl and Cl\(_2\), respectively.

The Knudsen diffusion coefficient \( (D_{\text{HClk}}) \) for HCl can be expressed as
D_{HCl,k} = \frac{2r}{3} \sqrt{\frac{8RT}{\pi M_{HCl}}} \quad (4.26)

In the present study, the activation overpotentials are evaluated using the Butler-Volmer equation:

\[ E_{\text{act},i} = \frac{RT}{F} \sinh^{-1} \left( \frac{1}{2J_{0,i}} \right), i = a, c \quad (4.27) \]

where \( J_{0,i} \) is the exchange current density, and \( a \) and \( c \) represent the anode and cathode, respectively. Note in the present study that, due to lack of experimental data, and the use of similar materials as for the case of a proton conducting steam electrolyser, the exchange current density and electrolyte conductivity for a proton conducting steam electrolyser are used for the proposed electrolyser. If reliable experimental data for the proposed electrolyser become available, it will be possible to evaluate the exchange current densities more accurately.

4.3 Exergoeconomic Analysis

Economic analysis based on exergy is called exergoeconomics. It includes the cost of thermal systems considering capital and their running cost. The principle of exergy is generally utilised in determining the costs to the products as given by Dincer and Rosen (2012):

\[ \dot{C}_{q,k} + \sum_i \dot{C}_{i,k} + \dot{Z}_k = \sum_e \dot{C}_{e,k} + \dot{C}_{w,k} \quad (4.28) \]

\[ \dot{Z} = \frac{Z_k \text{CRF}\emptyset}{N \times 3600} \quad (4.29) \]

where \( Z_k \) is the purchase cost of the \( k \)th component, and \( \text{CRF} \) is the capital recovery factor.

The capital costs are taken from the experimental setup costs as listed above. Exergy cost for the streams in any cost rate balance is given as

\[ \dot{C} = c \dot{E}_x \quad (4.30) \]

Here, \( c \) is in given in $/kWh and \( \dot{E}_x \) is given in W. The capital costs of the components is given as \( \dot{Z} \) in $/h.

Typical cost rate balance for a component is given below:

\[ \sum \dot{C}_{\text{in}} + \dot{W} c_{\text{in}} + \dot{Z} = \sum \dot{C}_{\text{out}} + \dot{W} c_{\text{out}} \quad (4.31) \]
CRF refers to capital recovery factor and depends on the interest rate and equipment life time, and is determined here as follows:

\[
\text{CRF} = \frac{i (1+i)^n}{(1+i)^n-1}
\]  

(4.32)

Here, \(i\) denotes the interest rate and \(n\) the total operating period of the system in years. Total costs for each of the components in the system are needed in $/h in order to use them in cost rate balance equations. The capital cost and the operating and maintenance costs are added. The total costs are then divided by the number of hours in a year to get a cost in $/h. Operating and maintenance costs are assumed to be a ratio of the capital costs as

\[
\text{OM} = \text{CC} \times \text{OM}\_\text{ratio}
\]  

(4.33)

where \(\text{OM}\_\text{ratio}\) depends on the type of application and material.

The total cost balance is written as follows:

\[
\text{TCC} = \text{CRF} \times (\text{CC} + \text{OM})
\]  

(4.34)

The annual investment cost rate of any component, \(\dot{Z}\) is calculated for the components of the integrated system. It is the summation of the annual capital investment cost rate and the annual O&M cost rate and defined as follows:

\[
\dot{Z} = \frac{TCC}{t\_\text{operation}}
\]  

(4.35)

where \(t\_\text{operation}\) is the total operational hours in a year.

The cost rate of exergy destruction for each component is expressed as

\[
\dot{C}\_D = c \dot{E}\_x\_d
\]  

(4.36)

Summation of additional cost caused by exergy destruction, \(\dot{C}\_D\) and final capital and operating cost rate \(\dot{Z}\) gives a critical parameter named as total cost rate \(\dot{C}\_\text{total}\) + \(\dot{Z}\):

\[
\dot{C}\_\text{total} = \dot{C}\_D + \dot{Z}
\]  

(4.37)

Total cost rates of the system consists of the total investment cost and cost of exergy destruction. The exergoeconomic factor, which is a measure of system effectiveness in terms of cost, obtained through exergoeconomic analysis is given as
\[ f = \frac{\dot{Z}}{\dot{Z} + \dot{C}_D} \]  
(4.38)

The exergoeconomic variables \( \dot{Z} \) and \( \dot{C}_D \) provide the significance of component in the system optimisation, whereas the variable \( f \) exergoeconomic factor is a relative measure of the component cost effectiveness.

The purchase cost of the components of Scheme 4 is calculated based on the following equipment capacity based equation (Almahdi, 2016; Turton et al., 2009):

\[
\log(Z) = K_1 + K_2 \log(A) + K_3 [\log(A)]^2
\]  
(4.39)

where \( Z \) is the resultant cost value in 2001$, \( K_1, K_2 \) and \( K_3 \) are the equipment specific coefficients (see Table 4.1) and \( A \) is the component capacity (For example; for heat exchanger \( A \) is the area while for compressor is the required power).

Table 4.1 Cost coefficient of equipment for purchase cost estimations

<table>
<thead>
<tr>
<th>Component/coefficient</th>
<th>Compressor</th>
<th>Pump</th>
<th>Reactor</th>
<th>Mixer</th>
<th>Heat exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_1 )</td>
<td>2.2897</td>
<td>3.8696</td>
<td>3.4974</td>
<td>5.0141</td>
<td>4.3247</td>
</tr>
<tr>
<td>( K_2 )</td>
<td>1.3604</td>
<td>0.3161</td>
<td>0.4485</td>
<td>-0.4133</td>
<td>-0.303</td>
</tr>
<tr>
<td>( K_3 )</td>
<td>-0.1027</td>
<td>0.122</td>
<td>0.1074</td>
<td>0.3224</td>
<td>0.1643</td>
</tr>
<tr>
<td>( A )</td>
<td>Power (kW)</td>
<td>Power (kW)</td>
<td>Volume (m³)</td>
<td>Volume (m³)</td>
<td>Area (m²)</td>
</tr>
</tbody>
</table>

Source: Turton et al., (2009)

The capital cost of the gas turbine of System 2 is evaluated as

\[
Z_{gt} = \left( \frac{1536 \dot{m}_1}{0.92 - \eta_{gt}} \right) \ln \left( \frac{P_i}{P_e} \right) \left( 1 + \exp(0.036 T_i - 54.4) \right)
\]  
(4.40)

where \( P_i \) and \( P_e \) are the inlet and exit pressures of the gas turbine, respectively and \( T_i \) is the inlet temperature of the gas turbine.

The compressor capital cost is calculated as follows:

\[
Z_C = \left( \frac{75 \dot{m}_1}{0.9 - \eta_C} \right) \ln \left( \frac{P_e}{P_i} \right) \frac{P_e}{P_i}
\]  
(4.41)

where \( \eta_C \) is the isentropic efficiency of the compressor.
For the exergoeconomic analysis of the proposed Scheme 4, following reasonable assumptions have been made (Bicer, 2017; Ferrandon et al., 2008):

- 10% interest rate is assumed.
- Lifetime of 20 years is considered.
- Maintenance factor of 1.06 is selected.
- Cost of thermal energy is considered to be 0.02$/kWh.
- Electricity cost is considered to be 0.06$/kWh.

4.4 Optimisation Study

In this thesis, the genetic algorithm is used to optimise the system to evaluate the best operating condition and to maximise the exergy efficiency since it works with multiple design variables, finds global optima (as opposed to local optima), and utilises populations (as opposed to individuals). The genetic algorithms are the class of search techniques that primarily constructed on the biological procedure of growth. The genetic algorithm is based on the following four steps as shown in Figure 4.1 (Stender, 1993):

1. A string of population is created.
2. Each string is then evaluated based on the performance.
3. The best string is then survived based on the performance.
4. The manipulation is then carried out to create the new strings.

In this thesis, the systems are analysed both thermodynamically and exergoeconomically. Therefore, the objective function is the combinations of exergy efficiency (to be maximised) and the exergoeconomic factor (to be minimised). Engineering Equation Solver (EES) is used for optimisation purposes using the genetic algorithm. The genetic algorithm is not affected by the guessed values like conjugate directions and variable metric methods. However, lower and upper bounds are important since the initial population and subsequent stochastic selections are chosen from within the bounds. Compared to other available methods, the genetic algorithm is more reliable since it is a more robust method; however it requires a longer period of time relative to other methods. In this thesis computation time is not a problem as the number of variables to be searched for are not great. EES requires finite lower and upper bounds to be set for each
independent variable which are chosen based on the parametric study conducted. Mathematically, the objective function that is used for multi-objective optimisation can be written as
\[ f_3 = a_1 f_1 - a_2 f_2 \]  
where \( a_1 \) and \( a_2 \) are the weighing factors, each having a value of 0.5, while \( f_1 \) and \( f_2 \) are the exergy efficiency and exergoeconomic factor respectively.

The thermodynamic and exergoeconomic model of the developed system (System 2) reveals that performance of the system depends upon following factors:

- Pressure ratio, \( r_p \)
- Temperature of the steps of Scheme 4 i.e. \( T_{\text{Step1}}, T_{\text{Step2}}, \) and \( T_{\text{Step3}} \)
- Hydrogen production rate
- Interest rate
- Lifetime
- Energy efficiency of the power plant
- Gas turbine inlet temperature, \( T_1 \)

Figure 4.1 Genetic algorithm cycle (adapted from Stender, 1993)
The independent variables chosen for the optimisation of System 2 with the upper and lower bounds are provided in Table 4.2. It is to be noted from the table that the pressure ratio of the gas turbine ($r_p$) are varied from 2 to 4. The energy efficiency of the power plant are set in a range of 30% to 50%, while the interest rates are changed from 2.5% to 10.0%.

Table 4.2 Independent variables chosen for optimisation of System 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_{en,pp}$</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>i (%)</td>
<td>2.5</td>
<td>10</td>
</tr>
<tr>
<td>$\dot{m}_{H_2}$ (kg/s)</td>
<td>0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>$T_{\text{Step}1}$ (K)</td>
<td>773</td>
<td>823</td>
</tr>
<tr>
<td>$T_{\text{Step}2}$ (K)</td>
<td>623</td>
<td>673</td>
</tr>
<tr>
<td>$T_{\text{Step}3}$ (K)</td>
<td>773</td>
<td>823</td>
</tr>
<tr>
<td>$T_1$ (K)</td>
<td>1073</td>
<td>1173</td>
</tr>
<tr>
<td>$T_{11}$ (K)</td>
<td>523</td>
<td>553</td>
</tr>
<tr>
<td>$r_p$</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>n (year)</td>
<td>10</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 4.3 Independent variables chosen for optimisation of System 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_{en,pp}$</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>i (%)</td>
<td>2.5</td>
<td>10</td>
</tr>
<tr>
<td>$\dot{m}_{H_2}$ (kg/s)</td>
<td>0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>$T_{\text{Step}1}$ (K)</td>
<td>773</td>
<td>823</td>
</tr>
<tr>
<td>$T_{\text{Step}2}$ (K)</td>
<td>623</td>
<td>673</td>
</tr>
<tr>
<td>$T_{\text{Step}3}$ (K)</td>
<td>773</td>
<td>823</td>
</tr>
<tr>
<td>$T_2$ (K)</td>
<td>813</td>
<td>833</td>
</tr>
<tr>
<td>$T_5$ (K)</td>
<td>798</td>
<td>803</td>
</tr>
<tr>
<td>$T_6$ (K)</td>
<td>623</td>
<td>633</td>
</tr>
<tr>
<td>$T_8$ (K)</td>
<td>778</td>
<td>788</td>
</tr>
<tr>
<td>n (year)</td>
<td>10</td>
<td>60</td>
</tr>
</tbody>
</table>

Similarly for System 1, the independent variable chosen for the optimisation with the upper and lower bound are listed in Table 4.3. As one can see from the Tables 4.2-4.3 that, for Systems 1 and 2, most of the parameters used in the optimisation are common except few such as pressure ratio, and turbine inlet temperature. For System 1, the temperature for Step 1 of Scheme 4 is set in the
range of 773 K to 823 K, while for Step 2 the range was 623 K to 673 K. The plant lifetime for both the systems are kept in between 10 years to 60 years.

4.5 Analyses of Schemes and Systems

In this section, the thermodynamic analysis for the proposed schemes and integrated system is presented as follows:

4.5.1 Analysis of the Proposed Schemes of Cu-Cl Cycle for Hydrogen Production

Energy and exergy analyses are performed for the proposed schemes (see Figures 3.1-3.5), in order to provide the information about their performances, efficiencies and emissions. The following assumptions, which are reasonable for the schemes, are invoked in the analysis:

1. All chemical reactions are taken to go to completion, according to their stoichiometry.
2. The changes in kinetic and potential energies and exergies are negligible.
3. The quantities like specific enthalpy and specific exergy are evaluated per mole of hydrogen produced.
4. All reactants and products are assumed to be at a pressure of 1 atm.
5. The ambient temperature and pressure are 299 K and 100 kPa, respectively.
6. The energy efficiency of the electrical power plant supplying electricity to electrolytic step is taken to be 40.0% (Orhan et al., 2012).

