Mass Transfer and Particle Dissolution in Liquid-Gas and Solid-Liquid Flows: Application to Hydrogen Production Processes

by

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Abstract

Many environmental problems are related to the production, transformation and use of energy. Some of the concerns include, but are not limited to, acid rain, ozone depletion and climate change. Therefore, “greener” alternatives for energy production are sought. The hydrogen economy is one potential avenue to a clean energy system, and a promising option for hydrogen production is the thermochemical Cu-Cl cycle for water decomposition.

When hydrogen or oxygen is produced from water splitting by electrolysis, thermochemical cycles or solar-based photocatalytic methods in water, bubble flow and vapour transfer into the gas phase occur during phase transition. This undesirable vapour transfer requires the use of more energy input to compensate for the evaporation heat requirement as well as for subsequent gas purification in the downstream unit. This work examines the thermodynamics and kinetics of vapour diffusion and entrainment for ascending bubbles in a vertical column through experimental studies for various gas production rates. Vapour entrainment is interpreted in terms of the phase transition rate and its dependence on various operating parameters such as gas bubble size, liquid depth, temperature and concentration is examined analytically and experimentally. A phase transition correlation is obtained to analyze these parameters and predict the amount of water carried to the surface of the liquid. It was determined that mass transfer is a function of Reynolds number (characterizes the flow regime), Eotvos number (characterizes bubbles’ shape) and distance the bubbles travel through liquid.
Additionally, this work presents experimental studies of particle dynamics, dissolution and transport processes for hydrogen production via thermochemical water decomposition. The processes involve multiple steps, some consisting of multiphase reaction systems. It examines the importance of design optimization of liquid-solid phase systems and process integration of a thermochemical copper-chlorine cycle for hydrogen production. The dissolution of cuprous chloride particles in hydrochloric acid is examined in order to provide a predictive modeling method for more complex multiphase reacting systems that determine the thermodynamic equilibrium, which regulates the final state that the transport processes can approach. A ternary system consisting of cuprous chloride (CuCl), hydrochloric acid (HCl) and water exists in different variations of the Cu-Cl cycle, and the modeling of the solubility for the ternary system is essential to providing the mathematical boundary conditions for the transport processes occurring in the system. This work examines the transport processes involving the ternary system and the constituent solubilities. A semi-mechanistic model is obtained that formulates the solubility of the ternary system. It was found that the reaction kinetics is accelerated when the solution is turbulent and when the concentration of HCl is increased, until the thermodynamic limit is achieved. These findings are of importance in the integration of the electrolysis with other reactors of the Cu-Cl cycle.
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Nomenclature

$A_s$ Surface area (m$^2$ or mm$^2$)

$C$ Concentration of CuCl (mol/m$^3$ or mol/l)

$C^*$ Saturation concentration of the dissolved CuCl

$D_{AB}$ Diffusivity of CuCl (m$^2$/s)

$E_0$ Eotvos number

$G$ Gibbs free energy (kJ/mol)

$h_{mass}$ Mass transfer coefficient (m/s)

$H$ Water level (m)

$J_{dis}$ Diffusion flux (mol/m$^2$s)

$K$ Equilibrium constant

$L$ Position of dissolved CuCl in the diffusion path (m)

$L_c$ Characteristic length (mm or m)

$m$ Mass (kg)

$Mo$ Morton number

$n$ Moles of substance

$R$ Universal gas constant (J/mol·K)
<table>
<thead>
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<tr>
<td>Re</td>
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<tr>
<td>S</td>
<td>Molar entropy (J/mol·K)</td>
</tr>
<tr>
<td>Sc</td>
<td>Schmidt number</td>
</tr>
<tr>
<td>Sh</td>
<td>Sherwood number</td>
</tr>
<tr>
<td>t</td>
<td>Time (s)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>V</td>
<td>Velocity (m/s)</td>
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<tr>
<td>w</td>
<td>Mass mole fraction</td>
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**Chemical Compounds**

- CuCl: Cuprous chloride
- CuCl₂: Cupric chloride
- Cu₂OCl₂: Copper oxychloride
- H₂: Hydrogen
- HCl: Hydrogen chloride
- H₂O: Water
- O₂: Oxygen
Greek Symbols

\( \eta \)  
Mean relative error

\( \mu \)  
Dynamic viscosity of a fluid (kg/m)

\( \rho \)  
Density (kg/m\(^3\))

\( \sigma \)  
Surface tension (N/m)

Subscripts

A  
species A

B  
species B

g  
gas

l  
surrounding liquid

i  
interface
Chapter 1

Introduction

"There is a great satisfaction in building
good tools for other people to use."

FREEMAN DYSON

1.1 Background and Rationale

Most human activities and practices are emitting greenhouse gases into the atmosphere, releasing compounds that diminish the Earth’s stratospheric ozone layer and polluting water supplies, to name a few of the environmental concerns. Many unsustainable characteristics are exhibited by energy processes, which are one of the largest contributors to climate change. Therefore, engineers, scientists and others are increasingly pursuing clean energy technologies and one approach is based on a hydrogen economy, in which the two main energy carriers are hydrogen and electricity. Although hydrogen is one of the most abundant elements on earth’s surface, H₂ does not exist in nature and it is therefore necessary to manufacture it from larger molecules such as water where it is predominantly found. The majority of hydrogen is currently used in applications such as oil refineries and fertilizers, which bring the world consumption of hydrogen to over 42 million tons/year [1]. The drawback of producing hydrogen is that the commonly applied methods for production emit vast amounts of CO₂ in the atmosphere and deplete the earth’s finite fossil fuel reserves since the vast majority of H₂ is produced from steam reforming of natural gas. Therefore, hydrogen production is a key
aspect of a hydrogen economy, and one promising renewable option for large-scale hydrogen production is thermochemical water decomposition. The copper-chlorine thermochemical cycle uses mainly thermal energy to split water into hydrogen and oxygen through intermediate copper and chlorine compounds, which are recycled continuously without releasing pollutants into the environment.

A thermochemical hydrogen production cycle usually involves multiple steps, some consisting of multiphase reaction systems. After investigating the performance of 10 different thermochemical cycles, Andress et al. [2] predicted base efficiencies from 35% to 49%. To improve the system efficiency, it is important to optimize the multiphase system design and the process integration.

This thesis presents novel research pertaining to the multiphase system design and process integration of the Cu-Cl. The findings of this research enable the full integration of the Cu-Cl cycle, which is currently undertaken in an advanced research facility for the copper-chlorine thermochemical hydrogen production cycle located at UOIT. Upon successful integration and scale-up of the cycle, it is expected to obtain a production capacity of 3000 kg of H₂ per day, which is double the capacity of current technologies.

1.2 Objectives and Scope

During hydrogen production by electrolysis, thermochemical cycles or solar-based photochemical catalysts submerged/dissolved in water, vapour diffuses into the bubbles of hydrogen and oxygen due to phase transition. Therefore, the quality of hydrogen and oxygen produced is diminished and the use of additional purifying components and
energy input is required. As a result, it is necessary to investigate the factors affecting diffusion across boundaries of bubbles in bubbly flows so that the mass transfer can be minimized and purification systems can be omitted.

Mass transfer is a process occurring in any flow with bubbles due to convection caused by motion and diffusion due to change in concentration. In this thesis, the thermodynamics of vapour entrainment for ascending bubbles in a vertical column was examined experimentally for various gas production rates. The dependence of vapour entrainment on the phase transition rate, which is influenced by gas bubble size, liquid depth, temperature and concentration, was investigated experimentally. The objective of this research is to develop a phase transition correlation to relate mass transfer to the parameters influencing it. Additionally, the amount of liquid carried out of the reactors is determined from the correlation.

Mass transfer also occurs in liquid solid conditions in the form of dissolution. Dissolution rate of a particle is limited by thermodynamics, which relates to the solubility equilibrium of a reaction. The reactant system between the decomposition reactor and electrolysis of the Cu-Cl cycle is a ternary system involving CuCl, HCl and H2O. For integration of the decomposition reactor with the electrolysis it is necessary to determine the solubility equilibrium. Hence, the objective of this investigation is to develop a correlation for the solubility of CuCl in a binary system (i.e. CuCl-H2O) and ternary system (i.e. CuCl-HCl-H2O). Additionally, the dissolution rate of solid CuCl in aqueous HCl solution is determined experimentally through a new technique in terms of change in area of the particle. The findings could be used for integration of the decomposition reactor with the anode of the electrolysis in a thermochemical Cu-Cl cycle for hydrogen production.
Lastly, the objective is to recommend an integration design for optimum dissolution rate of solid cuprous chloride in aqueous hydrochloric acid. In order to attain this objective, a set of studies pertaining to particle dynamics, dissolution and transport processes for hydrogen production via thermochemical water decomposition are performed. This dissolution step is investigated in order to provide a predictive modeling method for more complex multiphase reacting systems.

1.3 Outline of Thesis

This thesis is organized into eight chapters. In Chapter 2, a literature review focusing on bubble dynamics, mass transfer due to bubble dynamics, dissolution processes and applications such as the thermochemical Cu-Cl cycle for hydrogen production is presented. The gas-liquid mass transfer experimental loop used for investigation of bubble dynamics is presented in Chapter 3.

In Chapter 4, gas-liquid physical processes examining heat and mass transfer across bubble interface due to motion of bubbles are discussed. Also, a dimensional analysis is carried out and the correlation relating mass transfer to the parameters influencing it is obtained.

In Chapter 5, the experimental loop built at UOIT in order to study liquid solid interactions is introduced. Two different setups are described in this chapter. The first setup investigates dynamics of falling particles through liquid whereas the second setup focuses on dissolution of solid particles in liquid.
In Chapter 6, liquid-solid physical processes are investigated. Assumptions are being made, a dissolution analysis is presented, a comparison between binary and ternary systems is made, the system’s solubility is modeled and an investigation of particle dynamics for improved dissolution is carried out.

Obtained results are presented and discussed in Chapter 7. System optimizations for mass transfer minimization and design recommendations for gas-liquid processes are presented. Dissolution rate optimization and design recommendations for optimum dissolution rate is also discussed in this chapter.

Lastly, in Chapter 8, the conclusions are drawn and recommendations for improving current work and future work are specified.
Chapter 2

Literature Survey

“We never know the worth of water
till the well is dry.”

Thomas Fuller

2.1 Gas-Liquid Two-phase Flows

Two-phase flows exist in many engineering processes and other applications such as medicine, meteorology to name a few. The four different types are classified into gas-liquid, gas-solid, liquid-liquid and liquid-solid however the first and last types will be investigated in this thesis.

Out of the four types of two-phase flows, gas-liquid flows are among the most important and most complex. Their complexity lies in compressibility of the phases and the deformable interface, which can take many possible forms. These possible interfacial distributions have been classified into four different types of flow regimes in vertical columns, which are discussed in detail in Refs. [3-5]. The four classes of flow regimes are bubble flow, slug flow, churn flow and annular flow as represented in Figure 2.1 [6]. In bubble flow, bubbles are dispersed within a continuous liquid. When the number of bubbles and their size is increased, bubble coalescence is present and the flow becomes slug flow. As the bubbles number and size increases, a churn effect is noticed and the slug flow evolves into a churn flow. Lastly, annular flow is a flow of gas within the tube with
liquid flowing down the walls of the tube.

Figure 2.1 – Different flow regimes in two-phase gas-liquid flows – a) bubble flow, b) slug flow, c) churn flow, d) annular flow

Since researchers reported a laminar flow of the liquid phase and spherical hydrogen and oxygen bubbles rising in water decomposition processes based on experimental observations. A bubble flow is investigated in this thesis. Bubble flow is a two-phase flow in which gas bubbles are distinct and scattered within a liquid continuum. The bubbles in this flow are characterized by complex deformable interfaces caused by interactions between the liquid phase and gas pressure within the bubbles, which changes in time and space. Based on the magnitude of the interactions between the bubbles and fluid continuum, bubble flow is classified into an ideally-separated flow regime, interacting bubble flow regime, churn turbulent bubble flow regime and clustered bubble flow regime. These regimes are shown in Figure 2.2 [6].
In an ideally-separated bubble flow, there is no direct or indirect interaction between bubbles, therefore they are independent and the forces acting on them are represented in Figure 2.3. As the bubble density increases, bubbles start interacting directly as they collide, or indirectly due to wakes caused by adjacent bubbles. This type of flow is called interacting bubble flow. A further increase in bubble density causes bubbles to collide and coalesce which results in a flow of smaller and larger bubbles within a highly agitated bubble flow. This type of flow is called a churn turbulent bubble flow. The last type of bubble flow occurs when larger bubbles form a clustering that behaves as a single gas slug within a churn turbulent bubble flow. This flow is called a clustered bubble flow [7]. Hydrogen and oxygen bubble flows were reported in Refs. [8, 9]. An ideally-separated bubble flow was experimentally and numerically analyzed in this thesis.
In order to model an ideally-separated bubble flow, it is necessary to study the formation of bubbles. This formation can occur through nozzles or orifices submerged in viscous liquids. This represents an important process in gas–liquid flow contacting equipment such as bubble columns, sieve plate columns, and sparged vessels. In general, particulate systems are classified on the basis of the state of the particle present as gas bubbles, liquid drops, or solid particles/agglomerates [10].

Prediction of gas-liquid contact through bubbles is complex. To understand the process of gas bubbling in a liquid pool, it is desirable to understand the process of bubble formation. The process of bubble formation is governed by many operating parameters (i.e., gas flow rate through the orifice, mode of operation, flow/static condition of the liquid), system properties (dependent on orifice dimensions, orifice chamber volume), and also the thermophysical properties, such as liquid viscosity, liquid density, and nature.
of the liquid (i.e., polar or nonpolar), which affects the mode of bubble formation and subsequently reflects on bubble size [10]. The main forces acting on a moving bubble are gravity, buoyancy, drag, viscous forces, and the lift force. In many cases, the gas-liquid properties, orifice dimensions and the type of fluid govern these forces. The flow rate of gas through an orifice and orifice dimensions mainly affect the bubble frequency and thus the detachment time. Similarly, the orifice chamber volume affects the back pressure on the bubble and hence bubble sizes in general [10].

Studies by Clift at al. and Duineveld [11, 12] reported that bubbles with diameters less than 1 mm rise through water and retain their spherical shape due to surface tension. Also, their trajectory follows a straight line. However, this is not the case for larger bubbles. Researchers reported deformations due to the increase in hydrostatic and dynamic pressures over a bubble’s surface [13, 14]. Therefore, large bubbles first deform into oblate spheroids, then become ellipsoidal, and with further increase in size, they switch into a spherical or ellipsoidal cap shape [15]. The gas-phase density can be increased by increasing the pressure or by using a higher molecular weight gas. As a result of an increased gas density, the difference between the densities of two phases decreases, resulting in smaller sized bubbles and also a reduction in the buoyancy force [10]. According to this model, the bubble volume at the end of detachment remains the same for all bubbles generated from all holes on a porous plate [16].