4.5.1.1 Balance Equations

The balance equations for energy, entropy and exergy are written for each step in Scheme 1 as follows:

- Step 1 (Hydrolysis Step):
The specific energy balance for the hydrolysis step can be written as follows:

\[ h_1 + h_2 + q_1 = 2h_3 + 0.5h_4 \] (4.43)

The specific entropy balance for the hydrolysis step can be written as follows:

\[ s_1 + s_2 + q_1 \frac{\bar{q_1}}{T_1} + s_{\text{gen,Step1}} = 2s_3 + 0.5s_4 \] (4.44)

The specific exergy balance for the hydrolysis step can be written as follows:

\[ e_{x_1} + e_{x_2} + q_1 \left(1 - \frac{T_0}{T_1}\right) = 2e_{x_3} + 0.5e_{x_4} + e_{x_{d,\text{Step1}}} \] (4.45)

- Step 2 (Hydrogen Production Step):

![Figure 4.3 Schematic of Step 2](image)

The specific energy balance for the hydrogen production step can be written as follows:

\[ 2h_1 + 2h_2 + q_2 = 2h_3 + h_4 \] (4.46)

The specific entropy balance for the hydrogen production step can be written as follows:

\[ 2s_1 + 2s_2 + s_{\text{gen,Step2}} = 2s_3 + s_4 + \frac{q_2}{T_2} \] (4.47)

The specific exergy balance for the hydrogen production step can be written as follows:

\[ 2e_{x_1} + 2e_{x_2} = 2e_{x_3} + e_{x_4} + e_{x_{d,\text{Step2}}} + q_2 \left(1 - \frac{T_0}{T_2}\right) \] (4.48)

- Step 3 (Electrolytic Step):
Figure 4.4 Schematic of Step 3

The specific energy balance for the electrolysis step can be written as follows:

\[ 4h_1 + w_{in,\text{elec}} = 2h_2 + 2h_3 \]  

(4.49)

The specific entropy balance for the electrolysis step can be written as follows:

\[ 4s_1 + s_{\text{gen,Step3}} = 2s_2 + 2s_3 \]  

(4.50)

The specific exergy balance for the electrolysis step can be written as follows:

\[ 4ex_1 + w_{in,\text{elec}} = 2ex_2 + 2ex_3 + ex_{d,\text{Step3}} \]  

(4.51)

- Step 4 (Decomposition Step):

The specific energy balance for the decomposition step can be written as follows:

\[ 2h_1 + q_4 = h_2 + 2h_3 \]  

(4.52)

The specific entropy balance for the decomposition step can be written as follows:

\[ 2s_1 + \frac{q_4}{T_4} + s_{\text{gen,Step4}} = s_2 + 2s_3 \]  

(4.53)

The specific exergy balance for the decomposition step can be written as follows:

\[ 2ex_1 + q_4 \left( 1 - \frac{T_0}{T_4} \right) = ex_2 + 2ex_3 + ex_{d,\text{Step4}} \]  

(4.54)

The specific balance equations for the other schemes i.e. Schemes 2-4 can be written in a similar manner as above.
4.5.1.2 Performance Assessment of the Proposed Schemes

The exergy efficiency of a process is defined as the ratio of useful exergy output to the total exergy input. In order to assess the performance of each step of the proposed schemes, its exergy efficiency is used, defined as follows:

\[ \eta_{\text{ex, step}} = 1 - \frac{e_{\text{d, step}}}{e_{\text{in, step}}} \]  

(4.55)

Relevant energy and exergy efficiencies are used to evaluate the performance of the overall cycle. The energy efficiency is defined as the ratio of useful energy output to the total energy input. The energy efficiency of the overall scheme is calculated as

\[ \eta_{\text{en, ov}} = \frac{\text{LHV}_{\text{H}_2}}{\sum q + q_{eq}} \]  

(4.56)

where \( \text{LHV}_{\text{H}_2} \) is the lower heating value of hydrogen, \( q \) is the total specific heat required per mol of hydrogen to drive all the steps of the cycle (Scheme 1) and \( q_{eq} \) is the thermal equivalent of electric energy required by the electrolytic step (Step 3), which can be written as

\[ q_{eq} = \frac{w_{\text{in, elec}}}{\eta_{\text{en, pp}}} \]  

(4.57)

where \( w_{\text{in, elec}} \) is the amount of electricity required per mol of hydrogen in the Step 3, and \( \eta_{\text{en, pp}} \) is the energy efficiency of the electrical power plant supplying electricity to Step 3.

The exergy efficiency of the overall scheme can be expressed as
η_{ex,ov} = \frac{e_{xH_2}}{\sum e_{xQ} + w_{in,elec}}

(4.58)

where \(e_{xH_2}\) is the specific chemical exergy of the hydrogen product, and \(\sum e_{xQ}\) is the thermal exergy input to the scheme, which can be expressed as

\[\sum e_{xQ} = (q_1)\left(1 - \frac{T_0}{T_1}\right) + (q_2)\left(1 - \frac{T_0}{T_2}\right) + (q_4)\left(1 - \frac{T_0}{T_4}\right)\]

(4.59)

In order to assess the proposed electrolyser (presented in Section 3.2), voltage, energy and exergy efficiencies are calculated. The energy efficiency of the electrolyser can be expressed as

\[\eta_{en,elec} = \frac{\dot{m}_{H_2}LHV_{H_2}}{w_{in,elec}}\]

(4.60)

where \(w_{in,elec}\) is the amount of electricity required by the electrolyser and \(LHV_{H_2}\) is the lower heating value of hydrogen (in kJ/kg).

The exergy efficiency of the electrolyser can be expressed as

\[\eta_{ex,elec} = \frac{\dot{m}_{H_2}e_{xH_2}}{w_{in,elec}}\]

(4.61)

where \(e_{xH_2}\) is the specific chemical exergy of the hydrogen (in kJ/kg).

The electrolyser voltage efficiency is the ratio of standard voltage of the electrolyser to actual voltage of the electrolyser, that is

\[\eta_{voltage} = \frac{E_0}{E_{tot}}\]

(4.62)

4.5.2 Analysis of System 1

Energy and exergy analyses are performed for the proposed system (System 1) to provide information about their performances, efficiencies and emissions. The reference-environment state is specified as having a temperature \(T_0 = 299\) K and a pressure \(P_0 = 100\) kPa. Exergy values of sea water are calculated using EES software and its external library function. The following assumptions are made to facilitate the analyses and assessments:

- The changes in kinetic and potential energies and exergies are negligible.
- The turbine and pumps operate adiabatically.
- The isentropic efficiencies of the pumps and turbine are 85% (Srinivas et al., 2007).
\begin{itemize}
  \item The pressure losses in all heat exchangers and pipelines are negligible.
  \item The throttling process is adiabatic.
\end{itemize}

\subsection*{4.5.2.1 Balance Equations}

The rate balance equations for each component of system 1 follow:

**Nuclear Reactor:** The mass rate balance equation can be written for the nuclear reactor as follows:

\[ \dot{m}_1 = \dot{m}_2 \]  \hspace{1cm} (4.63)

The energy rate balance equation can be written for the nuclear reactor as follows:

\[ \dot{m}_1 h_1 + \dot{Q}_r = \dot{m}_2 h_2 \]  \hspace{1cm} (4.64)

The entropy rate balance equation can be written for the nuclear reactor as follows:

\[ \dot{m}_1 s_1 + \frac{\dot{Q}_r}{T_0} + \dot{S}_{\text{gen,r}} = \dot{m}_1 s_1 \]  \hspace{1cm} (4.65)

The exergy rate balance equation can be written for the nuclear reactor as follows:

\[ \dot{m}_1 e_{x1} + \dot{Q}_r \left( 1 - \frac{T_0}{T_r} \right) = \dot{m}_2 e_{x2} + \dot{E}_{x_{d,r}} \]  \hspace{1cm} (4.66)

**Steam Generator:** The mass rate balance equation can be written for the steam generator as

\[ \dot{m}_2 = \dot{m}_3 \text{ and } \dot{m}_4 = \dot{m}_5 \]  \hspace{1cm} (4.67)

The energy rate balance equation can be written for the steam generator as

\[ \dot{m}_2 h_2 + \dot{m}_4 h_4 = \dot{m}_3 h_3 + \dot{m}_5 h_5 \]  \hspace{1cm} (4.68)

The entropy rate balance equation can be written for the steam generator as

\[ \dot{m}_2 s_2 + \dot{m}_4 s_4 + \dot{S}_{\text{gen,sg}} = \dot{m}_3 s_3 + \dot{m}_5 s_5 \]  \hspace{1cm} (4.69)

The exergy rate balance equation can be written for the steam generator as

\[ \dot{m}_2 e_{x2} + \dot{m}_4 e_{x4} = \dot{m}_3 e_{x3} + \dot{m}_5 e_{x5} + \dot{E}_{x_{d,sg}} \]  \hspace{1cm} (4.70)

**Pump 1:** The mass rate balance equations can be written for pump 1 as

\[ \dot{m}_3 = \dot{m}_1 \]  \hspace{1cm} (4.71)
The energy rate balance equations can be written for pump 1 as
\[
\dot{m}_3 h_3 + \dot{W}_{p1} = \dot{m}_1 h_1
\] (4.72)

The entropy rate balance equations can be written for pump 1 as
\[
\dot{m}_3 s_3 + \dot{S}_{\text{gen},p1} = \dot{m}_1 s_1
\] (4.73)

The exergy rate balance equations can be written for pump 1 as
\[
\dot{m}_3 e_x_3 + \dot{W}_{p1} = \dot{m}_1 e_{x_1} + \dot{E}_{x_{d,p1}}
\] (4.74)

**Steam Turbine:** The mass rate balance equation can be written for the steam turbine as
\[
\dot{m}_5 = \dot{m}_6
\] (4.75)

The energy rate balance equation can be written for the steam turbine as
\[
\dot{m}_5 h_5 = \dot{W}_t + \dot{m}_6 h_6
\] (4.76)

The entropy rate balance equation can be written for the steam turbine as
\[
\dot{m}_5 s_5 + \dot{S}_{\text{gen},t} = \dot{m}_6 s_6
\] (4.77)

The exergy rate balance equation can be written for the steam turbine as
\[
\dot{m}_5 e_{x_5} = \dot{W}_t + \dot{m}_6 e_{x_6} + \dot{E}_{x_{d,t}}
\] (4.78)

**Condenser:** The mass rate balance equation can be written for the condenser as
\[
\dot{m}_6 = \dot{m}_7 \text{ and } \dot{m}_{10} = \dot{m}_{11}
\] (4.79)

The energy rate balance equation can be written for the condenser as
\[
\dot{m}_{10} h_{10} + \dot{m}_6 h_6 = \dot{m}_{11} h_{11} + \dot{m}_7 h_7 + \dot{Q}_{\text{loss,con}}
\] (4.80)

The entropy rate balance equation can be written for the condenser as
\[
\dot{m}_{10} s_{10} + \dot{m}_6 s_6 + \dot{S}_{\text{gen,con}} = \dot{m}_{11} s_{11} + \dot{m}_7 s_7 + \frac{\dot{Q}_{\text{loss,con}}}{T_0}
\] (4.81)

The exergy rate balance equation can be written for the condenser as
\[ \dot{m}_{10}\text{ex}_{10} + \dot{m}_6\text{ex}_6 = \dot{m}_{11}\text{ex}_{11} + \dot{m}_7\text{ex}_7 + \dot{E}_d,\text{con} + \dot{Q}_{\text{loss,con}} \left( 1 - \frac{T_0}{T_{\text{con}}} \right) \] (4.82)

**Pump 2:** The mass rate balance equation can be written for pump 2 as

\[ \dot{m}_7 = \dot{m}_4 \] (4.83)

The energy rate balance equation can be written for pump 2 as

\[ \dot{m}_7h_7 + \dot{W}_{p2} = \dot{m}_4h_4 \] (4.84)

The entropy rate balance equation can be written for pump 2 as

\[ \dot{m}_7s_7 + \dot{S}_{\text{gen,p2}} = \dot{m}_4s_4 \] (4.85)

The exergy rate balance equation can be written for pump 2 as

\[ \dot{m}_7\text{ex}_7 + \dot{W}_{p2} = \dot{m}_4\text{ex}_4 + \dot{E}_d,\text{p2} \] (4.85)

In order to analysis the reverse osmosis system, the following equations are used. The desalination process is in essence a separation process during which salt and water, comprising the feed seawater, are separated. The product water and brine are the two output streams of the desalination process, as shown in Figure 3.7. The product water has a low concentration of dissolved salts.

Based on the specified characteristics of the product water and the salinity of the source water, the mass flow rates and molar and mass fractions of salt and water in the solution at each point of the system can be expressed as follows:

**Sea Water:**

The feed mass flow rate of seawater can be determined based on the recovery ratio of the proposed RO plant as \( \dot{m}_{10} = \dot{m}_{23}/r_r \).

where the recovery ratio, \( r_r \), represents the ratio of product water relative to the total feed water to the RO plant.

The molar fraction of the salt and water in the seawater source can be calculated based on the defined salinity of seawater as \( x_{s,10} = \frac{\text{MW}_w}{\text{MW}_w + \text{MW}_s \left[ (1/y_{s,10}) - 1 \right]} \) and \( x_{w,23} = 1 - x_{s,23} \), respectively.

where \( y_{s,10} \) is the salt mass fraction in the seawater source and is equal to the salinity of the seawater in \( \text{PPM} \times 10^{-6} \).
Product Water:

The total mass flow rates of the product water and its salinity are given design parameters. The salt flow rate in the product water is calculated, $\dot{m}_{s,23} = y_{s,23} \cdot \dot{m}_{23}$.

The salt molar fraction is determined as $x_{s,23} = \frac{\text{MW}_w}{\text{MW}_w + \text{MW}_s \cdot (1/y_{s,23} - 1)}$.

The water mass flow rate, and water mass and molar fractions in the product water, can be expressed respectively using a simple mass balance of the product water as $\dot{m}_{w,p} = \dot{m}_{p} - \dot{m}_{s,p}$, $y_{w,p} = 1 - y_{s,p}$ and $x_{w,p} = 1 - x_{s,p}$.

Bypass Water:

The amount of bypass water, which mixes with the product water out of the RO to achieve the required salinity of final product, is calculated as $\dot{m}_{21} = \dot{m}_{23} \left[ \frac{y_{s,23} - y_{s,18}}{y_{s,10} - y_{s,18}} \right]$.

where $y_{s,18}$ is the mass ratio of salt in the outlet permeate flow of the RO.

Brine:

The mass flow rate of the brine, its salinity as the mass and molar ratio of salt, respectively can be evaluated as $\dot{m}_{20} = \dot{m}_{10} - \dot{m}_{23}$, $y_{s,20} = \frac{y_{s,10} - r_y y_{s,18}}{1 - r_y}$ and $x_{s,20} = \frac{\text{MW}_w}{\text{MW}_w + \text{MW}_s \cdot (1/y_{s,20} - 1)}$.

The water mass and molar ratios of the brine are calculated from the salt mass and molar ratios as $y_{w,20} = 1 - y_{s,20}$ and $x_{w,20} = 1 - x_{s,20}$.

The molecular weights of the source and product water and brine are calculated as $\text{MW}_i = x_{s,i} \cdot \text{MW}_s + x_{w,i} \cdot \text{MW}_w$.

where the salt molecular weight, $\text{MW}_s$, is taken to be the value of the NaCl salt molecular weight which is 58.5 kg/kmol. The salinity (in PPM) at each state is Salinity = $y_s \times 10^6$.

Pump 4: The mass rate balance equation for pump 4 can be written as

$$\dot{m}_{11} = \dot{m}_{12}$$

The energy rate balance equation for pump 4 can be written as

$$\dot{m}_{11} h_{11} + W_{p4} = \dot{m}_{12} h_{12}$$

The entropy rate balance equation for pump 4 can be written as
\[ \dot{m}_{11}s_{11} + \dot{S}_{\text{gen,p4}} = \dot{m}_{12}s_{12} \]  
(4.88)

The exergy rate balance equation for pump 4 can be written as
\[ \dot{m}_{11}\text{ex}_{11} + \dot{W}_p = \dot{m}_{12}\text{ex}_{12} + \dot{Ex}_{d,p4} \]  
(4.89)

**Filter**: The mass rate balance equation for the filter can be written as
\[ \dot{m}_{12} = \dot{m}_{13} \]  
(4.90)

The energy rate balance equation for the filter can be written as
\[ \dot{m}_{12}h_{12} = \dot{m}_{13}h_{13} \]  
(4.91)

The entropy rate balance equation for the filter can be written as
\[ \dot{m}_{12}s_{12} + \dot{S}_{\text{gen,f}} = \dot{m}_{13}s_{13} \]  
(4.92)

The exergy rate balance equation for the filter can be written as
\[ \dot{m}_{12}\text{ex}_{12} = \dot{m}_{13}\text{ex}_{13} + \dot{Ex}_{d,f} \]  
(4.93)

**Throttle Valve 1**: The mass rate balance equation for the throttle valve 1 can be written as
\[ \dot{m}_{14} = \dot{m}_{21} \]  
(4.94)

The energy rate balance equation for the throttle valve 1 can be written as
\[ \dot{m}_{14}h_{14} = \dot{m}_{21}h_{21} \]  
(4.95)

The entropy rate balance equation for the throttle valve 1 can be written as
\[ \dot{m}_{14}s_{14} + \dot{S}_{\text{gen,tv1}} = \dot{m}_{21}s_{21} \]  
(4.96)

The exergy rate balance equation for the throttle valve 1 can be written as
\[ \dot{m}_{14}\text{ex}_{14} = \dot{m}_{21}\text{ex}_{21} + \dot{Ex}_{d,tv1} \]  
(4.97)

**Pump 3**: The mass rate balance equation for pump 3 can be written as
\[ \dot{m}_{16} = \dot{m}_{17} \]  
(4.98)

The energy rate balance equation for pump 3 can be written as
\[ \dot{m}_{16}h_{16} + \dot{W}_{p3} = \dot{m}_{17}h_{17} \]  

(4.99)

The entropy rate balance equation for pump 3 can be written as

\[ \dot{m}_{16}s_{16} + \dot{\mathcal{S}}_{\text{gen, p3}} = \dot{m}_{17}s_{17} \]  

(4.100)

The exergy rate balance equation for pump 3 can be written as

\[ \dot{m}_{16}\text{ex}_{16} + \dot{W}_{p3} = \dot{m}_{17}\text{ex}_{17} + \dot{\mathcal{E}}_{\text{d, p3}} \]  

(4.101)

**RO Module:** The mass rate balance equation for the RO module can be written as

\[ \dot{m}_{17} = \dot{m}_{18} + \dot{m}_{19} \]  

(4.102)

The energy rate balance equation for the RO module can be written as

\[ \dot{m}_{17}h_{17} = \dot{m}_{18}h_{18} + \dot{m}_{19}h_{19} \]  

(4.103)

The entropy rate balance equation for the RO module can be written as

\[ \dot{m}_{16}s_{16} + \dot{\mathcal{S}}_{\text{gen, rm}} = \dot{m}_{18}s_{18} + \dot{m}_{19}s_{19} \]  

(4.104)

The exergy rate balance equation for the RO module can be written as

\[ \dot{m}_{16}\text{ex}_{16} = \dot{m}_{18}\text{ex}_{18} + \dot{m}_{19}\text{ex}_{19} + \dot{\mathcal{E}}_{\text{d, rm}} \]  

(4.105)

**Pelton Turbine:** The mass rate balance equation for the Pelton turbine can be written as

\[ \dot{m}_{19} = \dot{m}_{20} \]  

(4.106)

The energy rate balance equation for the Pelton turbine can be written as

\[ \dot{m}_{19}h_{19} = \dot{W}_{pt} + \dot{m}_{20}h_{20} \]  

(4.107)

The entropy rate balance equation for the Pelton turbine can be written as

\[ \dot{m}_{19}s_{19} + \dot{\mathcal{S}}_{\text{gen, pt}} = \dot{m}_{20}s_{20} \]  

(4.108)

The entropy rate balance equation for the Pelton turbine can be written as

\[ \dot{m}_{19}\text{ex}_{19} = \dot{W}_{pt} + \dot{m}_{20}\text{ex}_{20} + \dot{\mathcal{E}}_{\text{d, pt}} \]  

(4.109)

**Mixing Chamber:** The mass rate balance equation for the mixing chamber can be written as
\[ \dot{m}_{21} + \dot{m}_{18} = \dot{m}_{22} \]  \hfill (4.110)

The energy rate balance equation for the mixing chamber can be written as
\[ \dot{m}_{21} h_{21} + \dot{m}_{18} h_{18} = \dot{m}_{22} h_{22} \]  \hfill (4.111)

The entropy rate balance equation for the mixing chamber can be written as
\[ \dot{m}_{21} s_{21} + S_{\text{gen,mc}} + \dot{m}_{18} s_{18} = \dot{m}_{22} s_{22} \]  \hfill (4.112)

The exergy rate balance equation for the mixing chamber can be written as
\[ \dot{m}_{21} \text{ex}_{21} + \dot{m}_{18} \text{ex}_{18} = \dot{m}_{22} \text{ex}_{22} + E_{\text{d,mc}} \]  \hfill (4.113)

**Throttle Valve 2:** The mass rate balance equation for the throttle valve 2 can be written as
\[ \dot{m}_{22} = \dot{m}_{23} \]  \hfill (4.114)

The entropy rate balance equation for the throttle valve 2 can be written as
\[ \dot{m}_{22} h_{22} = \dot{m}_{23} h_{23} \]  \hfill (4.115)

The entropy rate balance equation for the throttle valve 2 can be written as
\[ \dot{m}_{22} s_{22} + S_{\text{gen,tv2}} = \dot{m}_{23} s_{23} \]  \hfill (4.116)

The exergy rate balance equation for the throttle valve 2 can be written as
\[ \dot{m}_{14} \text{ex}_{14} = \dot{m}_{23} \text{ex}_{23} + E_{\text{d,tv2}} \]  \hfill (4.117)

### 4.5.2.2 Performance Assessment of System 1

Here, the nuclear plant is used to generate three useful outputs, i.e. fresh water, hydrogen and electricity. The exergy efficiency of the trigeneration plant is an important measure. The trigeneration plant exergy efficiency follows:

\[ \eta_{\text{ex,ov1}} = \frac{E_{\text{out}}}{E_{\text{in}}} = \frac{W_{\text{pt}} + W_{\text{t}} + E_{\text{outwater}} - W_{\text{net,p}} - E_{\text{seawater}} + m_{\text{H}_2} \text{ex}_{\text{H}_2}}{Q_{\text{in}}} \]  \hfill (4.118)

where \( W_{\text{net,p}} \) denotes the sum of the work rates consumed by all pumps and the electrolyser.

In addition, to exergy efficiency, energy efficiency of System 1 is also evaluated as
\[ \eta_{en,ov1} = \frac{E_{out}}{E_{in}} = \frac{W_{pt} + W_t + E_{noutwater} - W_{net} - E_{nsaline} + m_{H_2} LHV_{H_2}}{Q_{in}} \]  

(4.119)

The exergy efficiency for the overall desalination system is defined here as the ratio between the minimum work rate required for the separation process to the actual work rate supplied:

\[ \eta_{ex,ro} = \frac{W_{min}}{W_{act}} \]  

(4.120)

Alternatively, using exergy flow rates through the RO system, we can rewrite this expression as follows:

\[ \eta_{ex,ro} = \frac{E_{xout}}{E_{xin}} = \frac{E_{xoutwater} - E_{xseawater}}{W_{net}} \]  

(4.121)

### 4.5.3 Analysis of System 2

In order to analyse the system some reasonable thermodynamic assumptions are made as follows:

- A steady state operation is considered.
- The changes in kinetic and potential exergies terms are negligible.
- The effectiveness of the precooler and recuperator is considered as 0.95.
- The pressure losses in all heat exchangers and pipelines are neglected.
- No heat losses in turbines and pumps are considered.