Since the sizes of bubbles after their formation and the wakes affect the rise velocity and also the direction of rise, i.e., trajectory in the liquid, they influence the above-mentioned dynamic processes, overall turbulence in the system and hence the performance of the equipment to some extent [10, 17, 18].
Figure 2.4 – Path of bubbles in an ideally-separated bubble flow; bubbles start a quasi-rectilinear path, continue in zig-zag motion and end in a spiralling motion.

As previously mentioned, the path of a rising bubble is generally not straight. Researchers showed that a rectilinear path becomes a zig-zag or spiral pattern, then quasi-rectilinear as the bubble size increases until it becomes a spherical cap. This has been observed in liquids of small Morton number [15]. The bubble size does not affect the trajectory at large Morton numbers as a rectilinear path is observed regardless of diameter [19]. Researchers also observed rocking motions for different Reynolds numbers [20].
Ohta et al. [17] discussed the trajectory of a larger bubble consisting of primary and secondary structures. The primary structure is defined as the bubble begins to oscillate and rise in a zig-zag motion as soon as the bubble is released until it reaches the terminal velocity. The secondary structure follows soon after when the bubble attains a special shape at terminal velocity.

It has been determined that the trajectories of bubbles are strongly influenced by the bubble deformations and the surrounding liquid flow [13]. However, researchers have shown that the Reynolds (Re), Eotvos (Eo) and Morton (Mo) numbers are essential for describing a rising bubble motion because the shape and terminal velocity of the bubble are determined by these three dimensionless parameters [17].

It is well known that when a droplet deforms, its surface area increases with respect to a spherical droplet of the same volume. Since mass transfer between a droplet and a liquid is proportional to the surface area of the droplet, one can expect the deformed droplets to be more efficient than spherical droplets in mass transfer operations [21].

### 2.2 Mass Transfer in Bubbles

Mass transfer between a droplet and a fluid has been extensively studied in past literature. Theoretical models for mass transfer rate predictions from rising bubbles have been developed. Some of these models are used for non-Newtonian fluids [22-25], whereas others apply to different Reynolds numbers [22, 23, 26-31]. In general, whenever there is an imbalance in the concentration in a medium, diffusive mass transfer tends to redistribute the concentration until a balance is achieved. Similar to the flow of
heat from a hot medium to a cold medium, the flow of species occurs in the direction of decreasing concentration. Mass transfer requires the presence of two different media with different concentrations. It refers to the movement of molecules from the medium with high concentration to the medium of low concentration. This change in concentration occurs as a result of diffusion and convection. The rate of mass diffusion of a chemical species A in a stationary medium in the direction of x is proportional to the concentration gradient \( dC/dx \) in that direction. Different types of diffusion processes were examined in past literature [32]. Diffusion occurs when the primary driving mechanism of mass diffusion is the concentration gradient. Thermal diffusion takes place as a result of temperature gradients. Similarly, pressure diffusion arises when pressure gradients are present. Forced diffusion occurs when an external force field such as electric or magnetic field is applied to the mixture in order to separate molecules from the mixture. Knudsen diffusion refers to diffusion between a porous solid with pores smaller than the mean free path of a gas molecule. Lastly, surface diffusion results when the size of gas molecules is comparable to the pore size and molecules are absorbed along the pore walls. All of these diffusion types occur when the two mediums are stationary.

A different type of mass transfer occurs when the mediums are in motion. Convection mass transfer is the transfer of mass between a surface and a moving medium as a result of both mass diffusion and bulk fluid motion [32]. Similar to heat transfer, mass transfer is influenced by surface geometry, flow velocity, flow regime, fluid properties and composition. Due to the processes that arise as a result of fluid motion and its properties, mass transfer is often determined based on experimental data. Therefore, the relative magnitudes of molecular momentum and mass diffusion in the velocity and
concentration boundary layers are expressed by the dimensionless Schmidt number. In heat transfer analysis, it is convenient to express the heat transfer coefficient in terms of the dimensionless Nusselt number. Likewise, in mass transfer, the mass transfer coefficient is expressed in terms of the dimensionless Sherwood number [32].

Another method to determine the Sherwood number reported in past literature is given in terms of the Reynolds number and Schmidt number [33]. To the author’s knowledge, there are no studies that represent mass transfer in bubbles in terms of bubble shape and diameter to distance traveled ratio, which are important parameters in determining the amount of liquid entrainment. This gap in knowledge is addressed in this research and a correlation to represent Sh in terms of Re, Eo and D/H is presented. This correlation will later be applied to determine the quantity of liquid entrainment in hydrogen and oxygen bubbles in hydrogen production cycles, i.e., thermochemical Cu-Cl cycle, water electrolysis and photoelectrolysis.

2.3 Liquid-Solid Two-Phase Flows

As mentioned previously, the problem of modeling two-phase flows in practical applications is challenging. Aside from the gas-liquid flows presented in the previous section, a two-phase flow can be a gas-solid flow, liquid-liquid flow or a liquid-solid flow. Flows of solids suspended in gases are commonly found in fluidized beds where the solid remains within the fixed container while the gas passes through. Within these systems, both the gas and solids are undergoing complex motions. Liquid-liquid flows are commonly found in pipelines and a common application is an oil-water mixture in the oil
industry. Other applications are found in liquid-liquid solvent extraction mass transfer systems which include packed columns, pulsed columns, stirred contactors and pipeline contactors. The last class of two-phase flows is liquid-solid flow, which is found in hydraulic conveying of solid materials, crystallization systems and dissolution systems with suspended particles [34], as addressed in this thesis.

Similar to gas-liquid flows, in liquid-solid flows, there is a liquid continuum carrying dispersed solids which are suspended due to drag and pressure forces. These types of flows are called slurry flows and they comprise two different flows; one that regards the mixture as a whole and another that is the relative flow between solid particles and the liquid. One key aspect in solid-liquid flows is to understand the particle’s behavior in the mixture; that is, whether they distribute evenly within the mixture and remain suspended or segregate and deposit. Particle behavior within the liquid continuum depends of the grain size, shape and density, properties of the liquid such as viscosity and density of the liquid, on the velocity of the flow, flow direction, pipe diameter and solid concentration. Researchers have found that there is a tendency towards segregation in vertical flows which is due to symmetrical configurations of forces. A uniform solid distribution can be expected as long as the condition for conveyance is satisfied. It was also found that the only particles that can be kept suspended without any turbulence have $Re < 10^{-6}$ and they are conveyed by Brownian molecular movement [35]. Additionally, little turbulence is necessary for particles with $10^6 < Re < 0.1$ to be suspended within the liquid continuum when the solid has low density and irregular shape. As expected, particles with $0.1 < Re < 2$ need a higher turbulence and higher velocity for suspension. To guarantee suspension, the ratio of the settling velocity of the particles and fluid velocity must be kept constant.
In this research, the critical settling velocity of course particles is investigated in order to determine a fluid velocity that would keep the particles suspended. This is a necessary condition to ensure CuCl particles dissolve evenly in liquid HCl and the dissolution rate is accelerated.

In dissolution, a solute dissolves in a solvent to form a solution. In this process, the solute’s structure is disintegrated into separate ions, atoms and molecules. This is governed by thermodynamics and kinetics. The outcome of the process is limited by the heat of solution and entropy of solution (i.e. thermodynamic energies) while the dissolution itself is a kinetic process and not governed by such energies. Solubility is determined by the concentration of solute in a saturated solution, which is determined by the thermodynamic limit. Dissolution is not always an instantaneous process as it depends on the rate of solubilization and the surface area of the material.

Solubilities of solids in liquids are required to determine mass transfer in liquid-solid systems. Studies of solubility of solid cuprous chloride (CuCl) in aqueous hydrochloric acid (HCl) and water (H₂O) have been reported in past literature [36-38]. Shashikant et. al. [36] investigated the solubility in an oxygen free environment since the presence of oxygen forms soluble cupric salts. O’Conor et al. performed solubility experiments in order to determine a solubility curve. Their study investigated the conversion rate from CuCl to CuCl₂ ions in order to determine the crystal size of chloro complexes [37]. Frits investigated the solubility in order to determine the equilibrium constants for formation and a set of viral parameters representing the activity coefficients of the ions formed in dissolution [38]. Hikita et al. investigated the oxidation of CuCl by O₂ in aqueous HCl in order to clarify the kinetics of chemical absorption of O₂ in the aqueous ternary system.
Gavrish and Galinker [39] investigated the dissolution of CuCl in water and determined that even a relatively low concentration of HCl (0.6M) can significantly increase the solubility of CuCl.

Researchers have been developing techniques to monitor reactions over small timescales in the range of femtoseconds to large timescales over hours or days. As expected, it is relatively straightforward to monitor the kinetics of a slow reaction and challenging to monitor fast reactions, which in general require highly specialized techniques for accurate monitoring. In general, kinetics experiments consist of initiating a reaction by mixing the reactants, however, the timescale of the initiation is negligible relative to that of the reaction. Once the reaction is initiated, the concentrations of the reactants and products are monitored. Most of the techniques studied by researchers are batch or continuous. In batch techniques, concentrations are monitored as a function of time after the reaction is initiated. In a continuous technique, the reaction initiation occurs on a continuous basis and the different concentration regions in the reaction vessel infer to the reaction mixture composition and time [40-42].

Since the dissolution of solid CuCl in aqueous HCl is not spontaneous, a different method of monitoring the reaction rate was utilized in this work. In this research, the reaction was initiated and the size of particles was monitored via a camera system. The dissolution of CuCl in HCl is an important aspect of the thermochemical Cu-Cl cycle for hydrogen production as the reactor integration design depends on determining the reaction kinetics.
2.4 Hydrogen Production

It is becoming increasingly important to reduce the greenhouse gas (GHG) emissions and at the same time meet the growing demand for a sustainable future of energy supply. Engineers and scientists have developed sustainable energy solutions, such as solar, nuclear, hydroelectric, wind, and geothermal energy, to meet the targets. However, some clean energy forms such as solar and wind are either intermittent or hindered by the necessity of power load fluctuations. Hydrogen production from intermittent and off-peak nuclear energy is a promising option for the storage and fluctuation buffering of nuclear energy [43].

2.4.1 Thermochemical Cu-Cl Cycle

Thermochemical cycles are promising alternatives for large-scale hydrogen production. In recent years, the copper-chlorine (Cu-Cl) cycle has increasingly attracted the interest of engineers and scientists due to its lower temperature requirement than most other thermochemical cycles. These cycles for hydrogen production use a series of reactions to achieve the overall splitting of water into hydrogen and oxygen:

\[ H_2O \rightarrow H_2 + \frac{1}{2}O_2 \] (2-10)

Thermochemical water decomposition generally involves at least three distinct steps: hydrogen production, oxygen production and re-cycling. The advantage of this cycle is that chemical reactions form a closed internal loop and re-cycle all chemicals on a continuous basis, without emitting any greenhouse gases externally to the atmosphere. This process is shown in Figure 2.5 [44].
One of the advantages of thermochemical cycles over direct one-step thermal water decomposition is their ability to achieve water splitting into hydrogen and oxygen at much lower temperatures (usually below 1,000˚C) [45]. One of the promising thermochemical cycles that operates at even lower temperatures is the thermochemical Cu-Cl cycle. The Cu-Cl cycle splits water into hydrogen and oxygen through intermediate copper and chlorine compounds. There are several variations of the Cu-Cl cycle reported in past literature. Such variations include 5-step, 4-step and 3-step cycles [46]. A 5-step cycle with its chemical reactions is summarized in Table 2.1 [47].

![Diagram of the Cu-Cl cycle]

Figure 2.5 – Schematic of the Cu-Cl cycle
Table 2.1 – Process flow and reactions of the thermochemical Cu-Cl cycle for hydrogen production

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Process and heat flow</th>
<th>Major reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Electrolysis for hydrogen production</td>
<td>2CuCl(aq) + 2HCl(aq) + $V_E = H_2(g) + 2CuCl_2(aq)$ in aqueous solution, at 30-90°C</td>
</tr>
<tr>
<td>B</td>
<td>Hydrolysis of cupric chloride, endothermic</td>
<td>2CuCl_2(s) + H_2O(g) + $Q = Cu_2OCl_2(s) + 2HCl(g)$, 400°C</td>
</tr>
<tr>
<td>C</td>
<td>Oxygen production, endothermic</td>
<td>Cu_2OCl_2(s) + $Q = 2CuCl$(molten) + 0.5O_2(g), at 500-530°C</td>
</tr>
<tr>
<td></td>
<td>Summation of all reactions</td>
<td>H_2O(l) = H_2(g) + $\frac{1}{2}$O_2(g) (net reaction)</td>
</tr>
</tbody>
</table>


As mentioned previously, hydrogen generation involves several steps. The first step of the cycle is electrolysis. In this step, hydrogen is generated as a result of Cu(I) chloride (CuCl) oxidation in the presence of hydrochloric acid (HCl) during an electrochemical reaction. The overall cell reaction is given by [46]:

$$2CuCl(aq) + 2HCl(aq) \rightarrow 2CuCl_2(aq) + H_2(g) \quad (2-11)$$

As indicated in Ref. [47], different relatively inexpensive electrode materials have been tested and hydrogen production has been achieved at potentials as low as 0.5V. Also, three different membranes were investigated in Ref. [46] so that membranes with lower copper diffusion rates but similar proton conductivity can be identified.
The reactant system in electrolysis (reaction A) is a ternary system involving CuCl, HCl and H₂O. Improving the electrolytic reaction kinetics of this hydrogen production process may lead to a smaller reactor for the same hydrogen production rate [45]. The general form of the reaction kinetics can be written as:

\[ k_{\text{electrolysis}} = k(C_{\text{CuCl}}, C_{\text{HCl}}, T) \]  \hspace{1cm} (2-12)

where \( C_{\text{CuCl}} \) and \( C_{\text{HCl}} \) are the concentrations of CuCl and HCl, respectively, in units of mol/l or kg/l, depending on the usage of convenience. Also, \( T \) is temperature and \( k_{\text{electrolysis}} \) is the electrolysis kinetics whose units depend on the form of the equation. Currently, the kinetics are being studied by researchers at the University of Ontario Institute of Technology (UOIT), Canada. It is observed that an option for improving the kinetics is to increase the concentrations of both CuCl and HCl. However, the increase of the electrolysis kinetics is limited by the thermodynamic solubility equilibrium of CuCl and HCl in water. In other words, the solubility equilibrium is a boundary or constraint condition of the model of the electrolysis kinetics. Therefore, the solubility equilibrium should be examined in detail.

Currently, proof-of-principle experiments for each reaction of Table 2.1 have been performed [47-50]. The experimental results have been reported for most of the processes of the Cu-Cl cycle, and large laboratory scale reactors for the processes have been tested successfully at UOIT [51]. Although the summation of the reactions shown in Table 2.1 can form a closed cycle, most previous studies focused on individual reactors rather than an integrated Cu-Cl cycle with a holistic approach. Only a limited number of past studies have examined the auxiliary processes and mutual impacts between upstream and
downstream reactions. For example, in the last step of the cycle, (i.e. reaction C in Table 2.1), molten CuCl salt is produced. By comparison, the aqueous state of the CuCl is used in the first step (reaction A) with the coexistence of HCl in the aqueous solution. This clearly indicates the necessity of the following auxiliary processes for the material flow linkage of reactions A and C:

\[ 2\text{CuCl (molten)} = 2\text{CuCl (solid)} \]  \hspace{2cm} (2-13)

\[ 2\text{CuCl (solid)} + \text{water} = 2\text{CuCl (aqueous)} + \text{water}, \text{binary system} \]  \hspace{2cm} (2-14)

The operation indicated by equation (2-13) is a solidification process, which has been examined by researchers at UOIT [52, 53]. It is not the focus of this thesis. As for the process of equation (2-14), it is not feasible from an engineering perspective due to the poor solubility of solid CuCl in water, although in theory the aqueous CuCl can be prepared with equation (4). This will be discussed in later sections of this thesis.

The second step of the cycle consists of removing the water from aqueous Cu(II) chloride [34]. Once the water is removed, the solid CuCl\(_2\) is supplied to the hydrolysis reactor to produce copper oxychloride (Cu\(_2\)OCl\(_2\)) and HCl gas [46]. This is achieved in an endothermic non-catalytic gas-liquid or gas-solid reaction.

The last step in the cycle is the decomposition reaction. This reaction is expressed by:

\[ \text{Cu}_2\text{OCl}_2(s) = 2\text{CuCl(molten)} + 0.5\text{O}_2(g) \]  \hspace{2cm} (2-15)

This is a decomposition reaction in which oxygen gas and molten CuCl are obtained from copper oxychloride. Several gaseous products are leaving the reactor such as oxygen gas, CuCl vapour and some products from side reactions such as HCl gas, Cl\(_2\) gas and water.
vapour [34, 35]. When particles enter the reactor at a temperature below 430˚C, bubbles may develop in the molten salt. These bubbles and their aggregate formation will decrease the contact area between the reactant particle and heating medium, therefore, aggregations may float to the surface. This is a major safety concern reported in Ref. [47].

Another promising solution to hydrogen production is water splitting using solar energy. Numerous methods have been developed such as thermolysis, thermochemical, water electrolysis, photoelectrolysis, photoelectrochemical, photochemical, photodissociation, photodecomposition, photolysis photodegradation, photocatalytic, photobiological and hybrid methods [51]. In some of the methods, mass transfer occurs due to the rising hydrogen and oxygen gas bubbles.

### 2.4.2 Hydrogen Production by Water Electrolysis

Combined with solar cell systems or wind power systems, hydrogen produced with water electrolysis will have an important role as an energy carrier for sustainable development in the future. Electrolysis has been used for the production of hydrogen since the early nineteenth century. It gives hydrogen at about 99.99% purity compared with 98% purity obtained from fossil fuel based methods [54]. On the one hand, electrolysis is convenient, as hydrogen is already separated from oxygen. Also, the gas is produced with high purity. On the other hand, electrolysis is relatively costly compared to other methods such as steam methane reforming (SMR). In water electrolysis, the water is split into hydrogen and oxygen using an electric current. Direct current passes through two electrodes immersed in water as depicted in Figure 2.6 [51].
The reactions taking place on the surface of the electrodes are given as follows [51]:

$$2\text{H}_2\text{O}(l) = \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \quad (2-16)$$

$$2\text{H}^+(aq) + 2e^- = \text{H}_2(g) \quad (2-17)$$

The overall efficiency of hydrogen production through water electrolysis depends on two factors: electricity-to-hydrogen efficiency and solar-to-electricity conversion efficiency [51]. Therefore, the electricity-to-hydrogen performance of such electrolytic processes is intrinsically related to mass transfer effects, which are influenced by hydrodynamics. Past research showed that the electrical and thermal properties of the electrolyte, diffusive transport of electroactive species and current density are modified by the dispersed phase (i.e. gas bubbles) and therefore this affects the macroscopic cell
performance [55]. Fluid flow in the cell depends on the release of gas bubbles, which in turn depends on the cell design. Thus, the understanding of gas–liquid flows in electrolytic systems is very important from the view-point of understanding mass transport, system optimization and improving efficiency.

The gases released at the electrode surface rise upward due to buoyancy. The presence of the gas phase at the electrodes can be detrimental to the overall performance of the process as it blocks the active surface area of the electrodes and increases the resistance of the electrolyte [56]. The presence of gas bubbles and their motion has a significant impact on the performance of the electrolytic cell [57]. Boissonneau and Byrne [56] investigated the velocity field in an electrolytic cell with vertical electrodes through Laser Doppler Anemometry and Particle Image Velocimetry. Their experiment relates gas evolution to the hydrodynamics of electrolyte flow through a narrow vertical channel. Although the flow was laminar in terms of the Reynolds number, the bubbles induce local turbulence which causes velocity fluctuations due to the interactions with the continuous phase.

Ali and Pushpavanam [58] studied the effects of gas evolution on hydrodynamics of water electrolysis in a partitioned electrolytic system using PIV. Their research was carried out for various electrode designs and different operating conditions such as voltage and concentration. As a result, they determined that the optimum condition for mixing was based on liquid circulation through circulation. Circulation was computed as a measure of irrotationality or irreversibility in the system. Such results were verified further quantitatively by analyzing time averaged velocity profiles along a line. The
temporal variation of liquid velocity at a point was also analyzed. It was found that velocity components exhibit turbulent fluctuations about a mean value [58].

### 2.4.3 Hydrogen Production by Photoelectrolysis

Photoelectrolysis uses sunlight to directly decompose water into hydrogen and oxygen. This process is shown in Figure 2.7.

![Figure 2.7 – Components of a photoelectrolysis system for hydrogen production](image)

The process uses two doped semiconductor materials. A p-type and n-type are brought together forming a p–n junction [51, 59]. A permanent electric field is formed at the junction when the charges in the n-type material rearrange. When a photon with energy greater than the semiconductor material’s bandgap is absorbed at the junction, an electron is released and a hole is formed [60]. The hole and electron are forced to move in opposite directions due to the electric field. As a result, an electric current is created when an external load is connected [49].
In photoelectrolysis, water is split into hydrogen and oxygen when a photocathode, p-type material with excess holes, or a photoanode, n-type material with excess electrons, is immersed in an aqueous electrolyte [51, 61, 62]. This process is shown in Figure 2.8. Holladay et al. [60] summarized the process into four steps. First, a photon with greater energy than the bandgap strikes the anode creating an electron–hole pair. Second, the holes decompose water at the anode’s front surface to form hydrogen ions and gaseous oxygen, while the electrons flow through the back of the anode, which is electrically connected to the cathode. Third, the hydrogen ions pass through the electrolyte and react with the electrons at the cathode to form hydrogen gas. In the last step, the oxygen and hydrogen gases are separated by the use of a semi-permeable membrane. The separated gases are then processed and stored [60].

The efficiency is directly related to the semiconductor band gap. This is the energy difference between the bottom of the conduction band and the top of the valence band.
Efficiency is also related to the band edge alignments, since the material or device must have the correct energy to split water [60]. In order to increase the efficiency of the system, electron transfer catalysts may be used; however these can minimize the surface over-potentials in relationship to the water and facilitate the reaction kinetics, decreasing the electricity losses in the system [60]. As a result, appropriate surface catalysts for the systems are being sought. Such catalysts must remain active for as many as $10^8$ redox reaction cycles, which is the equivalent of 20 years of operation [51]. Researchers also suggested the use of suspended metal complexes in solution as the photochemical catalysts [63]. Typically, nano-particles of ZnO, Nb$_2$O$_5$ and TiO$_2$ have been used [59, 60].
Chapter 3

Gas-Liquid Experimental System

“It is the weight, not numbers of experiments that is to be regarded.”

ISAAC NEWTON

In the electrolysis step of the thermochemical Cu-Cl cycle for hydrogen production, a ternary solution consisting of H₂O-HCl-CuCl is supplied to produce H₂ and CuCl₂. In the process of producing H₂ some of the aqueous HCl is evaporated due to mass transfer between liquid (HCl) and gas (H₂) phases of the system. Since the HCl is evaporated, the concentration of the solution decreases affecting the performance of the electrolyzer. Therefore, it is important to determine the amount of HCl loss due to mass transfer in this gas-liquid flow. This step is similar to conventional water electrolysis where water is split into hydrogen and oxygen. Hydrogen gas is produced on the cathode of the electrolyzer, whereas oxygen gas is produced on the anode. In this process gas bubbles rise to the surface carrying a certain amount of moisture from the water which affects the purity of the gasses. Additionally, a similar multiphase interaction is observed in the oxygen reactor where solid copperoxychloride (CuOCuCl₂) is fed to the reactor to produce liquid CuCl and O₂ gas. As CuOCuCl₂ decomposes, O₂ rises through the liquid CuCl and some of the liquid enters the gas due to mass transfer across the boundary of the bubble. For a better understanding of the multiphase flow in the electrolysis and oxygen reactor of the
thermochemical Cu-Cl cycle for hydrogen production, a cold modeling experiment has been designed and built at the University of Ontario Institute of Technology (UOIT) in the Clean Energy Research Laboratory (CERL). Although mass transfer in gas-liquid flows is enhanced with increasing temperature due to a higher diffusion coefficient, in this study the experimental loop was designed to examine bubble dynamics through fluids and determine the amount of mass transferred from the liquid to the gas that is carried out to the surface of the liquid due to bubble motion. Therefore, this research focuses on mass transfer due to motion of the bubbles, shape of the bubbles and distance traveled. Also, the experimental loop was designed in order to quantify the amount of moisture entering the gas bubbles due to diffusion as they travel through the liquid so that the purity of the hydrogen gas can be determined. Furthermore, by quantifying the amount of unwanted moisture that is carried out to the surface of the liquid, a proper condenser can be designed in conventional electrolysis, the concentration of HCl can be monitored in the electrolysis step of the thermochemical Cu-Cl cycle for hydrogen production and design considerations for the oxygen reactor can be implemented.

3.1 Description of the Experimental Apparatus

A schematic of the cold modeling apparatus is illustrated in Figure 3.1. The experimental apparatus consists of a 2708 mm high, 203 mm diameter, clear PVC vertical column and a camera system described in the following section.
Figure 3.1 – Schematic of apparatus

The flow rate of nitrogen was set manually using rotameters as shown in Figure 3.2. Due to availability and density similarity between nitrogen and oxygen (i.e.
\[ \rho_{N_2} = 1.251 \text{ g/L and } \rho_{O_2} = 1.429 \text{ g/L at STP}, \]

nitrogen gas was used to simulate hydrogen and oxygen gas bubbles rising through liquid. The nitrogen was injected from the bottom of the vertical column by means of a porous surface.

![Figure 3.2 – Experimental system](image)

It was observed that the bubbles generated are different in size and shape, which enables the study of a wider range of real life gas-liquid scenarios. The flow rate of gas was regulated by means of a control panel consisting of rotameters arranged in series. The
control panel designed and built in CERL regulates the flow such that a better accuracy is obtained. The experiments were performed for different scenarios of flow rates ranging from 0.5 L/min to 2 L/min. These flow rates were investigated due to inability to process images for higher flow rates because of bubble coalescence. The size and number of bubbles varies with the nitrogen flow rate such that less bubbles with bigger diameters are formed for lower flow rates, while more bubbles with smaller diameters are formed for higher flow rates. Bubbles flowing through the porous surface rise up through the water. Due to the motion of a bubble through water, some of the water molecules from the liquid diffuse across the boundary of the bubble and they are carried out of the water column. In order to examine whether or not there is water carried to the surface, a humidity analyzer was installed at gas exit as shown in Figure 3.2.

Type K thermocouples have also been installed at five different locations to record the temperature of the water as well as the temperature of gas exiting the experimental apparatus. LabVIEW software is used to view and record the data captured by the humidity sensor and thermocouples. Figures 3.3 and 3.4 show schematics of the programs written in order to collect data from the humidity sensor and thermocouples, respectively.

Figure 3.3 – LabVIEW diagram for humidity sensor
Although the temperature of the liquid is not varied in this research, the thermocouples were installed to determine the heat transfer due to liquid motion. A heat transfer analysis to determine the temperature change is performed in Chapter 4.

### 3.2 Shadow Imaging System

For a better understanding of flows with bubble generation and dynamics, it is important to map the size and velocity of bubbles as they rise through the liquid. Mass transfer across the boundary of bubbles is a function of Re, Eo and distance bubbles travel through liquid. Since Re is a function of velocity of bubbles and Eo is a function of the size of the bubbles, DynamicStudio Shadow Sizer is employed to measure these parameters so an analysis to determine mass transfer can be performed. The method presented in this section is widely used in literature [3-8] since it has the ability to freeze the bubbles in motion so accurate measurements can be attained.

Particles rising through the medium are backlit with an LED light source with a trigger frequency of 400 Hz, pulse of 100 µs and delay of 10 µs. The bubbles are...
therefore ‘frozen’ in place so that there is no distortion when acquiring the image due to
the motion. A glass diffuser is used in order to obtain an even light sheet so that the
camera can acquire the shadow image of the moving particles. A high speed FlowSense
2ME camera with an effective sensor size of 1600 by 300 pixels is used to capture images.
The shadow imaging system consisting of the three above-mentioned components is
shown in Figure 3.5.

![Figure 3.5 – Shadow imaging system consisting of LED light, camera, diffuser and timer box](image)

Images are captured in single frame mode with a trigger frequency of 91 Hz (i.e. 91
captured images per second), delay to open of 3.5 µs, delay to close of 10920 µs and
exposure time of 40.950 µs. The high trigger frequency is needed to ensure that the
bubbles are still within the camera’s reference frame in subsequent images therefore the
velocity may be determined. The delay to open and close was chosen so that the
uncertainty associated with experimental results is minimized. The exposure time has a 
dramatic impact on the appearance of moving bubbles and the smaller the value the less 
the distortion in the appearance of the bubbles therefore the smallest value the camera can 
sustain was chosen.

In order to ‘freeze’ the bubble in motion, the camera and LED light source are 
synchronized using a timer box. The timer box for imaging applications starts 
automatically so that the camera and LED light array are synchronized at the start of the 
acquisition process. The camera and light system are set up as shown in Figure 3.2. The 
stands were custom built so that images can be taken at precise specified heights from gas 
exit.