#### 4.5.3.1 Balance Equations

Making appropriate use of mass, energy, entropy and exergy balance equations for each component of the System 2 a program is developed in Energy Equation Solver (EES). Thermodynamic values are calculated using Engineering Equation Solver (EES) software which is a widely used software package. It can generally be used to solve n non-linear equations for n unknowns. It can simplify problems including thermodynamic cycles and easily minimise the chances of calculation errors when such cycles solve manually. However, the code generated to solve problems can be very sensitive to initial guesses, and will sometimes not meet to a solution even though the entered equations are correct. The component wise energy and exergy balance equations that are used in the analyses are given in Table 4.4. By using the exergy balance equations given in the table, one may obtain the exergy destruction rate for each component.
<table>
<thead>
<tr>
<th>Name of the component</th>
<th>Energy balance equations</th>
<th>Exergy balance equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor core</td>
<td>$\dot{m}<em>8 h_8 + Q</em>{rc} = \dot{m}_1 h_1$</td>
<td>$\dot{m}<em>8 e_8 + Q</em>{rc} = \dot{m}<em>1 e_1 + \dot{Ex}</em>{d,rc}$</td>
</tr>
<tr>
<td>Gas turbine</td>
<td>$\dot{m}_1 h_1 = \dot{m}<em>2 h_2 + W</em>{gt}$</td>
<td>$\dot{m}<em>1 e_1 = W</em>{gt} + \dot{m}<em>2 e_2 + \dot{Ex}</em>{d,gt}$</td>
</tr>
<tr>
<td>Recuperator</td>
<td>$\dot{m}_7 h_7 + \dot{m}_2 h_2 = \dot{m}_8 h_8 + \dot{m}_3 h_3$</td>
<td>$\dot{m}_7 e_7 + \dot{m}_2 e_2 = \dot{m}_8 e_8 + \dot{m}<em>3 e_3 + \dot{Ex}</em>{d,rec}$</td>
</tr>
<tr>
<td>Compressor</td>
<td>$\dot{m}_6 h_6 + W_c = \dot{m}_7 h_7$</td>
<td>$\dot{m}_6 e_6 + W_c = \dot{m}<em>7 e_7 + \dot{Ex}</em>{d,c}$</td>
</tr>
<tr>
<td>Steam generator</td>
<td>$\dot{m}<em>3 h_3 + \dot{m}</em>{14} h_{14}$</td>
<td>$\dot{m}<em>3 e_3 + \dot{m}</em>{14} e_{14}$</td>
</tr>
<tr>
<td></td>
<td>$= \dot{m}<em>{11} h</em>{11} + \dot{m}_4 h_4$</td>
<td>$= \dot{m}<em>{11} e</em>{11} + \dot{m}_4 e_4$</td>
</tr>
<tr>
<td></td>
<td>$= \dot{m}<em>{12} h</em>{12}$</td>
<td>$= \dot{m}<em>{12} e</em>{12} + \dot{Ex}_{d,sg}$</td>
</tr>
<tr>
<td>Precooler</td>
<td>$\dot{m}<em>9 h_9 + \dot{m}<em>6 h_6 + \dot{m}</em>{10} h</em>{10}$</td>
<td>$\dot{m}<em>9 e_9 + \dot{m}<em>6 e_6 + \dot{m}</em>{10} e</em>{10} + \dot{Ex}_{d,pre}$</td>
</tr>
<tr>
<td>Steam turbine</td>
<td>$\dot{m}<em>{11} h</em>{11} = W_{st} + \dot{m}<em>{12} h</em>{12}$</td>
<td>$\dot{m}<em>{11} e</em>{11} = W_{st} + \dot{m}<em>{12} e</em>{12} + \dot{Ex}_{d,st}$</td>
</tr>
<tr>
<td>Heat exchanger 1</td>
<td>$\dot{m}<em>{16} h</em>{16}$</td>
<td>$\dot{m}<em>{16} e</em>{16}$</td>
</tr>
<tr>
<td></td>
<td>$= \dot{m}<em>{17} h</em>{17} + \dot{m}_5 h_5$</td>
<td>$= \dot{m}<em>{17} e</em>{17} + \dot{m}_5 e_5$</td>
</tr>
<tr>
<td></td>
<td>$= \dot{m}<em>{18} h</em>{18}$</td>
<td>$= \dot{m}<em>{18} e</em>{18} + \dot{Ex}_{d,hex1}$</td>
</tr>
<tr>
<td>Heat exchanger 2</td>
<td>$\dot{m}<em>{19} h</em>{19}$</td>
<td>$\dot{m}<em>{19} e</em>{19}$</td>
</tr>
<tr>
<td></td>
<td>$= \dot{m}<em>{17} h</em>{17} + \dot{m}_5 h_5$</td>
<td>$= \dot{m}<em>{17} e</em>{17} + \dot{m}_5 e_5$</td>
</tr>
<tr>
<td></td>
<td>$= \dot{m}<em>{18} h</em>{18}$</td>
<td>$= \dot{m}<em>{18} e</em>{18} + \dot{Ex}_{d,hex2}$</td>
</tr>
<tr>
<td>Condenser</td>
<td>$\dot{m}<em>{12} h</em>{12} + \dot{m}<em>{15} h</em>{15}$</td>
<td>$\dot{m}<em>{12} e</em>{12} + \dot{m}<em>{15} e</em>{15}$</td>
</tr>
<tr>
<td></td>
<td>$= \dot{m}<em>{13} h</em>{13} + \dot{m}<em>{16} h</em>{16}$</td>
<td>$= \dot{m}<em>{13} e</em>{13} + \dot{m}<em>{16} e</em>{16}$</td>
</tr>
<tr>
<td></td>
<td>$+ Q_{loss,con}$</td>
<td>$+ \dot{Ex}<em>{d,con} + \dot{Ex}</em>{loss,con}$</td>
</tr>
<tr>
<td>Pump 1</td>
<td>$\dot{m}<em>{13} h</em>{13} + W_{p1} = \dot{m}<em>{14} h</em>{14}$</td>
<td>$\dot{m}<em>{13} e</em>{13} + W_{p1} = \dot{m}<em>{14} e</em>{14} + \dot{Ex}_{d,p1}$</td>
</tr>
<tr>
<td>Pump 2</td>
<td>$\dot{m}<em>{20} h</em>{20} + W_{p2} = \dot{m}<em>{21} h</em>{21}$</td>
<td>$\dot{m}<em>{20} e</em>{20} + W_{p2} = \dot{m}<em>{21} e</em>{21} + \dot{Ex}_{d,p2}$</td>
</tr>
<tr>
<td>Filter</td>
<td>$\dot{m}<em>{21} h</em>{21} = \dot{m}<em>{22} h</em>{22}$</td>
<td>$\dot{m}<em>{21} e</em>{21} = \dot{m}<em>{22} e</em>{22} + \dot{Ex}_{d,f}$</td>
</tr>
<tr>
<td>Throttle valve 1</td>
<td>$\dot{m}<em>{31} h</em>{31} = \dot{m}<em>{32} h</em>{32}$</td>
<td>$\dot{m}<em>{31} e</em>{31} = \dot{m}<em>{32} e</em>{32} + \dot{Ex}_{d,tv1}$</td>
</tr>
<tr>
<td>Throttle valve 2</td>
<td>$\dot{m}<em>{27} h</em>{27} = \dot{m}<em>{28} h</em>{28}$</td>
<td>$\dot{m}<em>{27} e</em>{27} = \dot{m}<em>{28} e</em>{28} + \dot{Ex}_{d,tv2}$</td>
</tr>
<tr>
<td>Pump 3</td>
<td>$\dot{m}<em>{24} h</em>{24} + W_{p3} = \dot{m}<em>{25} h</em>{25}$</td>
<td>$\dot{m}<em>{24} e</em>{24} + W_{p3} = \dot{m}<em>{25} e</em>{25} + \dot{Ex}_{d,p3}$</td>
</tr>
<tr>
<td>RO module</td>
<td>$\dot{m}<em>{25} h</em>{25} = \dot{m}<em>{26} h</em>{26} + \dot{m}<em>{29} h</em>{29}$</td>
<td>$\dot{m}<em>{25} e</em>{25} = \dot{m}<em>{26} e</em>{26} + \dot{m}<em>{29} e</em>{29} + \dot{Ex}_{d,rm}$</td>
</tr>
<tr>
<td>Mixing chamber</td>
<td>$\dot{m}<em>{32} h</em>{32} = \dot{m}<em>{26} h</em>{26}$</td>
<td>$\dot{m}<em>{32} e</em>{32} + \dot{m}<em>{26} e</em>{26}$</td>
</tr>
<tr>
<td></td>
<td>$= \dot{m}<em>{27} h</em>{27}$</td>
<td>$= \dot{m}<em>{27} e</em>{27} + \dot{Ex}_{d,mc}$</td>
</tr>
<tr>
<td>Pelton turbine</td>
<td>$\dot{m}<em>{29} h</em>{29} = W_{pt} + \dot{m}<em>{30} h</em>{30}$</td>
<td>$\dot{m}<em>{29} e</em>{29} = W_{pt} + \dot{m}<em>{30} e</em>{30} + \dot{Ex}_{d,pt}$</td>
</tr>
</tbody>
</table>
4.5.3.2 Performance Assessment of System 2

The performance assessment of System 2 is made in terms of exergy efficiency. In order to analyse the reverse osmosis process, the exergy efficiency of the electricity generation process is defined as

$$\eta_{\text{ex, power}} = \frac{P_e}{Q_{rc}} \quad (4.122)$$

The exergy efficiency of the electricity generation without steam turbine work output process is defined as

$$\eta_{\text{ex, power1}} = \frac{P_{e1}}{Q_{rc}} \quad (4.123)$$

Since the System 2 is designed to produce three useful outputs i.e. electricity, hydrogen and fresh water. The exergy efficiency of the overall system is defined as follows:

$$\eta_{\text{ex, ov2}} = \frac{m_{28}\text{ex}_{28} + m_{30}\text{ex}_{30} - m_{19}\text{ex}_{19} + P_e}{Q_{rc}} \quad (4.124)$$

4.6 Uncertainty Analysis

There are certain quantities which cannot be measured directly. However, they can be calculated in terms of variables that can be measured directly. The measured variable may be denoted as X1, X2, etc. having an uncertainty. In this thesis, EES is used to calculate the uncertainty for the quantities like exergy efficiencies, exergy destruction, heat etc. as they are mostly dependent upon the temperature. EES uses the method proposed by Taylor and Kuyatt (1994) to find the uncertainty in the calculated variable (Y). The uncertainty in the calculated quantity can be determined as

$$U_Y = \sqrt{\sum \left( \frac{\partial Y}{\partial X_i} \right)^2 U_X^2} \quad (4.125)$$

where U represents the uncertainty of the variable.

Table 4.5 lists the measurement range and accuracies of the devices used in the experiment and are listed based on the datasheets given by the manufacturer. The experimental uncertainty is calculated using the systematic (S_i) and random (R_E_i) errors of the measurement process and is defined as:
\[ \delta X_i = \sqrt{S_i^2 + RE_i^2} \]  \hfill (4.126)

During the experiment, there are some errors that arise due to the common complications such as instrument resolution, calibration, zero offset, instrument drift, personal errors and physical variations. To find the random (precision) errors, a Relative Standard Deviation (RSD) is defined and is calculated using the standard deviation \((s)\) using equation 4.127. RSD is useful in comparing the uncertainties between different measurements of varying absolute magnitude. RSD is also termed as the coefficient of variance.

\[
RSD = \frac{s}{\bar{x}} \times 100\% 
\]  \hfill (4.127)

Table 4.5 The measurement range and accuracies of the measurement devices

<table>
<thead>
<tr>
<th>Name of device</th>
<th>Measurement parameter</th>
<th>Measurement range</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamry Reference 3000</td>
<td>Voltage</td>
<td>±11 V</td>
<td>±1 mV ±0.3% of reading</td>
</tr>
<tr>
<td>Gamry Reference 3000</td>
<td>Current</td>
<td>±3 A</td>
<td>±10 pA ±0.3% of range</td>
</tr>
<tr>
<td>OM-DAQPRO-5300 Thermocouple K Type</td>
<td>Temperature</td>
<td>-250 to 1200°C</td>
<td>±0.5%</td>
</tr>
</tbody>
</table>

Source: (Omega, 2017; Gamry, 2017)

Table 4.6 Calculated values of different errors and total uncertainty

<table>
<thead>
<tr>
<th>Device</th>
<th>Measurement parameter</th>
<th>Reference value</th>
<th>Absolute bias error</th>
<th>Relative bias error (%)</th>
<th>Relative percentage error (%)</th>
<th>Total uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamry Reference 3000</td>
<td>Voltage</td>
<td>2.5 V</td>
<td>0.006 V</td>
<td>0.3</td>
<td>1.75</td>
<td>1.77</td>
</tr>
<tr>
<td>Gamry Reference 3000</td>
<td>Current</td>
<td>0.271 A</td>
<td>0.001 A</td>
<td>0.3</td>
<td>1.28</td>
<td>1.32</td>
</tr>
<tr>
<td>Thermocouple K Type</td>
<td>Temperature</td>
<td>500°C</td>
<td>1°C</td>
<td>0.2</td>
<td>0.313</td>
<td>0.37</td>
</tr>
</tbody>
</table>
The calculated bias error, precision error and the total uncertainty percentage is provided in Table 4.6. It is to be noted from the table that precision error dominates the total error, hence the total uncertainty. However, the precision error can be further reduced by conducting or repeating more experiments i.e. increasing the number of experiments. The total uncertainty in the temperature is 0.37% while in the voltage 1.77% of uncertainty is observed.
CHAPTER 5: EXPERIMENTAL SETUP AND PROCEDURE

In this chapter, the detailed about experimental setup is presented. In addition, experimental procedure is also briefly discussed. An experiment is conducted to see whether the proposed electrolytic reaction for Scheme 1 is physically possible or not as this is the very first time when this reaction is reported.

5.1 Experimental Setup

An experimental investigation is made to establish the feasibility of the high temperature electrolytic step as this step in aqueous state is well studied in literature. However, to the authors’ knowledge, in molten state this step is not yet well understood. The schematic illustration of high temperature electrolyser (i.e., the high temperature reactor for Step 3) is shown in Figure 5.1.

![Figure 5.1 Schematic of experimental setup used for examining the electrolytic step ((Step 3) of Scheme 1](image)

As shown in Figure 5.1, it consists of a heating mantle (having two heating tapes of 630 W each) comprised of a glass vessel (in order to sustain high temperature), graphite rods (diameter 1/4"), an electricity supply, a potentiostat (Gamry Instruments Reference 3000), CuCl powder (CAS-7758-89-6, provided by Spectrum chemicals) an oxygen analyser (HHAQ-104, provided by OMEGA), two temperature controllers, an argon flowmeter, a condenser, a scrubber, and a
crucible. One of the temperature controller having a J-type thermocouple is used to monitor the temperature of the heating mantle while the other temperature controller having a K-type thermocouple is used to measure the inside temperature of the reactor. The condenser (made of quartz glass) is utilised to condense some of the CuCl vapour exiting the reactor (as it can be harmful). The purpose of the scrubber (made of quartz glass and having a mixture of 4.5 L of water and 390 g sodium hydrogen carbonate (NAHCO₃)) is to neutralise the gases from the condenser before exhausting them to the fume hood.

Figure 5.2 shows the actual experimental setup for examining the electrolytic step.

![Figure 5.2 Actual experimental set up for examining the electrolytic step (Step 3)](image)

5.2 Experimental Procedure

Before starting the experiment, argon is fed to the reactor for purging the air completely. Throughout the experiment the flow rate of argon is set to 100 mL/min. The CuCl powder in the crucible is heated to 773 K. Once the required temperature is achieved, a voltage is applied to the graphite electrodes using the potentiostat. The potentiostat apply a voltage across a pair of electrodes and simultaneously measures the current which flows through a solution of an anolyte. The potentiostat used for this research is the Gamry 3000 high-performance Potentiostat/Galvanostat/ZRA which has a maximum current of ±3 A and a maximum voltage of
± 32 Volts. The product (a dark brown solid) is collected after the test and crushed to fine powder. The fine powder is examined using X-ray powder diffraction (XRD) (Rigaku Corporation, Japan).

Figure 5.3 shows the I-V curve of the proposed high temperature electrolytic step (Step 3) of Scheme 1. It can been seen that a current of 100 mA can be achieved when the applied voltage is 2.0 V. With increasing voltage, the current increases. It is to be noted from the figure that up to 1.5 V, the current varies almost linearly, however after 1.5 V the amount of current shoot-up following a non-linear relation. Some noise is observed due to the vibrations in the potentiostat device.

![Figure 5.3 I-V curve for proposed high temperature electrolytic step (Step 3)](image)

XRD measurements are necessary to observe the intensity of the substances. The XRD pattern of the obtained product (dark brown powder) is shown in Figure 5.4, which depicts the peak for a product called as melanothallite (Cu$_2$OCl$_2$). As shown in figure, the x-axis shows the scan range while y-axis shows the intensity. Melanothallite is formed from the reaction between CuCl$_2$ and CuO at a temperature of 773 K, suggesting that Step 3 is possible if it is ensured that there is no oxygen present throughout the experiment. This experimental result as a proof of concept suggests that Step 3 is possible if the presence of oxygen is avoided. A SEM image of the obtained product is required to obtain further details, but is not obtained here as it is beyond the scope of this study.
Figure 5.4 XRD pattern of the obtained product
CHAPTER 6: RESULTS AND DISCUSSION

In this chapter, the results obtained through the thermodynamic modeling are presented by using the procedure given in Chapter 4. Furthermore, results obtained from electrochemical modeling are given.

6.1 Results of Schemes of Cu-Cl Cycle for Hydrogen Production

The results obtained through the energy and exergy analyses for the schemes of Cu-Cl cycle for hydrogen production are presented in this sub-section.

6.1.1 Results of Scheme 1

The results of the energy and exergy analyses for Scheme 1 are presented in Table 6.1. It can be note from the table that the energy and exergy efficiencies of the proposed scheme are 31.8% and 69.7%, respectively. Ozbilen et al. (2014) found the energy efficiency of a similar four step Cu-Cl cycle for hydrogen production only, to be 35.7% for a heat-to-work conversion efficiency (i.e., an energy efficiency of the electrical power plant) of 50%, while in the present case an energy efficiency for Scheme 1 of 38.2% is achieved when a heat-to-work conversion efficiency of 50% is considered. This result suggests that the proposed scheme has a higher energy efficiency, although this observation is limited by the fact the processes have some differences. One may also note from the table that uncertainty observed in the energy and exergy efficiencies of Scheme 1 are ±0.02% and ±0.04%, respectively, which can be negligible when compared to the total energy and exergy efficiencies of the overall scheme. The uncertainty in the total specific heat is found to be ±0.04 kJ/kmol, while ±0.17 kJ/kmol of uncertainty is calculated in the theoretical specific amount of electricity required. The uncertainties values reported in the table are calculated based on the uncertainty in the temperature of the steps of the Scheme 1.

Figure 6.1 shows the specific exergy destruction of the various steps of the proposed Scheme 1. The maximum specific exergy destruction occurs in the electrolytic step (Step 3), mainly because electricity (a high quality energy form) is utilised. Thus effort is merited to reduce the specific exergy destruction in this electrolytic step in a cost effective manner. A significant amount of specific exergy destruction is observed in Step 2 while the specific exergy destructions in Step 1 and 4 are found to be negligible.
Table 6.1 Values of parameters calculated in the present study including uncertainties for Scheme 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy efficiency of Scheme 1 (%)</td>
<td>31.8</td>
<td>±0.02</td>
</tr>
<tr>
<td>Exergy efficiency of Scheme 1 (%)</td>
<td>69.7</td>
<td>±0.04</td>
</tr>
<tr>
<td>Theoretical specific amount of electricity required (kJ/mol)</td>
<td>251.7</td>
<td>±0.17</td>
</tr>
<tr>
<td>Exergy efficiency of Step 1 (%)</td>
<td>94.6</td>
<td>±0.01</td>
</tr>
<tr>
<td>Exergy efficiency of Step 2 (%)</td>
<td>68.9</td>
<td>±0.003</td>
</tr>
<tr>
<td>Exergy efficiency of Step 3 (%)</td>
<td>74.9</td>
<td>±0.002</td>
</tr>
<tr>
<td>Exergy efficiency of Step 4 (%)</td>
<td>99.4</td>
<td>±0.13</td>
</tr>
<tr>
<td>Total specific heat required by Scheme 1 (kJ/mol)</td>
<td>123.5</td>
<td>±0.04</td>
</tr>
<tr>
<td>Maximum temperature in Scheme 1 (K)</td>
<td>903</td>
<td>±1</td>
</tr>
</tbody>
</table>

Figure 6.1 Specific exergy destructions and exergy efficiencies of the various steps in Scheme 1

The effects of the operating temperature of Step 1 on the energy and exergy efficiencies of Scheme 1 are shown in Figure 6.2. As the temperature increases from 903 K to 953 K, there is no effect on the energy efficiency of the scheme while the exergy efficiency decreases from 69.7% to 69.5%. This result suggests that the reaction needs to be carried out at a temperature of around 900 K to achieve a higher exergy efficiency.
Figure 6.2 Effects of operating temperature of Step 1 on the energy and exergy efficiencies of Scheme 1

Figure 6.3 Effects of operating temperature of Step 1 on the specific exergy destruction and exergy efficiency of Step 1 in Scheme 1

Figure 6.3 shows the variations of specific exergy destruction and the exergy efficiency of Step 1 with the temperature of Step 1. It can be seen that, with increasing temperature, the exergy...
efficiency of the step decreases while the specific exergy destruction increases. To achieve a higher exergy efficiency for this step, the step operating temperature should be at around 900 K.

Figure 6.4 shows the effects of the operating temperature of Step 2 on the energy and exergy efficiencies of the scheme. No significant effects are observed on the overall energy and exergy efficiencies by changing the operating temperature of Step 2. Similar trends for the exergy efficiency of Step 2 and the specific exergy destruction of Step 2 are observed (see Figure 6.5) i.e. no significant changes are observed in the exergy efficiency and specific exergy destruction of Step 2.

It can be observed from Figure 6.6 that as the Step 3 temperature increases, the energy and exergy efficiencies of the overall cycle decrease from 69.7% to 68.7% and 31.8% to 31.3%, respectively. The reason for this trend is that, with increasing temperature, the Gibbs free energy change of this step increases, suggesting that this step needs to be carried out at a lower temperature, i.e., around 773 K.

Figure 6.4 Effects of operating temperature of Step 2 on the energy and exergy efficiencies of Scheme 1
Figure 6.5 Effects of operating temperature of Step 2 on the specific exergy destruction and exergy efficiency of Step 2 in Scheme 1

Figure 6.6 Effects of operating temperature of Step 3 on the energy and exergy efficiencies of Scheme 1
Figure 6.7 shows the effects of varying the operating temperature of Step 3 on its exergy efficiency and specific exergy destruction. As the temperature rises, the exergy efficiency of the step decreases while the specific exergy destruction increases.

Figure 6.7 Effects of operating temperature of Step 3 on the specific exergy destruction and exergy efficiency of Step 3 in Scheme 1

Figure 6.8 Effects of operating temperature of Step 4 on the energy and exergy efficiencies of Scheme 1
Figure 6.8 shows the effects of varying the operating temperature of Step 4 on the energy and exergy efficiencies of the overall cycle. No significant effect of step temperature is observed on either of the efficiencies of the overall cycle.

It can be observed from Figure 6.9 that, with increasing step temperature, the exergy efficiency decreases notably, from 99.4% to 94.0%, while the specific exergy destruction rises sharply from 1.18 kJ/mol to 12.2 kJ/mol. Note from this figure that it is not possible to carry out this reaction below 833 K as the specific exergy destruction becomes negative for lower temperature values. This result highlights the importance of applying exergy analysis to chemical reactions as energy analysis does not provide such insights.

The variations of the energy and exergy efficiencies of the overall cycle with the energy efficiency of the power plant is shown in Figure 6.10. As the energy efficiency of the power plant increases, the energy efficiency of the overall cycle increase significantly, suggesting that this type of cycle may be beneficial if coupled to a power plant having high efficiencies, such as High Temperature Nuclear Reactor based power plants.
Results of Scheme 2

The results of the energy and exergy analyses for Scheme 2 are presented in Table 6.2. It can be noted from the table that the energy and exergy efficiencies of the proposed scheme are 32.0% and 68.3%, respectively. For a heat-to-work conversion efficiency (i.e., an energy efficiency of the electrical power plant) of 50%, an energy efficiency for Scheme 2 of 37.2% is achieved while Ozbilen et al. (2014) reported an efficiency of 35.2% for a similar Cu-Cl cycle when a heat-to-work conversion efficiency of 50% is considered. This result suggests that the proposed scheme (Scheme 2) has a higher energy efficiency, although this observation is limited by the fact the processes have some differences. From the table, one can find that similar to Scheme 1, the values of uncertainties in the energy and exergy efficiencies of Scheme 2 are ±0.02% and ±0.04%, respectively. The uncertainties in the exergy efficiencies of each step of the proposed scheme (Scheme 2) are in the range of ±0.01 to ±0.1%. 

Figure 6.10 Variations of the energy and exergy efficiencies of Scheme 1 with the energy efficiency of the power plant
Table 6.2 Values of parameters calculated used in the study including uncertainties for Scheme 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy efficiency of Scheme 2 (%)</td>
<td>32.0</td>
<td>±0.02</td>
</tr>
<tr>
<td>Exergy efficiency of Scheme 2 (%)</td>
<td>68.3</td>
<td>±0.04</td>
</tr>
<tr>
<td>Theoretical specific amount of electricity required (kJ/mol)</td>
<td>216.7</td>
<td>±0.23</td>
</tr>
<tr>
<td>Exergy efficiency of Step 1 (%)</td>
<td>94.6</td>
<td>±0.01</td>
</tr>
<tr>
<td>Exergy efficiency of Step 2 (%)</td>
<td>74.3</td>
<td>±0.02</td>
</tr>
<tr>
<td>Exergy efficiency of Step 3 (%)</td>
<td>99.4</td>
<td>±0.1</td>
</tr>
<tr>
<td>Total specific heat required by Scheme 2 (kJ/mol)</td>
<td>207.3</td>
<td>±0.01</td>
</tr>
<tr>
<td>Maximum temperature in Scheme 2 (K)</td>
<td>903</td>
<td>±1</td>
</tr>
</tbody>
</table>

Figure 6.11 Specific exergy destructions and exergy efficiencies of the various steps in Scheme 2

Figure 6.11 shows the specific exergy destructions of the various steps of Scheme 2. The maximum specific exergy destruction occurs in the electrolytic step (Step 2), mainly because electricity (a high quality energy form) is utilised. Thus effort is merited to reduce the specific exergy destruction in this electrolytic step in a cost effective manner. The specific exergy destructions in Step 1 and 3 are found not to be significant.
Figure 6.12 Effects of operating temperature of Step 1 on the energy and exergy efficiencies of Scheme 2

Figure 6.13 Effects of operating temperature of Step 1 on the specific exergy destruction and exergy efficiency of Step 1 in Scheme 2
Figure 6.14 Effects of operating temperature of Step 2 on the energy and exergy efficiencies of Scheme 2

Figure 6.15 Effects of operating temperature of Step 2 on the specific exergy destruction and exergy efficiency of Step 2 in Scheme 2
The effects of the operating temperature of Step 1 on the energy and exergy efficiencies of Scheme 2 are shown in Figure 6.12. As the temperature increases from 903 K to 953 K, there is no effect on the energy efficiency of the scheme while the exergy efficiency decreases from 68.3% to 68.1%. This result suggests that the reaction needs to be carried out at a temperature of around 900 K to achieve a higher exergy efficiency. Note that Step 1 is a common step in both the schemes (Scheme 1 and Scheme 2).

Figure 6.13 shows the variations of specific exergy destruction and the exergy efficiency of Step 2 with the temperature of Step 2. It can be seen that, with increasing temperature, the exergy efficiency of the step decreases while the specific exergy destruction increases. To achieve a higher exergy efficiency for this step, the step operating temperature should be at around 900 K.

Figure 6.14 shows the effects of the operating temperature of Step 2 on the energy and exergy efficiencies of the scheme. No significant effects are observed on the overall energy and exergy efficiencies from changing the operating temperature of Step 2.