3.3 Shadow Imaging Results

DynamicStudio software [64], an advanced edge detection algorithm to extract the 
bubble shape information, was used to acquire and process captured images of rising 
bubbles. The “shadow sizer processing” method was applied so that information such as 
size, position, shape and velocity of bubbles could be extracted. In this method, the 
outline of the bubbles is obtained based on the grey level profile; that is, a value 
corresponding to the outline is assigned when the pixels intensity changes from high 
intensity to low intensity. Once determined, the outline is plotted and the size, position 
and shape are given in terms of pixels. For accurate processing, a set of calibration 
images was acquired prior to image processing. For the calibration images an electronic 
digital display caliper with an accuracy of 0.02 mm was set to 1 cm. Images of the caliper 
were acquired and then “Measure Scale Factor” function was employed in
DynamicStudio. This step is necessary as it enables the measurement of the scale factor used to determine the conversion of pixel units into metric units. The distance between the tips of the caliper in the acquired image was measured and the scale factor was obtained. To ensure that the scale factor is consistent across the diameter of the column, multiple images were acquired and the scale factors were determined. Also, images of the caliper were acquired outside and inside the water column to determine the distortion introduced by imperfections in the wall of the column as well as the circular shape of the column. Figure 3.6 depicts the acquired image at a flow rate of 0.5 L/min.

![Acquired image of gas bubbles rising through water for a gas flow rate of 0.5 L/min](image)

**Figure 3.6 – Acquired image of gas bubbles rising through water for a gas flow rate of 0.5 L/min**

The black shapes in Figure 3.6 are the gas bubbles rising through clear water that are backlit with the aid of the LED light source in order to freeze their motion for an accurate, nondistorted image. Therefore, the bright background is due to the high intensity light shining in front of the camera lense. Some of the light is reflected by the camera lense onto the surface of the bubble thus creating the white slits on the surface of the bubble. It can be seen that the gas bubbles are irregular in shape and their diameters are different. It is important to note that the irregular shape is due to bubble dynamics and fluid flow...
rather than distortion due to calibration. Also, the different diameters are a result of the porous surface used to inject nitrogen gas rather than the depth of field of the camera. Careful attention was given to the calibration of the camera and determining the depth of field as the shape and size of the bubble determines the amount of mass transfer across the boundary.

It is important to note that bubbles rise up in a spiral swarming motion which enhances the mass transfer across the boundary. It is suspected that the shape of the bubble is also determined by this swarming motion since bubbles generated from a higher flow rate are more spherical in shape than those generated at lower flow rates not exhibiting swarming behaviour.

Once the camera was calibrated, images of rising bubbles were acquired for different flow rates. Since mass transfer depends on velocity of the bubbles it was necessary to create double frame images so that the software can measure the distance each bubble traveled in subsequent images and in a given time thus determine the velocity. For this step to be effective one must ensure that the bubbles are detected and analyzed in subsequent images a grey level profile of the bubbles must be determined. A grey level profile is a histogram that gives the intensity value of each pixel in an image varying from black at the weakest intensity to white at the strongest. In determining the grey level profile, an area enclosing the bubble is selected and the threshold is determined. The threshold is the point at which the pixels go from high intensity to low intensity so that all pixels with a value higher than the threshold is considered background whereas the pixels with lower intensity than the threshold are considered to be objects in the captured image.
Figure 3.7 shows the grey level profile chosen when analyzing the image depicted in Figure 3.6.

![Grey level profile for bubbles at 0.5 L/min](image)

Figure 3.7 – Grey level profile for bubbles at 0.5 L/min

After the grey level profiles were determined, the images were analyzed using the Shadow Image module order to obtain useful information such as diameter, area, shape, position and velocity of the bubbles. The velocity information is extracted through combining a correlation algorithm and measuring displacement between two successive images via a dedicated particle-tracking algorithm. Figure 3.8 is the analyzed image of Figure 3.6 with velocity vectors pointing upwards depicting the direction of motion. The actual values for velocity as well as other data obtained after analysis is tabulated in Table 3.1.

It can be noted that in this instance all bubbles from the acquired image (i.e. Figure 3.8) were analyzed due to an adequate choice of the grey level profile. The choice of the
grey level profile is highly dependent on the amount of light such that a higher value (i.e. approximately 50%) is assigned for images captured using a stronger and more even light beam than those acquired using a weak light (i.e. ranging from approximately 15%).

![Figure 3.8 – Outline of gas bubbles rising through water for a flow rate of 0.5 L/min with velocity vectors](image)

Results obtained after analysis are tabulated in Table 3.1. The centroid gives information about the position of the bubbles with respect to the edges of the 2D image. This value does not reflect the distance traveled however it aids in obtaining the position relative to the wall of the column so the assumption that the bubbles are far from the wall is validated. The centroid in y-direction gives the position from the edge of the picture to the center of the bubble in the vertical direction. This helps determine the distance from the porous gas injection device to the center of the bubble so the exact distance traveled by bubbles can be determined. This distance is used in determining the mass transfer across the boundary due to bubble motion.

The parameters in Table 3.1 are tabulated in terms of the x-centroid with the smallest value being measured from the left edge of the picture across towards the right edge. The
tabulated area is the projected area of the bubble on the vertical axis. Equivalent diameter denotes the diameter of the sphere enclosing the bubble whereas the major axis and minor axis are the length (i.e. distance along horizontal axis) and height (i.e. distance along vertical axis) of the rectangle enclosing the bubble as indicated in Figure 3.8.

Table 3.1 – Results extracted using DynamicStudio for 0.5 L/min

<table>
<thead>
<tr>
<th>Centroid X* (mm)</th>
<th>Centroid Y* (mm)</th>
<th>Area (mm²)</th>
<th>Perimeter (mm)</th>
<th>Equivalent Diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.18</td>
<td>19.87</td>
<td>166.70</td>
<td>18.30</td>
<td>5.69</td>
</tr>
<tr>
<td>38.49</td>
<td>18.68</td>
<td>38.59</td>
<td>9.30</td>
<td>2.74</td>
</tr>
<tr>
<td>40.19</td>
<td>35.89</td>
<td>110.11</td>
<td>15.10</td>
<td>4.62</td>
</tr>
<tr>
<td>53.20</td>
<td>15.62</td>
<td>40.87</td>
<td>8.69</td>
<td>2.82</td>
</tr>
<tr>
<td>57.60</td>
<td>31.77</td>
<td>31.26</td>
<td>7.63</td>
<td>2.46</td>
</tr>
<tr>
<td>63.25</td>
<td>27.98</td>
<td>50.33</td>
<td>9.76</td>
<td>3.13</td>
</tr>
<tr>
<td>67.83</td>
<td>8.42</td>
<td>46.21</td>
<td>9.61</td>
<td>3.00</td>
</tr>
<tr>
<td>68.77</td>
<td>27.81</td>
<td>36.76</td>
<td>8.24</td>
<td>2.67</td>
</tr>
<tr>
<td>80.72</td>
<td>15.78</td>
<td>53.23</td>
<td>9.15</td>
<td>3.21</td>
</tr>
</tbody>
</table>

* measured with reference to the frame of the image

Table 3.1 – Results extracted using DynamicStudio for 0.5 L/min (continued)

<table>
<thead>
<tr>
<th>Major Axis** (mm)</th>
<th>Minor Axis*** (mm)</th>
<th>X-direction velocity (m/s)</th>
<th>Y-direction velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.28</td>
<td>1.90</td>
<td>0.00</td>
<td>0.30</td>
</tr>
<tr>
<td>2.30</td>
<td>0.82</td>
<td>-0.03</td>
<td>0.31</td>
</tr>
<tr>
<td>3.66</td>
<td>1.49</td>
<td>0.12</td>
<td>0.32</td>
</tr>
<tr>
<td>2.10</td>
<td>0.96</td>
<td>0.16</td>
<td>0.37</td>
</tr>
<tr>
<td>1.80</td>
<td>0.86</td>
<td>0.16</td>
<td>0.36</td>
</tr>
<tr>
<td>2.22</td>
<td>1.11</td>
<td>-0.06</td>
<td>0.28</td>
</tr>
<tr>
<td>2.35</td>
<td>0.97</td>
<td>0.01</td>
<td>0.30</td>
</tr>
<tr>
<td>1.97</td>
<td>0.92</td>
<td>0.18</td>
<td>0.32</td>
</tr>
<tr>
<td>2.06</td>
<td>1.28</td>
<td>0.21</td>
<td>0.21</td>
</tr>
</tbody>
</table>

** x-direction axis; *** y-direction axis

3.4 Closing Remarks
Quantifying the amount of mass transferred across boundaries of bubbles is critical in hydrogen production systems as the purity of the produced hydrogen is decreased with increasing mass transfer. In this chapter the experimental apparatus and method adopted to simulate bubbly flows in hydrogen production systems was presented. Additionally, the method used to measure bubbles diameter and velocity, which are parameters influencing mass transfer, were presented.

In the simulation process, nitrogen bubbles generated through a porous surface rose up through clear liquid water at room temperature. The dynamics of the rising bubbles were captured with the aid of a camera system, which had the ability to freeze the bubbles in motion in order to obtain accurate measurements of bubbles size and velocity. The acquired values are employed in the next chapter to calculate Sherwood, Reynolds and Eotvos numbers in order to obtain a correlation that determines the amount of mass transferred across the boundary of the gas bubble as it rises through the liquid.
Chapter 4

Gas Liquid Physical Processes

“Experience serves not only to confirm theory, but differs from it without disturbing it, it leads to new truths which theory only has not been able to reach.”

Dalembert

4.1 Assumptions

Gas bubbles rising through liquid have complicated physics to analyze, so simplifications are needed for purposes of analysis. In order to simplify the analysis in this chapter, some assumptions have been made (validated by past researchers [10]). The assumptions can be divided into four sections; pertaining to the apparatus, liquid, gas and gas bubbles themselves.

Since the column’s diameter is much larger than the diameter of the gas bubbles formed and the bubbles travel in the center of the column, it is reasonable to assume that the wall does not influence the ascending gas bubbles. Also, there are no obstacles in the path of the ascending gas bubbles. Additionally, the liquid within the column is not circulated except by the action of the bubbles themselves. Therefore the liquid is assumed stationary and circulation of the liquid is negligible. Since the volume of the liquid within the column is much larger than the volume of the bubbles, it is assumed that the liquid is a semi-infinite medium in comparison to bubble volume. Also, the added mass coefficient
of the fluid is assumed constant and the fluid flow field is inviscid; therefore, liquid viscous effects have no influence on bubble size.

One of the necessary assumptions is that the gas is ideal and the gas flow is incompressible. Also, the gas density changes are neglected. Since the gas injection rate is constant, it can be assumed that the bubble velocity is proportional to the flow rate with no allowance for a change in bubble cross-section during growth. Additionally, the motion of the bubble is not affected by the presence of another bubble immediately above it. During motion, the gas-liquid interface is affected by a pressure difference between the gas and liquid and also by surface tension forces, which are constant and uniform.

4.2 Heat Transfer Analysis

Although mass transfer is enhanced with an increasing temperature due to a higher diffusion coefficient, all gas-liquid bubble dynamics experiments were performed at room temperature conditions in order to determine the influence of other physical parameters on mass transfer. However, before performing the mass transfer analysis, it was essential to determine the amount of heat transferred due to motion of the bubbles through the liquid, as a change in temperature would affect the mass transfer analysis. The amount of heat transfer was determined analytically and validated experimentally.

The experimental apparatus was insulated to prevent heat from being transferred to the liquid from the surroundings. Initially, the liquid was allowed to reach the same temperature as the surroundings and then the vertical column was insulated with a 1.5 in
thick insulation. Type K thermocouples were installed at 4 different locations to obtain temperature readings.

For the analytical investigation, the factors affecting heat transfer were identified and tabulated in Table 4.1. The experiments were performed at 21°C hence the parameters in Table 4.1 pertain to this temperature [32].

Table 4.1 – Properties in heat transfer analysis

<table>
<thead>
<tr>
<th>P (kPa)</th>
<th>T (°C)</th>
<th>ρ_vap (kg/m³)</th>
<th>ρ_H₂O (kg/m³)</th>
<th>h_fg (kJ/kg)</th>
<th>C_p_H₂O (J/kgK)</th>
<th>C_p_vap (J/kgK)</th>
<th>C_p_air (J/kgK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>104.494</td>
<td>21</td>
<td>0.0231</td>
<td>997</td>
<td>2442</td>
<td>4180</td>
<td>1870</td>
<td>1038.5</td>
</tr>
</tbody>
</table>

In performing the analysis, the volume of water was first determined. After obtaining the volume of water, the mass of water was determined using the water density at 21°C. The volume of vapour was then calculated in order to obtain the net heat transfer. A net heat transfer of 0.327 kJ was obtained, which corresponds to a change in temperature of 0.2°C. These results were validated experimentally and the thermocouple data is tabulated in Table 4.2.

Table 4.2 – Experimental data results for heat transfer analysis

<table>
<thead>
<tr>
<th>Thermocouple</th>
<th>Initial Temperature (°C)</th>
<th>Final Temperature (°C)</th>
<th>Change in Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.93</td>
<td>24.09</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>23.38</td>
<td>23.45</td>
<td>0.08</td>
</tr>
<tr>
<td>3</td>
<td>23.33</td>
<td>23.44</td>
<td>0.11</td>
</tr>
<tr>
<td>4</td>
<td>23.31</td>
<td>23.37</td>
<td>0.06</td>
</tr>
</tbody>
</table>
The temperature was monitored for 2 hours at 4 different locations as shown in Figure 3.1. It can be noted that there is no significant change and the range is within the calculated value. Since the temperature change is negligible, the heat transfer is omitted in the mass transfer analysis.

4.3 Mass Transfer Analysis

Diffusive mass transfer occurs across the boundaries of the gas bubbles. In order to determine the amount of mass transferred and carried out of the column, a humidity sensor was installed at the gas exit to measure the change in relative humidity. The change in relative humidity is shown in Figure 4.1.

![Figure 4.1](image)

Figure 4.1 – Change in relative humidity for different flow rates
A correlation was developed to relate the change in relative humidity (i.e. mass transfer) to the parameters causing this change. A mass transfer analysis is necessary to interpret vapour entrainment in terms of the phase transition rate and its dependence on various operating parameters. The Buckingham PI theorem was used to develop a correlation representing the mass transfer in terms of various factors. This method was selected for analysis since it allows the generation of all key dimensionless groups which characterize the problem even if the general form of the equation to be developed is unknown. Therefore, with this method it was possible to select meaningful physical variables, such as the ones described in Section 4.4, prior to performing experiments. Although mass transfer is dependent on temperature, the temperature effects were not investigated in this thesis since all experiments were performed at the temperature shown in Table 4.2. However, in the future the temperature term should be included in the analysis as it would more accurately predict the amount of vapour entrainment not only in conventional electrolysis but in the Cu-Cl cycle electrolyzer which performs better at temperatures higher than 40°C.