It can be seen that, with increasing temperature, the exergy efficiency of the step decreases while the specific exergy destruction increases (see Figure 6.15). To achieve a higher exergy efficiency for this step, the step operating temperature should be at around 773 K. The reason for this trend is that, with increasing temperature, the Gibbs free energy change of this step increases, suggesting that this step needs to be carried out at a lower temperature, i.e., around 773 K.

Figure 6.16 shows the effects of varying the operating temperature of Step 3 on the energy and exergy efficiencies of the Scheme 2. No significant effect of step temperature is observed on either of the efficiencies of the scheme.

It can be observed from Figure 6.17 that, with increasing step temperature, the exergy efficiency decreases notably, from 99.4% to 94.0%, while the specific exergy destruction rises sharply from 1.18 kJ/mol to 12.2 kJ/mol. Note from this figure that it is not possible to carry out this reaction below 833 K as the specific exergy destruction becomes negative for lower temperature values. This result highlights the importance of applying exergy analysis to chemical reactions as energy analysis does not provide such insights.
Figure 6.16 Effects of operating temperature of Step 3 on the energy and exergy efficiencies of Scheme 2

Figure 6.17 Effects of operating temperature of Step 3 on the specific exergy destruction and exergy efficiency of Scheme 2
The variations of the energy and exergy efficiencies of the overall cycle with the energy efficiency of the power plant is shown in Figure 6.18. As the energy efficiency of the power plant increases, the energy efficiency of the overall cycle increases significantly, suggesting that this type of cycle may be beneficial if coupled to a power plant having high efficiencies, such as High Temperature Nuclear Reactor based power plants.

6.1.3 Results of Scheme 3

The results of the energy and exergy analyses for Scheme 3 are presented in Table 6.3. It can be noted from the table that the energy and exergy efficiencies of the proposed scheme are 38.9% and 88.0%, respectively. Ozbilen et al. (2014) found the energy efficiency of a similar four step Cu-Cl cycle, to be 35.7% for a heat-to-work conversion efficiency (i.e., an energy efficiency of the electrical power plant) of 50%, while in the present case an energy efficiency for Scheme 3 of 46.3% is achieved when a heat-to-work conversion efficiency of 50% is considered. This result suggests that the proposed scheme has a higher energy efficiency, although this observation is limited by the fact the processes have some differences. Similar to Schemes 1 and 2, the proposed scheme (Scheme 3) also have the uncertainty values of ±0.02% and ±0.04% in the energy and exergy efficiencies of the scheme. ±0.03 kJ/kmol of uncertainty is found in the total specific heat.
required by Scheme 3, while ±0.01 kJ/mol of uncertainty is calculated. In the theoretical specific amount of electricity required.

Table 6.3 Values of parameters calculated used in the study for Scheme 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy efficiency of Scheme 3 (%)</td>
<td>38.9</td>
<td>±0.02</td>
</tr>
<tr>
<td>Exergy efficiency of Scheme 3 (%)</td>
<td>88.0</td>
<td>±0.04</td>
</tr>
<tr>
<td>Theoretical specific amount of electricity required (kJ/mol)</td>
<td>198.6</td>
<td>±0.01</td>
</tr>
<tr>
<td>Total specific heat required by Scheme 3 (kJ/mol)</td>
<td>120.4</td>
<td>±0.03</td>
</tr>
<tr>
<td>Maximum temperature in Scheme 3 (K)</td>
<td>733</td>
<td>±1</td>
</tr>
</tbody>
</table>

![Figure 6.19 Variations of the energy and exergy efficiencies of Scheme 1 with the energy efficiency of the power plant](image)

One may also note from the table that the maximum temperature is less for Scheme 3 than Schemes 1 and 2, suggesting that the proposed Scheme 3 can operate at a lower temperature i.e. at 773 K.

From Figure 6.19 it shown that as the energy efficiency of the power plant increases, the energy efficiency of the Scheme 3 increases significantly, suggesting that this type of scheme may be
beneficial if coupled to a power plant having high efficiencies, such as High Temperature Nuclear Reactor based power plants.

![Graph showing the effects of operating temperature of Step 4 on specific exergy destruction and exergy efficiency.](image)

Figure 6.20 Effects of operating temperature of Step 4 (electrolytic step) on the specific exergy destruction and exergy efficiency of Step 4 in Scheme 3

It can be observed from Figure 6.22 that, as the Step 4 temperature increases, the exergy efficiencies decreases while the specific exergy destruction increases. The reason for this trend is that, with increasing temperature, the Gibbs free energy change of this step increases, suggesting that this step needs to be carried out at a lower temperature, i.e., around 773 K.

6.1.4 Results of Scheme 4

The results of the energy and exergy analyses for Scheme 4 are given in Table 6.4. One may note from the table that the energy and exergy efficiencies of the proposed scheme are 41.5% and 93.7%, respectively. Ozbilen et al. (2014) found the energy efficiency of a similar four step Cu-Cl cycle, for hydrogen production only, to be 35.7% for a heat-to-work conversion efficiency (i.e., an energy efficiency of the electrical power plant) of 50%, while in the present case an energy efficiency for Scheme 4 of 50.1% is achieved when a heat-to-work conversion efficiency of 50% is considered. This result suggests that the proposed scheme has a higher energy efficiency,
although this observation is limited by the fact the processes have some differences. For Scheme 4, the uncertainty in the energy and exergy efficiencies values are ±0.006% and ±0.05%, respectively.

Table 6.4 Values of parameters calculated used in the study for Scheme 4

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy efficiency of Scheme 4 (%)</td>
<td>41.5</td>
<td>±0.006</td>
</tr>
<tr>
<td>Exergy efficiency of Scheme 4 (%)</td>
<td>93.7</td>
<td>±0.05</td>
</tr>
<tr>
<td>Theoretical specific amount of electricity required (kJ/mol)</td>
<td>198.5</td>
<td>±0.01</td>
</tr>
<tr>
<td>Exergy efficiency of Step 1 (%)</td>
<td>98.6</td>
<td>±0.03</td>
</tr>
<tr>
<td>Exergy efficiency of Step 2 (%)</td>
<td>99.4</td>
<td>±0.03</td>
</tr>
<tr>
<td>Exergy efficiency of Step 3 (%)</td>
<td>98.1</td>
<td>±0.002</td>
</tr>
<tr>
<td>Total specific heat required by Scheme 4 (kJ/mol)</td>
<td>82.0</td>
<td>±0.07</td>
</tr>
<tr>
<td>Maximum temperature in Scheme 4 (K)</td>
<td>773</td>
<td>±1</td>
</tr>
</tbody>
</table>

Figure 6.21 Specific exergy destructions and exergy efficiencies of the various steps of Scheme 4
Figure 6.21 shows the specific exergy destruction of the various steps of the proposed Scheme 4. The maximum specific exergy destruction occurs in the electrolytic step (Step 3), mainly because electricity (a high quality energy form) is utilised. Note that the specific exergy destruction of this step is less compared to the specific exergy destructions of the other schemes (see Figures 6.1-6.2). A significant amount of specific exergy destruction is observed in Step 1 while the specific exergy destructions in Step 2 is found to be negligible.

![Figure 6.22](image)

Figure 6.22 Effects of operating temperature of Step 1 on the energy and exergy efficiencies of Scheme 4

The effects of the operating temperature of Step 1 on the energy and exergy efficiencies of Scheme 4 are shown in Figure 6.22. As the temperature increases from 903 K to 953 K, there is no effect on the energy efficiency of the scheme while the exergy efficiency decreases from 69.7% to 69.5%. This result suggests that the reaction needs to be carried out at a temperature of around 900 K to achieve a higher exergy efficiency.

Figure 6.23 shows the variations of specific exergy destruction and the exergy efficiency of Step 1 with the temperature of Step 1. It can be seen that, with increasing temperature, the exergy efficiency of the step decreases while the specific exergy destruction increases. To achieve a higher exergy efficiency for this step, the step operating temperature should be at around 773 K.
Figure 6.23 Variations of specific exergy destruction and the exergy efficiency of Step 1 with the temperature of Step 1

Figure 6.24 Effects of operating temperature of Step 2 on the energy and exergy efficiencies of Scheme 4
Figure 6.25 Effects of operating temperature of Step 2 on the specific exergy destruction and exergy efficiency of Step 2 in Scheme 4

Figure 6.26 Effects of operating temperature of Step 3 on the energy and exergy efficiencies of Scheme 4
Figure 6.24 shows the effects of the operating temperature of Step 2 on the energy and exergy efficiencies of Scheme 4. Significant effects are observed on the energy and exergy efficiencies of overall scheme by changing the operating temperature of Step 2.

Figure 6.25 shows the effects of varying the operating temperature of Step 2 on its exergy efficiency and specific exergy destruction. As the temperature rises, the exergy efficiency of the step increases while the specific exergy destruction decreases.

Figure 6.26 shows the effects of varying the operating temperature of Step 3 on the energy and exergy efficiencies of the scheme. No significant effect of step temperature is observed on either of the efficiencies of the scheme.

It can be observed from Figure 6.27 that, with increasing step temperature, no significant changes in the exergy efficiency, and the specific exergy destruction rises are observed.
Figure 6.28 Variations of the energy and exergy efficiencies of Scheme 4 with the energy efficiency of the power plant

The variations of the energy and exergy efficiencies of Scheme 4 with the energy efficiency of the power plant is shown in Figure 6.28. As the energy efficiency of the power plant increases, the energy efficiency of the overall scheme increase significantly, suggesting that this type of cycle may be beneficial if coupled to a power plant having high efficiencies, such as High Temperature Nuclear Reactor based power plants.

The variations of total cost flow rate with the lifetime of the plant are shown in Figure 6.29. With the increase in the lifetime of the plant, the total cost rate decreases while with the increase in interest rate, the total cost rate increases. For the proposed scheme (Scheme 4), the value of the exergoeconomic factor obtained is 0.384 while Ozbilen (2013) reported a value of 0.346 for a four step Cu-Cl cycle, suggesting that the proposed cycle performs better exergoeconomically compared to the other similar cycles.

The cost of exergy destruction rate of major steps of Scheme 4 is shown in Figure 6.30. It can be noted that the maximum cost is associated with Step 3 (electrolysis step). The cost of exergy destruction rate in Step 1 (hydrolysis step) is also significant. The results obtained exhibit the similar trends as observed by Ozbilen (2013), as he also reported that the electrolysis and hydrolysis are the two most significant steps where cost of exergy destruction rates is greatest.
Figure 6.29 The variations of the exergoeconomic factors of Scheme 4 with the lifetime for different interest rates

Figure 6.30 Cost of exergy destruction rates for the major steps of Scheme 4

Exergoeconomic factor evaluates the total cost with respect to the cost of exergy destruction. It can be considered as an optimising tool for the performance of a component suggesting that the cost of exergy destruction is minimised when the value of exergoeconomic factor reaches 1. The value of exergoeconomic factor is zero, when the cost rate of exergy destruction is very high.
compare to the capital cost. The variations of the exergoeconomic factor for the proposed Scheme 4 with lifetime of the scheme for different interest rate is illustrated in Figure 6.31. It is seen from the figure that with the increase in the interest rate the exergoeconomic factor increases while it decreases with the increases in lifetime.

Figure 6.31 Total cost flow rates of Scheme 4 with the lifetime for different interest rate

The effect of electricity price on the exergoeconomic factor and total cost flow rate of Scheme 4 is shown in Figure 6.32. It can be seen that with the increase in electricity price, the total cost flow rate increase while exergoeconomic factor decreases.

A cost comparison of the proposed cycle (Scheme 4) with the other hybrid thermochemical cycles is conducted and the results are shown in Figure 6.33. The Mg-Cl cycle presented in the figure is the four step cycle for hydrogen production proposed by Ozcan (2015). Ozbilen et al. (2014) made a cost assessment of hydrogen production for a modified four-step cycle Cu-Cl with heat exchanger network, and was found to be $3.74/kg H₂. Cost assessment of the Westinghouse HyS cycle has been found to be $4.56/kg H₂ in a study performed by Jeong and Kazimi (2006). These costs belong corresponding years of studies conducted, which are than updated to 2017 values by using US inflation calculator (US, 2017). However, in the present study the cost of hydrogen produced is $4.18/kg H₂ suggesting it to be feasible and may compete with other thermochemical cycles.
Figure 6.32 Variations of exergeconomic factor and cost flow rate of Scheme 4 with electricity price

Figure 6.33 Cost comparisons of the present study with the other hybrid thermochemical cycles

Figure 6.34 shows the variations of cost of hydrogen produced with the daily hydrogen production rate. It can be noted that cost of hydrogen produced can reduced to almost 3$/kg of H₂ for a daily production rate of around 120 tonnes per day.
6.1.5 Comparisons of the Proposed Schemes

Figure 6.35 shows the comparison of the proposed schemes on the basis of energy and exergy efficiencies.