As previously mentioned, mass transfer is dependent on bubble motion and its shape which is characterized by Re, Eo and Mo. In order to better understand how the three numbers describe the bubble’s motion, it is necessary to determine their values. The Reynolds number is the ratio of inertia forces to viscous forces in the fluid:

\[ \text{Re} = \frac{VL_c}{\nu} = \frac{\rho VL_c}{\mu} \]  \hspace{1cm} (4-1)
where $V$ is the bubble’s velocity, $L_c$ is the diameter of the bubble, $\mu$ is the dynamic viscosity of the fluid, $\rho$ is the density of the fluid and $\nu = \frac{\mu}{\rho}$ is the kinematic viscosity of the fluid. The Eotvos number characterizes the shape of the bubble and it is proportional to the buoyancy force divided by the surface tension force:

$$Eo = \frac{\Delta \rho g L_c}{\sigma}$$ (4-2)

where $\Delta \rho$ is the density change of the two phases and $\sigma$ is the surface tension. The Morton number is used together with $Eo$ in order to characterize the bubble’s shape and it is given by:

$$Mo = \frac{g \mu^4 \Delta \rho}{\rho_c^2 \sigma^3}$$ (4-3)

The rate of mass diffusion of a chemical species, $A$, in a stationary medium in the direction of $x$ is proportional to the concentration gradient $dC/dx$ in that direction and it is expressed by Fick’s law of diffusion [32]:

$$m_{diff} = -D_{AB} \frac{dC_A}{dx}$$ (4-4)

where $D_{AB}$ is the diffusion coefficient and $C_A$ is the concentration of species in the mixture at that location. Due to the processes that arise as a result of fluid motion and its properties, mass transfer is determined based on experimental data. Therefore, the relative magnitude of molecular momentum and mass diffusion in the velocity and concentration boundary layers are expressed by the dimensionless Schmidt number defined as [32]:

$$\text{Schmidt number}$$
In heat transfer analysis, it is convenient to express the heat transfer coefficient in terms of the dimensionless Nusselt number. Likewise, in mass transfer, the mass transfer coefficient is expressed in terms of the dimensionless Sherwood number [32]:

\[
Sc = \frac{\nu}{D_{AB}} \tag{4-5}
\]

where \( \nu \) is the kinematic viscosity and \( D_{AB} \) is the mass diffusivity.

Considering the flow over a plate with a free stream condition \( w_{A,\infty} \), the mass transfer condition at the surface can be expressed as [32]:

\[
j_{A,i} = -D_{AB} \left. \frac{\partial w_A}{\partial y} \right|_{y=0} = h_{mass} (w_{A,i} - w_{A,\infty}) \tag{4-7}
\]

where \( w_{A,i} \) is the mass mole fraction of medium A at the surface.

For an internal flow and using bulk motion properties, the above relation can be rewritten as [32]:

\[
\frac{d}{d\left(\frac{y}{L_c}\right)} \left[ \frac{(w_A - w_{A,j})}{(w_{A,\infty} - w_{A,j})} \right] = \frac{h_{mass} L_c}{D_{AB}} = Sh \tag{4-8}
\]

Another method to determine the Sherwood number is given in terms of the Reynolds number and Schmidt number. The expression is given as follows [33]:

\[
Sh = \frac{h_{mass} L_c}{D_{AB}} \tag{4-6}
\]
Sh = c Re^{1/2} Sc^{1/3} \quad (4-9)

where \( c \) is a constant. This expression is used when the bubble can be assumed to be rigid and therefore a solid sphere.

### 4.4 Dimensional Analysis

The non-dimensional correlation will have the following form [65]:

\[ y = C_0 t_1^{C_1} t_2^{C_2} \ldots t_n^{C_n} \quad (4-10) \]

where values of \( t \) are the various independent parameters influencing the mass transfer and \( C \) are the coefficients. A dimensional analysis is necessary in order to determine relations among physical quantities governing the mass transfer coefficient and obtain a general empirical equation. Mass transfer across the boundary of a gas bubble is dependent on different variables such as the velocity of the rising bubble, size and shape of the bubble, distance it travels and the temperature of the surrounding fluid.

The Buckingham \( \Pi \) theorem was used for the purpose of non-dimensional groups. Parameters affecting mass transfer have been identified and an equation expressing the mass transfer coefficient as a function of the mass transfer parameters can be written as follows:

\[ h_{\text{mass}} = f(\mu, \sigma, V, D, d, D_{AB}, g, H, \rho) \quad (4-11) \]

where \( h_{\text{mass}} \) is the mass transfer coefficient, \( \mu \) is the dynamic viscosity, \( \sigma \) is the surface tension, \( V \) is the instantaneous velocity of the bubble, \( D \) is the major diameter of the
bubble, d is the minor diameter of the bubble, $D_{AB}$ is the diffusivity, g is the standard gravity, H is the distance travelled by the bubble and $\rho$ is the average gas-liquid density. These parameters are tabulated in Table 4.3. Units of the physical quantity, dimensions of physical quantities and coefficients of the dimensions of the physical quantities are also tabulated.

Dimensions of physical quantities are expressed as a product of the basic physical dimensions of mass (M), length (L), time (T) and temperature (K) such that the dimensions of the velocity are length/time ($L/T$ or $LT^{-1}$). Incorporating the dimensions of the physical quantities in Eq. (4-11), the dimensional equation becomes:

$$LT^{-1} = (MT^{-1}L^{-1})^a (ML^{-3})^b L^c T^{-1} (L^2 T^{-1})^f (MT^{-2})^i (LT^{-2})^j L^l$$

Eq. (4-12)

The exponents of mass, length and time terms in Eq. (4-12) are then isolated to yield 3 equations and 9 unknowns and form the augmented matrix A:

$$A = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & -3 & 1 & 1 & 1 & 2 & 0 & 1 & 1 & 1 \\ -1 & 0 & 0 & 0 & -1 & -2 & -2 & 0 & -1 & 1 \end{bmatrix}$$

It can be noted that matrix A has a rank of 3 therefore 6 PI terms are obtained. In order to determine the 3 equations in terms the other unknowns, matrix A is written in row reduced echelon form through Gaussian elimination. Therefore A becomes:

$$rref(A) = \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 1 & 2 & 2 & 0 & 1 \\ 0 & 1 & 0 & 0 & -1 & -1 & -1 & -2 & 0 & -1 \\ 0 & 0 & 1 & 1 & -1 & 0 & -1 & -3 & 1 & -1 \end{bmatrix}$$
Table 4.3 – Dimensional analysis parameters for mass transfer analysis

<table>
<thead>
<tr>
<th>Factors Affecting Mass Transfer</th>
<th>Units</th>
<th>MLT</th>
<th>Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamic viscosity</td>
<td>(\frac{\text{kg}}{\text{s} \cdot \text{m}})</td>
<td>MT(^{-1})L(^{-1})</td>
<td>a</td>
</tr>
<tr>
<td>Surface tension</td>
<td>(\frac{\text{kg}}{\text{s}^2})</td>
<td>MT(^{-2})</td>
<td>b</td>
</tr>
<tr>
<td>Bubble velocity</td>
<td>(\frac{\text{m}}{\text{s}})</td>
<td>MT(^{-1})</td>
<td>c</td>
</tr>
<tr>
<td>Major diameter</td>
<td>(\text{m})</td>
<td>L</td>
<td>e</td>
</tr>
<tr>
<td>Minor diameter</td>
<td>(\text{m})</td>
<td>L</td>
<td>f</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>(\frac{\text{m}^2}{\text{s}})</td>
<td>L(^2)T(^{-1})</td>
<td>h</td>
</tr>
<tr>
<td>Gravity</td>
<td>(\frac{\text{m}}{\text{s}^2})</td>
<td>LT(^{-2})</td>
<td>i</td>
</tr>
<tr>
<td>Water level</td>
<td>(\text{m})</td>
<td>L</td>
<td>j</td>
</tr>
<tr>
<td>Density</td>
<td>(\frac{\text{kg}}{\text{m}^3})</td>
<td>ML(^{-3})</td>
<td>l</td>
</tr>
<tr>
<td>Mass transfer coefficient</td>
<td>(\frac{\text{m}}{\text{s}})</td>
<td>LT(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

M - mass; L - length; T - time
By combining terms in the above Eq. (4-13) and after rearranging, $h_{\text{mass}}$ can be written as follows:

$$h_{\text{mass}} = \frac{\mu}{\rho D} \left( \frac{d}{D} \right)^c \left( \frac{\rho D V}{\mu} \right)^{\frac{1}{f}} \left( \frac{\rho D \sigma}{\mu^2} \right)^{\frac{1}{g}} \left( \frac{\rho^2 D^3 g}{\mu^2} \right)^{\frac{1}{i}} \left( \frac{H}{D} \right)^{\frac{1}{j}}$$

(4-14)

Eq. (4-14) can be written in PI terms as:

$$\Pi_1 = \Pi_2 \Pi_3 \Pi_4 \Pi_5 \Pi_6 \Pi_7$$

(4-15)

where $\Pi_1 = \frac{h_{\text{mass}} \rho D}{\mu}$.

Table 4.4 – PI terms for mass transfer analysis

<table>
<thead>
<tr>
<th>PI Terms</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Pi_1 = \frac{h_{\text{mass}} D}{D_{AB}}$</td>
<td>Sherwood number</td>
</tr>
<tr>
<td>$\Pi_2 = \frac{d}{D}$</td>
<td>Aspect ratio</td>
</tr>
<tr>
<td>$\Pi_3 = \frac{\rho D V}{\mu}$</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>$\Pi_6 = \frac{\rho D^2 g}{\sigma}$</td>
<td>Eotvos number</td>
</tr>
<tr>
<td>$\Pi_7 = \frac{H}{D}$</td>
<td></td>
</tr>
</tbody>
</table>

53
From Eq. (4-14) it was noted that $\Pi_2$ is the aspect ratio of the bubble, $\Pi_3$ is the formulation for Re whereas Sh is obtained when dividing $\Pi_1$ by $\Pi_4$ and Eo is obtained when diving $\Pi_6$ by $\Pi_5$. These terms are tabulated in Table 4.4 below.

Therefore Eq. (4-14) can be written in terms of the terms described in Table 4.4 as follows:

$$Sh^{1-h} = Re^{f} Eo^{j-i} \left(\frac{d}{D}\right)^{e} \left(\frac{H}{D}\right)^{1}$$

(4-16)

Simplifying for optimization purposes,

$$Sh = Re^{m_1} Eo^{m_2} \left(\frac{d}{D}\right)^{m_3} \left(\frac{H}{D}\right)^{m_4}$$

(4-17)

where $m_1 = \frac{f}{1-h}$, $m_2 = \frac{j-i}{1-h}$, $m_3 = \frac{e}{1-h}$, $m_4 = \frac{l}{1-h}$ are coefficients to be determined.

In order to determine the coefficients in Eq. (4-17), experimental data were utilized. Diameters and velocities of gas bubbles were obtained using DynamicStudio using the steps described in the previous section.

### 4.5 Water quantification

It is required to determine the amount of liquid carried out of the electrolysis reactor in the thermochemical Cu-Cl cycle for hydrogen production and conventional water electrolysis techniques. In the electrolysis reactor of the Cu-Cl cycle, an aqueous solution
consisting of aqueous HCl and dissolved CuCl is used to split water. In this process, aqueous HCl enters the hydrogen bubbles and it is then carried out of the reactor. As a result, the purity of the produced hydrogen is affected and the concentration of aqueous HCl decreases, thereby affecting the efficiency of the electrolytic cell. Therefore, it is important to determine the amount of HCl carried out in order to determine the concentration change in the HCl-CuCl solution. By the same principle, the purity of hydrogen is affected in conventional electrolysis, making it necessary to determine the amount of water carried out due to mass transfer across the boundary of the gas bubbles.

To determine the amount of vapour entrainment, the correlation obtained in the previous section will be used. The rate of mass convection is:

\[ \dot{m}_{\text{conv}} = h_{\text{mass}} A_s \left( \rho_{A,s} - \rho_{A,\infty} \right) \]  \hspace{1cm} (4-18)

where \( h_{\text{mass}} \) is the mass transfer coefficient, in m/s; \( A_s \) is the surface area of the bubble, in \( m^2 \) and \( \rho_{A,s} \) and \( \rho_{A,\infty} \) are the densities of species A at the boundary and free stream respectively (i.e. \( \rho_{A,\infty} \) is gas density, \( \rho_{A,\infty} \) is liquid density). Also, \( h_{\text{mass}} \) may be determined from Eq. (4-18) by rearranging such that:

\[ h_{\text{mass}} = \frac{ShD_{AB}}{L_c} \]  \hspace{1cm} (4-19)

where Sh is given by Eq. (4-17).

A general formulation to determine \( A_s \) for an ellipsoid is given by:

\[ A_s = 2\pi c^2 + \frac{2\pi ab}{\sin \phi} \left( E\left(\phi,k\right)\sin^2 \phi + F\left(\phi,k\right)\cos^2 \phi \right) \]  \hspace{1cm} (4-20)
where \( \cos \phi = \frac{c}{a}, \quad k^2 = \frac{a^2 \left( b^2 - c^2 \right)}{b^2 \left( a^2 - c^2 \right)} \), \( a \geq b \geq c \) and \( F(\phi, k) \) and \( E(\phi, k) \) are incomplete elliptic integrals of the first and second kind respectively [66]. Assuming \( a = b \), an approximation to the surface area, which is employed in this research, is given by [54]:

\[
A_s = 2\pi a^2 + \frac{\pi c^2}{\ln \frac{1 + \sqrt{1 - \frac{c^2}{a^2}}}{\sqrt{1 - \frac{c^2}{a^2}}}}
\]  

(4-21)

The results of using the above procedure to determine the amount of liquid entrainment are given in Chapter 7.
Chapter 5

Liquid-Solid Experimental Loop

“Make everything as simple as possible, but not simpler.”

ALBERT EINSTEIN

The thermochemical Cu-Cl cycle consists of many steps, which must be integrated for continuous recycling of the products. In the integration of the electrolysis with the other reactors of the cycle cuprous chloride (CuCl) (the product out of the oxygen reactor) and hydrochloric acid (HCl) (product of hydrolysis reactor) are mixed together to obtain a ternary CuCl-HCl-H₂O solution, which is the input to the electrolysis step of the cycle. The dissolution of solid CuCl in aqueous HCl is of detrimental importance to the cycle integration. Thus, an experimental setup was designed and built by the author to investigate liquid-solid interactions and dissolution rates for successful integration of electrolysis with the upstream reactors.

Two different experimental setups are described; the first presents particle dynamics and simulates a quenching process of solid CuCl in water as CuCl flows out of the oxygen reactor whereas the second setup investigates the dissolution rates of CuCl in quiescent and turbulent HCl solution with different molarities. The findings of the experiments will aid in the design of an integration system of the electrolysis with the upstream reactors.
5.1 Description of Experimental Apparatus for Particle Dynamics

In the first setup of the experimental loop (Figure 5.1) the dynamics of CuCl particles travelling through liquid are examined so that the descending velocity of the particles can be determined. The obtained velocity is used in a force analysis to ultimately determine the velocity of a flow of liquid in the opposite direction the particle travels to ensure the particles are suspended for improved dissolution rate.

![Experimental setup for particle dynamics with camera system setup horizontally for capturing falling particles motion](image)

Figure 5.1 – Experimental setup for particle dynamics with camera system setup horizontally for capturing falling particles motion

To simulate the quenching process and investigate CuCl particle dynamics, the experimental apparatus consisting of a clear pyrex vessel and a camera system was arranged as seen in Figure 5.1. Since the CuCl particles travel in the vertical direction, the camera system was arranged horizontally in order to capture the particle in motion. In this
arrangement of the camera system, the LED light source freezes the particles in motion as the camera captures 91 frames per second. This ensures that the particles are not traveling out of the field of view of the camera between subsequent images acquired and the velocity of the particles can be determined.

Although the dissolution of CuCl in HCl is sought in this research, quiescent water at room temperature was used for these experiments. This is due to water’s density being comparable to that of HCl therefore the velocity of the descending particle through water is comparable to that of descending particles through HCl solution. Additionally, the scope of this part of the research is to investigate the dynamics of the particles without focusing on dissolution, which will be described in the next section. Also, water was chosen since CuCl particles coming out of the oxygen reactor of the thermochemical Cu-Cl cycle for hydrogen production are first quenched in quiescent water for heat recovery.

The dynamics of irregular shaped CuCl particles of mass ranging from 4 mg to 45 mg were observed with the aid of the camera system described. Captured images were analyzed and information such as size and velocity of the particle was obtained. This information is used to determine the counter flow velocity to keep particles suspended for improved dissolution.

5.2 Description of The apparatus for Particle Dissolution

As previously mentioned, for effective integration of the electrolysis with the upstream reactors in the thermochemical Cu-Cl cycle for hydrogen production it is necessary to investigate the kinetics of solid CuCl in aqueous HCl. For this, a second
setup was constructed with the purpose of acquiring images of the particle as it dissolves in HCl and obtain the particle’s surface area. Similar to the previous experiment, this setup consists of the pyrex vessel and the camera system as shown in Figure 5.2. It can be noticed in Figure 5.2 that the position of the camera system differs from the setup discussed in Section 5.1 since the scope of this investigation is to determine the dissolution rate of CuCl in quiescent and turbulent HCl with different molarities. Since the dropped CuCl particle descends through HCl and settles at the bottom of the pyrex vessel, the camera system was setup vertically as opposed to the setup in Figure 5.1. As the particle dissolves, a concentration gradient around the particle is observed, which would not be captured with the setup described in previous section.

Figure 5.2 – Experimental setup for dissolution rate with camera system setup vertically
These experiments also investigate different factors affecting reaction kinetics. The two factors presented in this thesis are concentration of HCl and mixing. Dissolution rate of CuCl in quiescent HCl with concentrations of 6M, 9M and 12M were investigated. These concentrations were chosen for consistency with electrolyzer studies performed at UOIT [51, 53, 54]. In order to study the effect of mixing, nitrogen gas was supplied from the bottom of the pyrex vessel. The flow of nitrogen generates a steady mixing quality of the liquid without disturbing the particle. Although disturbing the particle due to turbulence in the fluid would further enhance dissolution rate, it is necessary to keep the particle stationary so that the camera could capture pictures of the same surface so that the change of the surface area can be determined.

5.3 Dissolution Shadow Imaging Results

Similar to the method described in Section 3.1, a FlowSense 2ME camera with an effective sensor size of 1600 by 300 pixels was used to capture images. Images were captured in single frame mode with a trigger frequency of 91 Hz when observing the particle dynamics and 1 Hz when observing the dissolution rate. A glass diffuser (not shown) was placed between the particle and LED light source in order to obtain an even light sheet for accurate images of particles’ motion and dissolution. The calibration of the camera was performed as described in Section 3.1. The “shadow sizer processing” method is used to monitor dissolution and extract information regarding particles’ dynamics.
Figure 5.3 – Captured image of CuCl flowing through quiescent water at 0.956 s

Figure 5.4 – Image of outline of CuCl particle flowing through water with velocity vector at 0.956 s

This information is useful for calculating the force balance on the particle so that a flow of liquid in the opposite direction of the falling particles in order to suspend the particles may be introduced. Introducing this counter flow will also enhance dissolution by refreshing the interface of bulk liquid without introducing additional mechanical components. The effect of mixing through gas cross flow and counter flow for different injection angles has been reported [67-69]. However, the scope of this part of experiment was to investigate the motion of the particles without examining reaction kinetics that would occur when the particle is dropped in HCl and dissolution would occur.
Figures 5.5 and 5.3 depict the original acquired images at 0.956 s and 1.011 s, respectively, whereas Figures 5.4 and 5.6 depict the processed images with velocity vectors taken in the same reference frame at 0.956 s and 1.011 s, respectively from the time the camera started acquiring images. In Table 5.1, it is observed that the particle’s velocity changes as the particle changes its physical orientation. Due to the irregular shape, the particle changes orientation until it settles on the bottom of the vessel with a settling velocity [67, 68].
Table 5.1 - Parameters obtained using DynamicStudio

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Area  (mm$^2$)</th>
<th>EqDiab (mm)</th>
<th>MajAxisc (mm)</th>
<th>MinAxisd (mm)</th>
<th>Shape*</th>
<th>U vel$^f$ (m/s)</th>
<th>V vel$^g$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.956</td>
<td>18.559</td>
<td>0.418</td>
<td>0.249</td>
<td>0.184</td>
<td>0.896</td>
<td>0.005</td>
<td>-0.022</td>
</tr>
<tr>
<td>1.011</td>
<td>19.166</td>
<td>0.425</td>
<td>0.24</td>
<td>0.2</td>
<td>0.909</td>
<td>0</td>
<td>-0.023</td>
</tr>
</tbody>
</table>

* Cross-sectional area; b Diameter of the circle with an area equivalent to the cross-sectional area; c Longest axis of particle; d Shortest axis of particle; e Shape of the particle relative to a sphere enclosing it; f Horizontal velocity; g Vertical velocity

Table 5.1 shows the results pertaining to a 45mg particle falling through water at two different times as captured by the camera. The instantaneous velocities for different mass particles are tabulated in Table 5.2. It is important to note that the particles are irregular in shape and the area is the cross-sectional area of the particle parallel to the direction of motion. These results are explained in detail in Chapters 6 and 7.

Table 5.2 - Areas and velocities of particles of varying masses

<table>
<thead>
<tr>
<th>Area  (mm$^2$)</th>
<th>U vel (m/s)</th>
<th>V vel (m/s)</th>
<th>Mass (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.841</td>
<td>-0.003</td>
<td>-0.012</td>
<td>4.000</td>
</tr>
<tr>
<td>3.293</td>
<td>0.000</td>
<td>-0.017</td>
<td>7.000</td>
</tr>
<tr>
<td>5.042</td>
<td>-0.007</td>
<td>-0.020</td>
<td>7.000</td>
</tr>
<tr>
<td>6.971</td>
<td>-0.002</td>
<td>-0.016</td>
<td>8.000</td>
</tr>
<tr>
<td>7.060</td>
<td>-0.001</td>
<td>-0.017</td>
<td>8.000</td>
</tr>
<tr>
<td>12.950</td>
<td>-0.001</td>
<td>-0.020</td>
<td>21.000</td>
</tr>
<tr>
<td>9.228</td>
<td>0.005</td>
<td>-0.017</td>
<td>22.000</td>
</tr>
<tr>
<td>15.562</td>
<td>-0.003</td>
<td>-0.018</td>
<td>26.000</td>
</tr>
<tr>
<td>20.816</td>
<td>0.000</td>
<td>-0.026</td>
<td>31.000</td>
</tr>
<tr>
<td>13.764</td>
<td>-0.001</td>
<td>-0.023</td>
<td>32.000</td>
</tr>
<tr>
<td>8.591</td>
<td>0.004</td>
<td>-0.020</td>
<td>33.000</td>
</tr>
<tr>
<td>19.795</td>
<td>0.000</td>
<td>-0.023</td>
<td>45.000</td>
</tr>
</tbody>
</table>

* Projected area of the particle parallel to the direction of motion

To investigate the dissolution rate of CuCl in HCl, a second setup was constructed as described in Section 5.2. Although the CuCl particles start dissolving in HCl solution immediately, the camera starts recording when the particle settles at the bottom of the vessel. Also, it is assumed that dissolution occurs evenly across the surface of the particle. As the particle settles at the bottom of the vessel, molecular diffusion takes place until
equilibrium is achieved. However, it has been observed that local saturation around the particle significantly slows down the dissolution rate.

![Figure 5.7 - Actual mass transfer around a CuCl particle during dissolution process](image)

The local saturation can be observed in Figure 5.7, which shows images taken at 1 s, 60 s and 120 s after dropping the particle. This local saturation could be detrimental for the cycle since the byproducts are recycled continuously and a slow dissolution rate could result in an accumulation of byproducts. Hence, methods for enhancing the dissolution rate are necessary. Although a stirrer would be a common solution for mixing,
introducing mechanical components as well as coatings to prevent corrosion due to high concentrations of HCl would increase the cost of the cycle. Therefore, different methods of mixing for enhancing the dissolution rate such as introducing gas to create disturbance in the liquid were investigated.

Figure 5.8 - Actual mass transfer around a CuCl particle during dissolution process with introduced nitrogen gas for mixing purposes

In this set of experiments, nitrogen gas is supplied from the bottom of the pyrex vessel. The flow of nitrogen generates a steady mixing quality of the liquid without
disturbing the particle. This process is shown in Figure 5.8 in which it can be observed that the local saturation is diminished compared to Figure 5.7 in which the laminar layer is much darker representing a higher concentration surrounding the particle. Although disturbing the particle due to turbulence in the fluid would further enhance dissolution rate, it is necessary to keep the particle stationary so that the camera could capture pictures of the same surface so that the change of the surface area can be determined.

**5.4 Closing Remarks**

In this chapter, experimental setups for CuCl particle dynamics and reaction kinetics of CuCl in HCl with different molarities (i.e. 6M, 9M and 12M) were presented. The investigation aids in the integration of the electrolysis with the upstream reactors in the thermochemical Cu-Cl cycle for hydrogen production. The experimental setup for particle dynamics was design so that it simulates the quenching process of the particles in quiescent water whereas the setup for dissolution rates investigates the reaction kinetics and methods for improved dissolution. Based on the experiments, it was found that increasing the molarity of the HCl accelerates the dissolution of CuCl. Additionally, the dissolution rate is accelerated when mixing is introduced. Models for expressing the dissolution rate based on the described experiments were developed in this thesis and are discussed in detail in Chapter 7. Also, based on the particle dynamics results obtained, a counter flow to suspend the particle for improved dissolution and integration purposes is proposed in Chapter 7.
Chapter 6

Liquid-Solid Physical Processes

“I wanted to understand the secrets behind my chemical experiments and behind the processes in nature.”

RICHARD ERNST

6.1 Assumptions

Many dissolution models have been proposed in past literature [69-71], particularly in pharmaceutical research. In the modeling of dissolution processes, a set of assumptions is normally made in order to simplify the analysis. In this thesis, the following assumptions are made for the analysis of dissolving particles:

1. Particles dissolve isotropically;
2. Diffusion layer thickness is constant;
3. Dissolution occurs in sink conditions;
4. Solid-liquid interface saturated concentration $C^*$ is constant;
5. Diffusion coefficient is constant;
6. Quasi-static state exists.

Although CuCl at the bottom of the vessel is dispersing the HCl solution on the side being in contact with the vessel, the first assumptions calls for uniform physical properties in all directions. This assumption is valid when the particle is suspended. The second assumption is reasonable since the physical properties of the particle are uniform. The
sink condition is valid when the volume of liquid is more than five to ten times the saturation point and the particle does not reach its saturation point. This assumption is valid since a 7 mg CuCl particle was dissolved in 250 mL HCl solution. The diffusion coefficient changes with temperature and pressure. Since the temperature and pressure are constant during experiments, the diffusion coefficient is also constant, therefore the fifth assumption is also reasonable in this research. The quasi-equilibrium assumption is often used to simplify the analysis of reaction diffusion problems. The validation of this assumption is described in detail in [69-71].

6.2 Dissolution Analysis

Most dissolution studies are intended to determine the CuCl$_2$ crystal size and formation rate when CuCl dissolves in HCl in the presence of oxygen gas. Although dissolution of CuCl is more rapid in the presence of CuCl$_2$, the efficiency of electrolysis decreases when CuCl$_2$ ions are present. Therefore, it is important to determine the optimum dissolution rate while preventing the formation of CuCl$_2$ ions.

Since the electrolysis also includes HCl as a reactant, the solid CuCl obtained from the decomposition reactor can be directly dissolved in the aqueous HCl, because it has been found that the solubility of CuCl in aqueous HCl is much larger than in water only [27]. The dissolution process is expressed in the following equation:

\[
2\text{CuCl (solid)} + x \text{HCl (aqueous)} = [2\text{CuCl} + x\text{HCl }] \text{(aqueous, ternary system)} \quad (6-1)
\]

where x is a coefficient depending on the concentration of CuCl and temperature.
The dissolution kinetics should be modeled for synchronization with the electrolysis kinetics. According to boundary layer theory, the mass transfer close to the solid CuCl particle surface is dominated by molecular diffusion, because a laminar liquid layer exists on the particle surface, which cannot be eliminated by mechanical stirring. The near-surface process is shown in Figure 6.1.

![Figure 6.1 - Schematic of mass transfer process close to the particle surface during CuCl dissolution](image)

According to Fick’s law of steady state diffusion, the dissolution kinetics in the boundary layer can be expressed as [32]: 
\[ J_{\text{dis}} = -D_{AB} \frac{\partial C}{\partial L} \]  

(6-2)

where \( J_{\text{dis}} \) is the "diffusion flux" (often expressed in units of mol/m\(^2\)s), \( D_{AB} \) is the diffusivity of CuCl in the ternary system (m\(^2\)/s), \( C \) is the dissolved CuCl concentration (mol/m\(^3\) or mol/l) and \( L \) is the position of dissolved CuCl in the diffusion path (m). For one-dimensional diffusion over a short distance, Eq. (6-2) can be approximated as:

\[ J_{\text{dis}} = -D_{AB} \frac{\Delta C}{\Delta L} = -D_{AB} \frac{C^* - C}{\Delta L} \]  

(6-3)

where \( C^* \) is the saturation concentration of the dissolved CuCl in the ternary system.