As shown in the figure, Scheme 4 has the highest energy and exergy efficiencies while Scheme 1 has the least, suggesting that Scheme 4 performs better thermodynamically compared to all other
schemes. One may also note from the figure that there is no significant difference in the energy efficiencies of Scheme 1 and Scheme 2. The results of exergy and energy efficiencies of the Scheme 4 show that it performs better than other similar Cu-Cl cycle such as by Ozbilen (2013). Ozbilen et al. (2014) found the energy efficiency of a similar four step Cu-Cl cycle, for hydrogen production only, to be 35.7% for a heat-to-work conversion efficiency (i.e., an energy efficiency of the electrical power plant) of 50%, while in the present case an energy efficiency for Scheme 1 of 38.2% is achieved when a heat-to-work conversion efficiency of 50% is considered. This result suggests that the proposed scheme has a higher energy efficiency, although this observation is limited by the fact the processes have some differences.

6.2 Results of Electrochemical Modeling

Using the equations from the previous section, an electrochemical model is developed for the electrolyser. Table 6.5 provides values of input parameters used in the electrochemical analysis. These parameters are selected based on the study conducted by Ni et al. (2008) for high temperature proton conducting steam electrolysis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average electrode pore radius (μm)</td>
<td>0.5</td>
</tr>
<tr>
<td>Electrode tortuosity</td>
<td>5.0</td>
</tr>
<tr>
<td>Electrolyte resistivity (Ωm)</td>
<td>1.0</td>
</tr>
<tr>
<td>Electrolyte thickness (μm)</td>
<td>50</td>
</tr>
<tr>
<td>Cathode thickness (μm)</td>
<td>50</td>
</tr>
<tr>
<td>Anode thickness (μm)</td>
<td>500</td>
</tr>
<tr>
<td>Exchange current density at cathode (A/m²)</td>
<td>4000</td>
</tr>
<tr>
<td>Exchange current density at anode (A/m²)</td>
<td>1300</td>
</tr>
<tr>
<td>Electrode porosity</td>
<td>0.4</td>
</tr>
<tr>
<td>Operating temperature (K)</td>
<td>1073</td>
</tr>
<tr>
<td>Operating pressure (kPa)</td>
<td>101.325</td>
</tr>
<tr>
<td>Activation energy for ion transport (kJ/mol)</td>
<td>29.5</td>
</tr>
<tr>
<td>Pre-exponential factor (S/m)</td>
<td>339.34×10²</td>
</tr>
<tr>
<td>$\sigma_{\text{HCl}}$ (Å)</td>
<td>3.339</td>
</tr>
<tr>
<td>$\sigma_{\text{Cl}_2}$ (Å)</td>
<td>4.217</td>
</tr>
<tr>
<td>$\varepsilon_{\text{HCl}}/k$ (K)</td>
<td>344.7</td>
</tr>
<tr>
<td>$\varepsilon_{\text{Cl}_2}/k$ (K)</td>
<td>316.0</td>
</tr>
</tbody>
</table>

Source: (Reid et al., 1987; Ni et al., 2008; Menon et al., 2015)
Figure 6.36 shows the variations of electrolyser potential with current density for several operating temperatures. As the current density increases, the electrolyser potential increases drastically. For instance, at T=1073 K, the electrolyser potential changes from 1.5 V to 3.5 V with an increase in current density from 1000 A/m$^2$ to 5000 A/m$^2$. Note also from the figure that the electrolyser potential decreases with increasing operating temperature (in the range 773 K to 1073 K).

Figure 6.37 Effects of current density on activation overpotentials
Figure 6.37 shows the effects of current density on the activation overpotentials for the electrolyser. As the current density increases, both the anodic and cathodic activation overpotentials increase. It can be seen that the activation overpotential at the anode dominates.

Figure 6.38 Effects of current density on concentration overpotentials

Figure 6.39 Variations of ohmic overpotential with operating temperature of electrolyser
The effects of current density on the concentration overpotentials is shown in Figure 6.38. As the current density increases, the anodic and cathodic concentration overpotentials increases. The magnitude of anodic concentration overpotential is negligible compared to the cathodic concentration overpotential. The losses contributed by the concentration overpotentials are much less than the ohmic and activation overpotentials. For example, even at 5000 A/m² the cathodic concentration overpotential is 0.21 V, due to small resistance of porous electrode to the permeation of hydrogen.

The variations of ohmic overpotential with operating temperature is shown in Figure 6.39. As the temperature changes from 773 K to 1173 K for a current density of 1000 A/m², the ohmic overpotential decreases drastically, from 1.1 V to 0.35 V. This trend is due to increase in ionic conductivity of the proton conducting electrolyte with increasing temperature, suggesting that it is better to operate the proposed electrolyser at an elevated temperature.

The effects of current density on the ohmic overpotential is shown in Figure 6.40, where it is seen that the ohmic overpotential exhibits a linear relationship with current density. It should be noted that the ohmic overpotential dominates all other losses (e.g., concentration and activation). For example, at a current density of 5000 A/m², the ohmic overpotential is 2.2 V (see Figure 6.40).

Figure 6.40 Effects of current density on ohmic overpotential
Figure 6.41 Effects of current density on exergy destruction rate and work input rate for the electrolyser

Figure 6.41 shows the effects of current density on the exergy destruction rate and the work input rate of the proposed electrolyser. As the current density increases, both exergy destruction rate of and work input rate to the electrolyser increase. This trend is attributed to the fact that higher current densities lead to more losses, and that an increase in potential of the electrolyser eventually increases the work input rate to the electrolyser.

Figure 6.42 Effects of current density on the energy and exergy efficiencies and hydrogen production rate

It can be seen from the Figure 6.42 that, as the current density increases, the hydrogen production rate increases significantly whereas the energy and exergy efficiencies decrease. At higher current
densities, the energy and exergy efficiencies of the electrolyser both are not very high, suggesting that the proposed electrolyser needs to operate at moderate current densities.

Figure 6.43 Variations of work input rate and exergy destruction rate with hydrogen production rate

Figure 6.43 shows the effects of hydrogen production rate on the work input rate and exergy destruction rate of the electrolyser. It can be seen that, as the hydrogen production rate increases, both work input rate and exergy destruction rate increase.

Figure 6.44 Effects of hydrogen production rate on energy and exergy efficiencies of the electrolyser

From Figure 6.44, it can be seen that, no changes are observed in the electrolyser energy and exergy efficiencies with increasing hydrogen production rate. This is due to the fact that, as the
hydrogen production rate increases, the amount of work required by the electrolyser increases proportionally, leading to no change in energy and exergy efficiencies.

Figure 6.45 Variations of voltage efficiency with current density

The change of electrolyser voltage efficiency with the current density is shown in Figure 6.45. As the current density increases from 1000 A/m$^2$ to 5000 A/m$^2$, the voltage efficiency decreases from 69.4% to 30.4%, mainly due to there being more losses at higher current densities.

Figure 6.46 Variations of ideal voltage of different hydrogen halides with conversion factor
The effects of conversion factor on the ideal voltage requirement for different hydrogen halides is shown in Figure 6.46. It is to be noted from the figure that hydrogen iodide requires the least amount of voltage while the hydrogen chloride requires the most. The figure also emphasises that significant amount of conversion can be achieved with least amount of voltage supplied, suggesting that gas phase electrolysis of hydrogen halides is beneficial and need to be incorporated into the thermochemical or hybrid thermochemical cycle. This results also open a new avenue for the two step hydrogen halide cycles such as HI, HCl and HBr cycle utilising the proton conducting high temperature electrolyser as presented somewhere above. To the authors’ knowledge no study has been carried out for the gas phase electrolysis of hydrogen chloride utilising high temperature proton conducting solid electrolyte. However, Ni et al. (2008) have reported the electrolysis of steam utilising high temperature proton conducting solid electrolyte; the results obtained in this study exhibit similar trends.

6.3 Results of System 1

In performing the energy and exergy analyses of the proposed system, values of mass flow rate, temperature and pressure, are determined for each state of the systems. As noted earlier, thermodynamic values are calculated using EES software and the reference-environment conditions are taken to have a temperature and pressure of 26°C and 100 kPa, respectively.

![Figure 6.47 Exergy destruction rates for the major components of System 1](image)
Figure 6.48 Effects of hydrogen production rate on exergy efficiency and electrolyser power input for System 1

For the SFR-based system i.e. System 1 (Figure 6.47), the largest exergy destruction rate occurs in the primary heat exchanger, followed by the steam generator and the steam turbine. Large heat transfers across large temperature differences, resulting in a large exergy destruction rates. Thus efforts may be worth expending to reduce the exergy destruction rates in the above components, provided they are cost effective or advantageous in other ways.

Figure 6.49 Effects of fresh water production rate on various exergy efficiencies of System 1
Figure 6.48 shows the variations of the exergy efficiency of the overall system with the hydrogen produced. By increasing the amount of hydrogen produced the exergy efficiencies of the overall system decreases. With the increase in the hydrogen production it is seen that the efficiency of the overall system decreases and the power required by the electrolyser increases. However, produced hydrogen is an asset whenever there is an excess electricity generate by the system.

Figure 6.49 shows the behaviour of several exergy efficiencies of System 1 with variations in fresh water production rate. On increasing the fresh water production rate from 4000 kg/s to 8000 kg/s, the exergy efficiency of power generation increases from 36.5% to 37.7% resulting in an increase in the exergy efficiency of overall system from 37.2% to 39.3%, respectively.

![Graph showing the effect of preheating reverse osmosis feed water on various exergy efficiencies of System 1](image)

Figure 6.50 Effects of preheating reverse osmosis feed water on various exergy efficiencies of System 1

Figure 6.50 shows the effects of preheating the feed water of a reverse osmosis plant on the exergy efficiencies of RO, power generation and overall system. The exergy efficiency of RO increases with feed water temperature while the exergy efficiencies of power generation and trigeneration remains fixed. The reason for this behaviour is that, with increasing feed water temperature, the viscosity of the water decreases, allowing the RO membrane to become more permeable and leading to a decrease in the electrical power required for reverse osmosis.
Figure 6.51 shows the effects of the lifetime on the exergoeconomic factor for the major components and overall system. Increasing the lifetime causes a reduction in the exergoeconomic factor of all the devices. It is to be noted that the exergoeconomic factor of the proposed cycle is the highest, suggesting that the proposed cycle has better thermal management. For example, at a value of n=10 year, the value of the exergoeconomic factor is 0.41 while Ozbilen et al. (2016) reported a value of 0.33 (approx.).

Figure 6.51 Variations of the exergoeconomic factors for the major components and the overall system

6.4 Results of System 2

In order to perform the parametric study, values of mass flow rate, temperature and pressure, are determined for each state of the system. As mentioned earlier a program in EES is written for the detailed energy and exergy analyses of each component of the system. The exergy values of the seawater are calculated using EES external library function. The values of certain parameters that are used in the analysis are given in Table 6.6. It is noted from the table that the ambient temperature and pressure for the system are 26°C and 101.3 kPa, respectively. The pressure ratio is set to 2.5, while the generator efficiency is assumed to be 95.0%. The mathematical expressions for the isentropic efficiency of the gas turbine and compressor are also provided in the table.
Isentropic efficiency of 85.0% is assumed for all the pumps, steam turbine and Pelton turbine used in the system (System 2).

Table 6.6 Input data assumed in the analysis for System 2

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$ (°C)</td>
<td>26</td>
</tr>
<tr>
<td>$P_0$ (kPa)</td>
<td>101.3</td>
</tr>
<tr>
<td>$r_p$</td>
<td>2.5</td>
</tr>
<tr>
<td>$\eta_{igt}$</td>
<td>$0.932 - 0.0117 \ln(r_p)$</td>
</tr>
<tr>
<td>$\eta_c$</td>
<td>$0.916 - 0.0175 \ln(r_p)$</td>
</tr>
<tr>
<td>$\eta_{lp}, \eta_{lst}, \eta_{pt}$</td>
<td>0.85</td>
</tr>
<tr>
<td>$P_e$ (MW)</td>
<td>$\left[ (\eta_m \dot{W}<em>{t,net} - \dot{W}</em>{cons,net}) \eta_g \right] (1 - \varepsilon_{ut}) \eta_{switch}$</td>
</tr>
<tr>
<td>$P_{e1}$ (MW)</td>
<td>$\left[ (\eta_m \dot{W}<em>{t,net1} - \dot{W}</em>{cons,net1}) \eta_g \right] (1 - \varepsilon_{ut}) \eta_{switch}$</td>
</tr>
<tr>
<td>$\varepsilon_{ut}$</td>
<td>0.025</td>
</tr>
<tr>
<td>$\eta_{switch}$</td>
<td>0.994</td>
</tr>
<tr>
<td>$\eta_m$</td>
<td>0.99</td>
</tr>
<tr>
<td>$\eta_g$</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Source: El-Genk and Tournier (2008)

For the comparison, the exergy destruction ratios of some major components are determined and plotted in Figure 6.52. It is clearly shown from Figure 6.52 that reactor core has the maximum exergy destruction ratio followed by the recuperator. The next higher exergy destruction is found for heat exchanger 2 and compressor, respectively. So the effort should be made to optimise these exergy destruction in the above components.