The modeling of the CuCl dissolution kinetics always involves the saturation state of the dissolved CuCl. As the solubility of CuCl simultaneously depends on temperature and concentration of HCl, the solubility data of CuCl is not convenient for Eq. (6-3), plus there are insufficient data for different temperatures and HCl concentrations available in literature. As previously discussed, the same application difficulty exists for the usage of Eq. (2-12). To overcome the challenge, this thesis focuses on the modeling of the solubility of CuCl in the water and aqueous HCl solution. Since the solubility is a thermodynamic equilibrium property, it is not dependent on the equipment and processing scales. Consequently, the model can be incorporated into the electrolysis and dissolution kinetics for the equipment scale-up and process integration.
6.3 Solubility Comparison of the Binary and Ternary Systems

Figure 6.3 shows the solubility of solid CuCl in water at different temperatures with and without the presence of HCl [36-39].

Even a relatively low concentration of HCl (0.5M) can significantly increase the solubility of CuCl. At the same temperature, the solubility is increased by an order of magnitude with the low concentration of HCl. Also, to reach the same solubility levels at 20 and 50ºC resulting from the addition of HCl, the binary system consisting of only CuCl and water must be operated at about 130 and 190ºC, respectively. This means the binary system must be operated at a higher operating pressure in order to keep the water in liquid form. So it is greatly beneficial for the dissolution process of CuCl to be operated in aqueous HCl.
The solubility of CuCl at higher HCl concentrations such as 6M and 12M is not shown in this figure because the solubility difference spans several orders. This difference can be explained thermodynamically. The enthalpy change of the HCl dissolution in water has a negative value [72], but the enthalpy change for CuCl is positive. As a consequence, the increase of the HCl concentration in the ternary system favors the dissolution of CuCl, until other effects such as the diversified chemical bonding forces dominate.

Figure 6.3 – Increase of CuCl solubility with increasing concentration of HCl in the ternary system

Figure 6.3 shows the increase of the CuCl solubility with increasing concentration of HCl in the ternary system at 10, 25 and 80°C. The solubility of CuCl at 80°C in the ternary system is higher than that at 25°C and the value at 25°C is higher than that at 10°C,
which means a positive effect is observed from increasing temperature on the CuCl solubility, although the solubility of HCl decreases with increasing temperature.

6.4 Modeling of System Solubility

In an engineering operation of the CuCl-HCl-H$_2$O system, it is usually preferred to utilize HCl acid to dissolve the solid CuCl or binary slurry of CuCl and water, to prepare the ternary system, because the preparation of the two separate binary systems (i.e. aqueous HCl-H$_2$O and slurry CuCl-H$_2$O) is more convenient. The preparation of the binary system of HCl-H$_2$O is a mature operation in industry. It is beneficial for the solubility of CuCl in the ternary system to be well understood for the engineering design.

As discussed previously, the dissolution enthalpy of CuCl in water may counteract the counterpart of HCl in water. Then from a thermodynamic viewpoint, the ternary system can be divided into two subsystems: CuCl-H$_2$O and HCl-H$_2$O. However, this does not mean that the solubility of the binary systems of the CuCl-H$_2$O and HCl-H$_2$O can be simply summed together in a linear mode, because the interactions of the two subsystems in the ternary system are non-linear. As the non-linear interactions are complex, in this thesis, the non-linear behavior will be examined in a semi-empirical way instead of a fully mechanistic approach.

In order to develop a correlation, thermodynamic equilibrium theory is applied to the ternary system. In the following analysis, it should be noted that there are a number of complex transport and thermodynamic processes which have not been well understood or documented in the technical literature, particularly from a chemistry perspective. As a
result, the analysis involves simplifications in order to establish an initial formulation from which future developments can improve the accuracy of the predictive models. Experimental data will be presented in a subsequent chapter to provide verification and validation of the approximate analysis.

The dissolution process of CuCl(s) in the ternary system is given by:

\[
\text{CuCl}_\text{(s)} \rightleftharpoons \text{Cu}^{+\text{aq}} + \text{Cl}^{-\text{aq}} \quad (6-4)
\]

However, there may exist multiple equilibria and the cuprous cation can exist in different ion complexes [72-76] due to the introduction of more Cl\(^-\) from the dissolution of HCl in the system:

\[
\text{Cu}^{+} + \text{Cl}^{-} \rightleftharpoons \text{CuCl}_\text{(aq)} \quad (6-5)
\]

\[
\text{Cu}^{+} + 2\text{Cl}^{-} \rightleftharpoons \text{CuCl}_\text{2}^- \quad (6-6)
\]

\[
\text{Cu}^{+} + n\text{Cl}^{-} \rightleftharpoons \text{CuCl}^{(n-1)-}_n \quad (6-7)
\]

where \( n \) is a constant reported in literature as 3 or 4 [72-76]. These equilibria indicate that once the solid CuCl dissolves into Cu\(^+\) (aq) and Cl\(^-\) (aq), the ions will be consumed by processes (6-5) through (6-7) to form ion complexes, until all these processes reach their equilibria. Therefore, the solubility of the solid CuCl in the system should take into account all the ion complexes. Since any function of state depends on the path the system experiences and the ion complexes formed in the ternary system are not easy to obtain or measure, a dissolution state is assumed at equilibrium, as follows:
\[ \text{CuCl} \text{(s)} \Leftrightarrow \text{Cu}^{\text{cplx}} \text{(aq)} + \text{Cl}^{\text{cplx}} \text{(aq)} \quad (6-8) \]

where the superscript cplx refers to the ion complexes.

For reaction presented in Eq. (6-5), the standard Gibbs energy of formation can be expressed in terms of an equilibrium constant at any given temperature as:

\[ \Delta G^0_{\text{CuCl}} = -RT \ln K_{\text{CuCl}} \quad (6-9) \]

where \( K_{\text{CuCl}} \) is an equilibrium constant.

In order to predict the solubility, all the equilibrium constants of processes given by Eq. (6-4) through (6-8) should be calculated. For example, for process given by Eq. (6-4), the equilibrium constant is defined as follows:

\[ K_{\text{CuCl}} = \frac{a_{\text{Cu}} \cdot a_{\text{Cl}}}{a_{\text{CuCl}}} \quad (6-10) \]

where \( a_{\ast} \) denote the activities. Since activity can be written in terms of concentration \( C_{\ast} \) and an activity constant \( \gamma_{\ast} \) (i.e. \( a_{\ast} = C_{\ast} \gamma_{\ast} \)), Eq. (6-10) becomes:

\[ K_{\text{CuCl}} = \frac{C_{\text{Cu}} \cdot C_{\text{Cl}} \cdot \gamma_{\text{Cu}} \cdot \gamma_{\text{Cl}}}{a_{\text{CuCl}}} \quad (6-11) \]

Eq. (6-11) can be rewritten in terms of Gibbs free energy associated with Eqs. (6-4) and (6-5) as follows:

\[
\begin{bmatrix}
-\frac{\Delta_{\text{dis}} G^0_{\text{CuCl}}}{RT} \\
\end{bmatrix}
_{\text{ternary}}^\text{ternary} = \ln K_{\text{CuCl}} \quad (6-12)
\]
Since the molar concentration of the copper ions equals that of the chlorine ions, Eq. (6-11) can be written as:

\[ K_{CuCl} = \frac{C_{Cu^2}^2 \gamma_{Cu^2} \gamma_{Cl^-}}{a_{CuCl}} \]  

(6-13)

Substituting Eq. (6-13) into (6-12), the following expression is obtained:

\[ \left[ -\frac{\Delta_{\text{dis}} G_{\text{CuCl}}^0}{RT} \right]_{\text{ternary}} = \ln(S_{CuCl}^2 \gamma_{Cu^2} \gamma_{Cl^-}) \]  

(6-14)

and solving for \( S_{CuCl} \) in Eq. (6-14):

\[ S_{CuCl} = \frac{\exp\left[ -\frac{\Delta_{\text{dis}} G_{\text{CuCl}}^0}{RT} \right]_{\text{ternary}} \gamma_{Cu^2} \gamma_{Cl^-}}{\gamma_{Cu^2} \gamma_{Cl^-}} \]  

(6-15)

Following a similar approach, the chemical equilibria for dissolution of HCl(g) in H2O(l) is given by [77]:

\[ HCl_{(g)} \leftrightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)} \]  

(6-16)

\[ HCl_{(g)} \leftrightarrow HCl_{(aq)} \]  

(6-17)

\[ HCl_{(aq)} \leftrightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)} \]  

(6-18)

with equilibrium constant given by:
\[
K_{\text{HCl}} = \frac{a_{\text{H}^+}a_{\text{Cl}^-}}{a_{\text{HCl}}} = \frac{C_{\text{H}^+}C_{\text{Cl}^-} \gamma_{\text{H}^+} \gamma_{\text{Cl}^-}}{a_{\text{HCl}}} \quad (6-19)
\]

Eq. (6-19) can be rewritten in terms of the Gibbs free energy changes associated with Eqs. (6-17) and (6-18) as follows:

\[
-\frac{\Delta_{\text{dis}}G_0^0}{RT} = \ln K_{\text{HCl}} \quad (6-20)
\]

Eq. (6-20) can be rewritten as:

\[
-\frac{\Delta_{\text{dis}}G_0^0}{RT} = \ln(S_{\text{HCl}}^2 \gamma_{\text{H}^+} \gamma_{\text{Cl}^-}) \quad (6-21)
\]

and solving Eq. (6-21) for \( S_{\text{HCl}} \), the following expression is obtained:

\[
S_{\text{HCl}} = \sqrt[\gamma_{\text{H}^+} \gamma_{\text{Cl}^-}]{\exp \left[-\frac{\Delta_{\text{dis}}G_0^0}{RT}\right]} \quad (6-22)
\]

Dividing Eq. (6-15) by Eq. (6-22) for non-dimensionalization, the following is obtained:

\[
\frac{S_{\text{CuCl}}}{S_{\text{HCl}}} = \frac{\gamma_{\text{H}^+}}{\gamma_{\text{Cu}^+}} \sqrt[\gamma_{\text{H}^+} \gamma_{\text{Cl}^-}]{\exp \left[-\frac{\Delta_{\text{dis}}G_0^0 - \Delta_{\text{dis}}G_0^0_{\text{CuCl}}}{RT}\right]} \quad (6-23)
\]

At this point OLI Systems can be used to obtain an accurate expression for dissolution [73,77] however, since data for activity coefficients is unavailable due to the many complexes that can be formed in the solution, the ternary system was approximated by two binary aqueous subsystems as follows [80]:
\[
\left[ \frac{-\Delta_{\text{dis}} G_{\text{CuCl}}^{\text{plx}}}{RT} \right]_{\text{ternary}} = \left[ -\frac{-\Delta_{\text{dis}} G_{\text{CuCl}}^0}{RT} \right]_{\text{binary}} + \left[ -\frac{-\Delta_{\text{dis}} G_{\text{HCl}}^0}{RT} \right]_{\text{binary}}
\]  

(6-24)

where \( \Delta_{\text{dis}} G_{\text{CuCl}}^{\text{plx}}, \Delta_{\text{dis}} G_{\text{CuCl}}^0 \) and \( \Delta_{\text{dis}} G_{\text{HCl}}^0 \) are the standard Gibbs free energy changes of the dissolution of CuCl to complexes, standard Gibbs free energy of CuCl and HCl, respectively. Since data for the binary systems is easily obtained, it was used to obtain a correlation to represent the solubility of CuCl in aqueous HCl for integration purposes.

Although expressing the ternary system in terms of binary systems is not a completely strict approach in thermodynamics, the analysis is employed in literature for complex systems with unavailable thermodynamic data [79, 80]. Following this approach and from the mass conservation law, the molar ratio of all solutes (i.e. CuCl(s) and HCl(g)) to solvent (i.e. H_2O(l)) in the ternary system can be expressed as follows:

\[
\frac{n_{\text{CuCl}} + n_{\text{HCl}}}{n_{\text{H}_2\text{O}}} = \frac{n_{\text{CuCl}}}{n_{\text{H}_2\text{O}}} + \frac{n_{\text{HCl}}}{n_{\text{H}_2\text{O}}}
\]  

(6-25)

where \( n_{\text{CuCl}}, n_{\text{HCl}} \) and \( n_{\text{H}_2\text{O}} \) are the moles of CuCl, HCl, and water in the ternary system, respectively.

For nondimensionalization, the following terms have been defined:

\[
S_{\text{CuCl}} = \frac{n_{\text{CuCl}}}{n_{\text{H}_2\text{O}}}
\]  

(6-26)

\[
S_{\text{HCl}} = \frac{n_{\text{HCl}}}{n_{\text{H}_2\text{O}}}
\]  

(6-27)
which represent the solubility of CuCl and HCl in the ternary system. Hence, Eq. (6-25) becomes:

\[
\frac{n_{\text{CuCl}} + n_{\text{HCl}}}{n_{\text{H}_2\text{O}}} = S_{\text{CuCl}} (\text{III}) + S_{\text{HCl}} (\text{III})
\] (6-28)

Both \(S_{\text{CuCl}}\) and \(S_{\text{HCl}}\) are dimensionless and indicate the solubility of CuCl and HCl in the ternary system, respectively, so they can be used for modelling purposes.

Figure 6.4 – Molar solubility of \(S_{\text{CuCl}}\) and \(S_{\text{HCl}}\) for different temperatures

Figure 6.4 shows the relationship between \(S_{\text{CuCl}}\) and \(S_{\text{HCl}}\) for temperatures of 0, 25, and 100\(^\circ\)C in the ternary system. There are many mathematical equations that can correlate the curve of each temperature. Since Figure 6.4 clearly shows that the solubility is increased with the addition of HCl, the solubility of CuCl and HCl in the ternary system could be correlated by the following calculation:
\[ S_{\text{CuCl}} = aS_{\text{HCl}}^b \]  

(6-29)

where \( a \) and \( b \) are coefficients independent of \( S_{\text{HCl}} \) and \( S_{\text{CuCl}} \). For modelling convenience, the temperature influence on the solubility is assumed to be reflected by these two coefficients:

\[ a = a(T) \]  

(6-30)

\[ b = b(T) \]  

(6-31)

Then Eq. (6-28) was applied to the solubility data of CuCl [36-39] in the ternary system at the temperatures of 0, 10, 15, 25, 35, 40, 50, 60, 80, and 100°C to obtain the following optimum expressions of \( a \) and \( b \) through the least squares method:

\[ a = 1.0993 \cdot 10^3 \left( \frac{RT}{\Delta G_{\text{HCl}}}^0 \right)^2 - 64.9082 \frac{RT}{\Delta G_{\text{HCl}}}^0 + 1.6322 \]  

(6-32)

\[ b = 4.0217 \cdot 10^2 \left( \frac{RT}{\Delta G_{\text{HCl}}}^0 \right)^2 - 44.0585 \frac{RT}{\Delta G_{\text{HCl}}}^0 + 1.9769 \]  

(6-33)

where \( \Delta G_{\text{HCl}}^0 \) is the standard Gibbs free energy change of the dissolution of HCl from gaseous form to an aqueous state with a value of 35.94 kJ/mol [72].