Figure 6.53 shows the variations of exergy efficiencies for various cases namely electricity generation, electricity generation without steam turbine work output, reverse osmosis, and overall processes with pressure ratio ($r_p$). It can be observed that with the increase in pressure ratio, the exergy efficiencies of all the processes change except the reverse osmosis process. It is also observed that increase in pressure ratio after certain point results in the decrease of exergy efficiencies of all three processes. Increase in pressure ratio results in the increase compressor work as well as gas turbine but once the certain point is reached the rate at which compressor work increase exceed the rate at which gas turbine works resulting in the decrease of the exergy efficiencies of all the three processes.
Figure 6.52 Exergy destruction ratios for the major components of System 2

Figure 6.53 Variations of the exergy efficiencies for various cases
Figure 6.54 shows the effects of gas turbine inlet temperature \( T_1 \) on the four exergy efficiencies namely electricity generation, electricity generation without steam turbine work output, reverse osmosis, and overall processes. It is clearly seen in the figure that, on increasing the gas turbine inlet temperature, the exergy efficiencies of all the processes increase except the reverse osmosis process as it is not directly related to the gas turbine inlet temperature. For example, on increasing the gas turbine inlet temperature from 700°C to 900°C, the exergy efficiency of the overall process increases from 23.7% to 30.9%.

![Exergy Efficiency vs. T1]  
Figure 6.54 Effects of gas turbine inlet temperature \( T_1 \) on the four exergy efficiencies

Figure 6.55 shows the effects of preheated feed seawater inlet temperature \( T_{20} \) on all exergy efficiencies. It is seen from the figure that on increasing the preheated feed seawater inlet temperature \( T_{20} \) all the four exergy efficiencies increase. It is also noted from figure that exergy efficiencies of electricity generation, electricity generation without steam turbine work output, and overall processes increase slowly while the exergy efficiency of reverse osmosis processes increases drastically suggesting that preheating the feed seawater is a good choice.
Figure 6.55 Effects of preheated feed seawater inlet temperature ($T_{20}$) on all exergy efficiencies

Figure 6.56 Variations of all four exergy efficiencies with the recovery ratio ($r_r$). It is seen from the figure that on increasing the recovery ratio the exergy efficiency of the RO process increases significantly from 86.1% to 92.7%, while it is observed that the exergy efficiencies of the electricity generation, electricity generation without steam turbine work output processes
decreases. The main reason for the increase in the exergy efficiency of the reverse osmosis process is that on increasing the recovery ratio, the work output of the Pelton turbine increases resulting in the exergy efficiency of reverse osmosis process.

Figure 6.57 Variations of the exergy efficiency of the overall system with the hydrogen produced

Figure 6.58 Variations of exergoeconomic factors for various components of System 2
Figure 6.57 shows the variations of the exergy efficiency of the overall system with the hydrogen produced. By increasing the amount of hydrogen produced the exergy efficiencies of the overall system decreases. With the increase in the hydrogen production it is seen that the efficiency of the overall system decreases and the power required by the electrolyser increases. However, produced hydrogen is an asset whenever there is an excess electricity generate by the system.

The exergoeconomic factor of the various components of System 2 is shown in Figure 6.58. It is to be noted that higher plant lifetime, the exergoeconomic factor decreases. This is attributed due to the fact that at higher plant lifetime, the cost of component is lower. It is to be noted from the figure that the compressor has the highest exergoeconomic factor while the recuperator has the least one. The value of exergoeconomic factor of various components such as reactor core, recuperator etc. are in the agreement with those obtained by Mohammadkhani et al. (2014).

As discussed in Section 4.4, the multi-objective optimisation for System 1 is conducted and values of various optimised parameters are provided in Table 6.7. For the optimum performance of System 1, the temperature of Step 2 of the Cu-Cl cycle is found to be 651 K i.e. at this temperature, the proposed system (System 1) will exhibit the maximum exergy efficiency and minimum exergoeconomic factor. Similarly for an interest rate of 2.5% the system is optimised. A lifetime of 59 years will result in the best exergy efficiency and the lowest exergoeconomic factor for the system (System 1).

<table>
<thead>
<tr>
<th>Decision Parameter</th>
<th>Lower Bound</th>
<th>Upper Bound</th>
<th>Optimised Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>η_{en,pp}</td>
<td>0.3</td>
<td>0.5</td>
<td>0.31</td>
</tr>
<tr>
<td>i (%)</td>
<td>2.5</td>
<td>10</td>
<td>2.55</td>
</tr>
<tr>
<td>\dot{m}_{H_2} (kg/s)</td>
<td>0.3</td>
<td>1.5</td>
<td>0.30</td>
</tr>
<tr>
<td>T_{Step1} (K)</td>
<td>773</td>
<td>823</td>
<td>804</td>
</tr>
<tr>
<td>T_{Step2} (K)</td>
<td>623</td>
<td>673</td>
<td>651</td>
</tr>
<tr>
<td>T_{Step3} (K)</td>
<td>773</td>
<td>823</td>
<td>797</td>
</tr>
<tr>
<td>T_2 (K)</td>
<td>813</td>
<td>833</td>
<td>816</td>
</tr>
<tr>
<td>T_5 (K)</td>
<td>798</td>
<td>803</td>
<td>800</td>
</tr>
<tr>
<td>T_6 (K)</td>
<td>623</td>
<td>633</td>
<td>632</td>
</tr>
<tr>
<td>T_8 (K)</td>
<td>778</td>
<td>788</td>
<td>786</td>
</tr>
<tr>
<td>n (year)</td>
<td>10</td>
<td>60</td>
<td>58.8</td>
</tr>
</tbody>
</table>
Table 6.8 Optimised values of the decision parameters for System 2

<table>
<thead>
<tr>
<th>Decision Parameter</th>
<th>Lower Bound</th>
<th>Upper Bound</th>
<th>Optimised Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_{\text{en,pp}}$</td>
<td>0.3</td>
<td>0.5</td>
<td>0.39</td>
</tr>
<tr>
<td>$i$ (%)</td>
<td>2.5</td>
<td>10</td>
<td>2.5</td>
</tr>
<tr>
<td>$m_{\text{H}_2}$(kg/s)</td>
<td>0.3</td>
<td>1.5</td>
<td>0.3</td>
</tr>
<tr>
<td>$T_{\text{Step1}}$ (K)</td>
<td>773</td>
<td>823</td>
<td>778</td>
</tr>
<tr>
<td>$T_{\text{Step2}}$ (K)</td>
<td>623</td>
<td>673</td>
<td>673</td>
</tr>
<tr>
<td>$T_{\text{Step3}}$ (K)</td>
<td>773</td>
<td>823</td>
<td>777</td>
</tr>
<tr>
<td>$T_1$ (K)</td>
<td>1073</td>
<td>1173</td>
<td>1172</td>
</tr>
<tr>
<td>$T_{11}$ (K)</td>
<td>523</td>
<td>553</td>
<td>540</td>
</tr>
<tr>
<td>$r_p$</td>
<td>2</td>
<td>4</td>
<td>2.5</td>
</tr>
<tr>
<td>$n$ (year)</td>
<td>10</td>
<td>60</td>
<td>55.7</td>
</tr>
</tbody>
</table>

Table 6.8 provides the optimised values of different parameters used for the optimisation of the proposed system (System 2). It can be noted from the table that for a lifetime of 56 years, System 2 exhibits its optimum performance. For System 2, the maximum exergy efficiency and minimum exergoeconomic factor is observed for the pressure ratio of 2.5. Similarly for the turbine inlet temperature of 1172 K, the optimum performance of the proposed system (System 2) is found.

6.5 Comparisons of the Proposed Systems

The overall exergy efficiencies for Systems 1 and 2 are found to be 33.4% and 29.3%, respectively. On the basis of overall plant exergy efficiency, the SFR-based system (System 1) is found to be superior compared to GT-MHR based system (System 2). The prime reason being that the SFR-based system has a higher electricity output than that of System 2.

The values of exergy efficiency for the systems closely matches to the value reported by Ozcan (2015). Ozcan considers a Super Critical Water Reactor (SCWR) based system for hydrogen production and reported exergy efficiency of 31.3% while Al-Zareer et al. (2017a) reported an energy efficiency of 25.7% for a lead cooled reactor coupled to Cu-Cl cycle. For a SCWR based system coupled to Cu-Cl cycle for hydrogen production and electricity, Al-Zareer et al. (2017b) found energy efficiency of the overall system as 16.9%. However, in both the studies conducted by Al-Zareer et al. (2017a; b), compressed hydrogen is produced which is ready to be delivered. Khalid et al. (2016) have also reported the exergy value of 36.8% for a SFR based system producing electricity and fresh water. Qureshi and Zubair (2016) found the exergy efficiency of
the RO process with an energy recovery device is 40.2% while in the present study the value of the RO process is 63.3%. The prime reason for the much higher value of the RO process in the present study is due to the effect of preheating of the RO feed water as Qureshi and Zubair (2016) do not consider the effect of preheating.
7.1 Conclusions
A number of thermochemical cycles have been investigated to produce hydrogen from water. However, most of these cycles operate at over 800°C making them extremely high temperature processes. The relatively lower temperature (550°C) requirement and use of inexpensive chemicals make the copper-chlorine (Cu-Cl) thermochemical cycle a promising process for hydrogen production. To build large scale hydrogen production facilities based on this cycle some challenges need to be resolved. This thesis addresses the challenges of the Cu-Cl cycle by incorporating high temperature electrolysis to propose and assess four novel configuration of Cu-Cl cycle. Some of the key findings from the thesis can be summarised as:

- Four novel Cu-Cl cycle with the incorporation of a high temperature electrolytic step for hydrogen production are proposed and thermodynamically assessed. In addition, a novel hybrid Cu-Cl cycle for the co-production of hydrogen and copper using copper waste is proposed and assessed thermodynamically.
- Experimental investigation is made to establish the feasibility of the high temperature electrolytic step, as this step in aqueous state is well studied in literature. However, to the authors’ knowledge in molten state this step is not yet well understood.
- The energy and exergy efficiencies of the proposed scheme (Scheme 4) are 41.5% and 93.7%, respectively. This result suggests that the proposed scheme has a higher energy efficiency relative to similar Cu-Cl cycles.
- The energy and exergy efficiencies of the novel hybrid Cu-Cl cycle for co-production of copper and hydrogen using copper waste are found to be 31.8% and 69.7%, respectively. The results suggest that using high temperature electrolysis in the Cu-Cl cycle may be beneficial as it provides a higher energy efficiency (about 4% increase) than some similar cycles reported in the literature. The other benefit of the proposed cycle is that pure copper can be obtained and copper waste can be more advantageously managed, potentially enhancing the sustainability of the relevant through improved environment protection and resource recovery.
- A novel high temperature electrolyser for gas phase electrolysis of hydrogen chloride with a detailed electrochemical model is presented and assessed. To the authors’ knowledge no
study has been carried out for the gas phase electrolysis of hydrogen chloride utilising high
temperature proton conducting solid electrolyte.

- Simulation results show that the proposed electrolyser can achieve 69.4% of voltage
  efficiency at current density of 1000 A/m$^2$ and operating temperature of 1073 K, showing
  that this type of electrolyser is beneficial if coupled to High Temperature Nuclear Reactor
  based power plants. The present study provides a better understanding of the operation
  mechanism of high temperature electrolyser for gas phase electrolysis of hydrogen
  chloride.
- The proposed electrolyser required 1.6 V to produce 1 mole of hydrogen which is 0.3 V
  (approx.) less than the voltage required by the high temperature steam electrolyser.
- The cost of hydrogen production from the three step Cu-Cl cycle (Scheme 4) is $4.11 per
  kg of hydrogen. This results in a lower cost for hydrogen production than that of hybrid
  sulfur cycle and slightly higher than the four step Cu-Cl cycle. The cost of the proposed
  cycle is within the feasible range and can be competitive among other hybrid cycles.
- The effect of feed water preheating in reverse osmosis is advantageous as it provide higher
  efficiency. This shows that coupling the reverse osmosis process with the condenser of the
  nuclear power plant can be beneficial.
- The overall exergy efficiencies for Systems 1 and 2 are found to be 33.4% and 29.3%,
  respectively. On the basis of overall plant exergy efficiency, the SFR-based system
  (System 1) is found to be superior compared to the GT-MHR based system (System 2).

7.2 Recommendations

Based on the results obtained in this thesis, following recommendations can be made for future
research:

- A study should be conducted to assess the effect of the conversion factor of each reaction
  on the performance of the proposed schemes.
- A study should also be performed to observe the effect of pressure on the various steps of
  the proposed schemes.
- Comprehensive experimental investigations should be carried out to investigate gas phase electrolysis of hydrogen chloride utilising high temperature proton conducting solid electrolyte.

- Further experimental investigations are needed to have a better understanding of the high temperature electrolytic step of Scheme 1.

- A detailed kinetic study should be conducted to further determine the rate of the reaction for the chlorination step (Step 2) of Scheme 4.

- In electrochemical modeling, the effect of permeation phenomena on the concentration overpotential is neglected. Therefore, a study should also be conducted to observe the effect of permeation on the concentration overpotential.

- Gas phase electrolysis of Hydrogen Halide (HX) gases (such as HBr or HI) should also be investigated for their potential use in other thermochemical cycles.

- In order to reduce the temperature of the reaction, the reverse deacon reaction (Hydrolysis Step) of Schemes 1 and 2 should be combined with the other renewable sources such as solar, and biomass.

- Renewable energy sources such as biomass, solar, geothermal, wind etc., should be considered to supply the required heat and electricity for the proposed Cu-Cl cycle and its integrated systems.
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