However, as the concentration of HCl approaches zero, the ternary system reduces to a binary system and consequently the solubility of CuCl in aqueous HCl should also reduce to the solubility of CuCl in water only. Thus, the modeling should be both mathematically and physically correct. The binary solubility behavior must be determined
and incorporated into the model. Experimental data for the solubility of CuCl in water at different temperatures is represented in Figure 6.5 [82].

A predictive model for the binary system is represented by:

\[
S_{\text{CuCl}} = 3.48 \cdot 10^4 \left( \frac{RT}{\Delta G_{\text{CuCl}}^0} \right)^{3.5}
\]  

(6-34)

where \( \Delta G_{\text{CuCl}}^0 \) is the Gibbs free energy of formation of CuCl with a value of 201.089 kJ/mol [72]. By combining Eqs. (6-29) and (6-34), a complete solubility model of the ternary system is given by:

\[
S_{\text{CuCl}} = a S_{\text{HCl}}^b + 3.48 \cdot 10^4 \left( \frac{RT}{\Delta G_{\text{CuCl}}^0} \right)^{3.5}
\]  

(6-35)

where coefficients \( a \) and \( b \) are given by Eqs. (6-32) and (6-33), respectively. Also, variables \( S_{\text{HCl}} \) and \( S_{\text{CuCl}} \) and the coefficients \( a \) and \( b \) in Eq. (6-35) are dimensionless.

The predictive performance of the model and the relative error will be discussed in Chapter 7. It is found that the mean relative error is mostly below 10\% in the temperature range of 10-60\(^\circ\)C. The small prediction error suggests that the assumptions for the solubility modeling are satisfactory for the temperature and concentration ranges of interest, although the correlation is not strict in thermodynamics.
6.5 Particle Dynamics and Dissolution Model

Consider a particle of mass \( m_p \) moving through a fluid under the action of an external force \( F_e \). Define the velocity of the particle relative to the fluid as \( v_p \), buoyant force on the particle, \( F_b \), and drag force, \( F_D \), then

\[
m_p \frac{dV}{dt} = F_e + F_b + F_D
\]  

(6-36)

where

\[
F_e = m_p g
\]  

(6-37)

\[
F_b = \rho g V_p
\]  

(6-38)

\[
F_D = \frac{1}{2} C_D \rho v_p^2 A_p
\]  

(6-39)

and \( C_D \) is the drag coefficient, \( V_p \) is the volume of the particle, \( A_p \) is the projected area of the particle. For the solid particle to be conveyed upward or suspended, the transport condition must be well-satisfied, meaning that the fluid velocity, \( v_f \), exceeds the hindered settling velocity of a non-spherical particle, \( v_s \):

\[
v_f \gg v_s
\]

The hindered settling velocity can be calculated using the model of Webber [83] as follows:

- Calculate particle related Re using Eq. (6-40);
\[
\text{Re}_s = \frac{v_p D_{\text{eq}}}{v_L}
\]

where \(D_{\text{eq}}\) is the equivalent diameter of the particle and \(v_L\) is the kinematic viscosity of the liquid. In this case, \(v_L\) is the kinematic viscosity of water at \(25^\circ\text{C}\) with a value of \(8.96 \times 10^{-7} \text{m}^2/\text{s}\).

- **Calculate drag coefficient, \(C_D\):**

\[
C_D = \frac{24}{\text{Re}_s} + \frac{4}{\sqrt{\text{Re}_s}} + 0.4
\]

- **Calculate particle’s settling velocity, \(v_t\):**

\[
v_t = \sqrt{\frac{4 D_{\text{eq}} \rho_s - \rho_l}{3 \rho_l \text{Re}_s C_D}}
\]

where \(\rho_s\) and \(\rho_l\) are densities of the solid and liquid, respectively. In this case, the density of the solid is the density of CuCl with a value of \(4,145 \text{ kg/m}^3\) and density of the liquid is the density of water at \(25^\circ\text{C}\) with a value of \(1,000 \text{ kg/m}^3\). The above equations were used to calculate quantities pertaining to particle dynamics. The data from experiments and analyzed by the methods described in Chapter 5 is tabulated in Table 6.1. There are two effects that must be taken into account when investigating particle dynamics. One of the effects is related to the concentration of the solids; however this effect was not investigated in this work as the particles were dropped one at a time and the concentration is very small. A second effect is related to the particle’s shape, which is described by the sphericity \(\psi\). Figure 6.5 shows the relationship between the sphericity, \(\text{Re}_s\), and the ratio.
of the hindering settling velocity and the terminal velocity of the particle where the hindered settling velocity is the velocity of the particles as a result of increasing the number of particles in the liquid and therefore creating wakes, increasing mixture viscosity and altering buoyancy effects. As a result, the hindered settling velocity should be used when analyzing CuCl dynamics in water or HCl.

Table 6.1 - Areas and velocities of particles of varying masses

<table>
<thead>
<tr>
<th>Area (mm²)</th>
<th>Equivalent Diameter (mm)</th>
<th>Major Axis (mm)</th>
<th>Minor Axis (mm)</th>
<th>Ecc</th>
<th>Orient (rad)</th>
<th>Shape</th>
<th>U vel (m/s)</th>
<th>V vel (m/s)</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.706</td>
<td>3.132</td>
<td>2.440</td>
<td>1.099</td>
<td>4.931</td>
<td>1.126</td>
<td>0.450</td>
<td>-0.155</td>
<td>-0.281</td>
<td>0.10</td>
</tr>
<tr>
<td>12.249</td>
<td>3.949</td>
<td>2.998</td>
<td>1.388</td>
<td>4.666</td>
<td>1.424</td>
<td>0.463</td>
<td>0.001</td>
<td>-0.016</td>
<td>0.10</td>
</tr>
<tr>
<td>5.340</td>
<td>2.608</td>
<td>1.662</td>
<td>1.062</td>
<td>2.449</td>
<td>-0.397</td>
<td>0.639</td>
<td>0.020</td>
<td>-0.242</td>
<td>0.40</td>
</tr>
<tr>
<td>12.695</td>
<td>4.020</td>
<td>2.191</td>
<td>1.929</td>
<td>1.290</td>
<td>0.543</td>
<td>0.880</td>
<td>0.000</td>
<td>-0.018</td>
<td>0.40</td>
</tr>
<tr>
<td>12.736</td>
<td>4.027</td>
<td>3.344</td>
<td>1.265</td>
<td>6.986</td>
<td>1.287</td>
<td>0.378</td>
<td>0.004</td>
<td>-0.017</td>
<td>0.50</td>
</tr>
<tr>
<td>4.556</td>
<td>2.409</td>
<td>2.531</td>
<td>0.597</td>
<td>17.992</td>
<td>-1.523</td>
<td>0.236</td>
<td>-0.005</td>
<td>-0.014</td>
<td>0.50</td>
</tr>
<tr>
<td>5.435</td>
<td>2.631</td>
<td>1.756</td>
<td>1.067</td>
<td>2.712</td>
<td>-1.123</td>
<td>0.608</td>
<td>-0.005</td>
<td>-0.010</td>
<td>0.50</td>
</tr>
<tr>
<td>6.436</td>
<td>2.863</td>
<td>2.418</td>
<td>0.880</td>
<td>7.541</td>
<td>1.347</td>
<td>0.364</td>
<td>0.000</td>
<td>-0.013</td>
<td>0.70</td>
</tr>
<tr>
<td>5.868</td>
<td>2.733</td>
<td>2.469</td>
<td>0.793</td>
<td>9.689</td>
<td>1.425</td>
<td>0.321</td>
<td>0.001</td>
<td>-0.017</td>
<td>0.70</td>
</tr>
<tr>
<td>12.898</td>
<td>4.052</td>
<td>2.437</td>
<td>1.783</td>
<td>1.870</td>
<td>1.519</td>
<td>0.732</td>
<td>0.000</td>
<td>-0.018</td>
<td>0.80</td>
</tr>
<tr>
<td>9.667</td>
<td>3.508</td>
<td>2.952</td>
<td>1.078</td>
<td>7.505</td>
<td>-1.559</td>
<td>0.365</td>
<td>0.007</td>
<td>-0.014</td>
<td>0.80</td>
</tr>
<tr>
<td>11.817</td>
<td>3.879</td>
<td>2.795</td>
<td>1.377</td>
<td>4.119</td>
<td>-1.307</td>
<td>0.493</td>
<td>-0.002</td>
<td>-0.014</td>
<td>0.90</td>
</tr>
<tr>
<td>8.126</td>
<td>3.216</td>
<td>1.842</td>
<td>1.473</td>
<td>1.564</td>
<td>-0.118</td>
<td>0.800</td>
<td>-0.005</td>
<td>-0.020</td>
<td>1.10</td>
</tr>
<tr>
<td>8.802</td>
<td>3.348</td>
<td>2.226</td>
<td>1.285</td>
<td>3.001</td>
<td>1.559</td>
<td>0.577</td>
<td>0.002</td>
<td>-0.015</td>
<td>1.10</td>
</tr>
<tr>
<td>15.413</td>
<td>4.430</td>
<td>2.652</td>
<td>1.920</td>
<td>1.908</td>
<td>-0.962</td>
<td>0.724</td>
<td>-0.004</td>
<td>-0.023</td>
<td>1.20</td>
</tr>
<tr>
<td>8.382</td>
<td>3.267</td>
<td>1.976</td>
<td>1.418</td>
<td>1.942</td>
<td>1.560</td>
<td>0.718</td>
<td>-0.005</td>
<td>-0.022</td>
<td>1.40</td>
</tr>
<tr>
<td>12.952</td>
<td>4.061</td>
<td>2.434</td>
<td>1.784</td>
<td>1.861</td>
<td>0.838</td>
<td>0.733</td>
<td>0.001</td>
<td>-0.020</td>
<td>2.10</td>
</tr>
<tr>
<td>23.079</td>
<td>5.421</td>
<td>2.821</td>
<td>2.719</td>
<td>1.076</td>
<td>-1.314</td>
<td>0.964</td>
<td>-0.001</td>
<td>-0.018</td>
<td>2.10</td>
</tr>
<tr>
<td>16.860</td>
<td>4.633</td>
<td>3.498</td>
<td>1.692</td>
<td>4.272</td>
<td>0.864</td>
<td>0.484</td>
<td>0.005</td>
<td>-0.017</td>
<td>2.20</td>
</tr>
<tr>
<td>16.900</td>
<td>4.639</td>
<td>3.128</td>
<td>1.830</td>
<td>2.921</td>
<td>1.371</td>
<td>0.585</td>
<td>-0.004</td>
<td>-0.017</td>
<td>2.60</td>
</tr>
<tr>
<td>36.207</td>
<td>6.790</td>
<td>3.998</td>
<td>3.027</td>
<td>1.745</td>
<td>-0.987</td>
<td>0.757</td>
<td>0.000</td>
<td>-0.024</td>
<td>3.10</td>
</tr>
<tr>
<td>14.980</td>
<td>4.367</td>
<td>2.667</td>
<td>1.897</td>
<td>1.977</td>
<td>-0.127</td>
<td>0.711</td>
<td>-0.004</td>
<td>-0.026</td>
<td>3.20</td>
</tr>
<tr>
<td>22.984</td>
<td>5.410</td>
<td>4.160</td>
<td>1.845</td>
<td>5.084</td>
<td>1.269</td>
<td>0.444</td>
<td>0.003</td>
<td>-0.019</td>
<td>3.30</td>
</tr>
<tr>
<td>32.475</td>
<td>6.430</td>
<td>3.767</td>
<td>2.830</td>
<td>1.771</td>
<td>-1.098</td>
<td>0.751</td>
<td>0.005</td>
<td>-0.022</td>
<td>4.50</td>
</tr>
</tbody>
</table>

*a Projected area of the particle parallel to the direction of motion, \(b\) Velocity in the horizontal plane, \(c\) Velocity in the vertical plane
Figure 6.5 - Influence of the sphericity $\Psi$ on settling velocity replotted from Ref. [83]

From Figure 6.5, it can be noted that the hindered settling velocity can be obtained based on $\text{Re}_s$, sphericity and particle terminal velocity. The next step is to calculate sphericity, which is obtained using the following expression:

\[
\Psi = \frac{2^{\frac{3}{2}} \sqrt{R_{\text{maj}} R_{\text{min}}^2}}{R_{\text{max}} + \frac{R_{\text{min}}^2}{\sqrt{R_{\text{maj}}^2 - R_{\text{min}}^2}} \ln \left( \frac{R_{\text{maj}} + \sqrt{R_{\text{maj}}^2 - R_{\text{min}}^2}}{R_{\text{min}}} \right)}
\]  

(6-43)

where $R_{\text{min}}$ and $R_{\text{maj}}$ are the minor and major radii of the particle, respectively. Results pertaining to this procedure will be presented and discussed in detail in the following chapter.
Chapter 7

Results and Discussion

“However beautiful the strategy, you should occasionally look at the results.”

Winston Churchill

In this chapter, the results pertaining to the analyses described in Chapters 4 and 6 are described. All the results are based on experimental data obtained from the setups described in Chapters 3 and 5. In Section 7.1, the proposed correlation for vapour entrainment in gas-liquid flows is obtained based on experimental data. The proposed correlation is applied to the electrolysis step in the thermochemical Cu-Cl cycle for hydrogen production to quantify the amount of HCl carried out of the vessel as it could degrade the efficiency of the cycle. The performance of the model and the error associated with the results are discussed. A design recommendation for vapour entrainment minimization during electrolysis and uncertainties associated with experimental data are discussed in Sections 7.2 and 7.3, respectively. Results pertaining to dissolution of CuCl in HCl are discussed in Section 7.4 where predictive models are proposed for reaction thermodynamics and reaction kinetics. Particle dynamics, design recommendations for improved dissolution and uncertainties associated with the experiments are discussed in Sections 7.4, 7.5 and 7.6, respectively. The design
recommendations are for integration of the oxygen reactor with the electrolysis in the Cu-Cl cycle for hydrogen production.

Once the factors affecting mass transfer have been identified and discussed in Chapter 4, it was necessary to obtain a correlation representing mass transfer in terms of the factors affecting it. In this section results pertaining to mass transfer in bubbly flows are presented and the correlation described in Chapter 4 is finalized. Furthermore, the amount of moisture carried to the surface of the liquid is determined for different gas flow rates.

7.1 Mass transfer Correlation in Gas-Liquid Systems

As previously mentioned, DynamicStudio software was used to acquire and process the images necessary for this analysis. Useful information such as size, position, shape and velocity of bubbles were extracted using the “shadow sizer processing” method. This was done after a set of calibration images was acquired so that conversion from pixels to metric was possible via a scale factor. After processing images, it was determined that the gas bubbles are irregular in shape and their diameters are different therefore each bubble carries a different amount of moisture. Also, the bubble’s shape is that of an ellipsoid which means that more mass is transferred across the boundary compared to spherical bubbles. The size of the bubbles also affects the amount of mass transferred across the boundary; more moisture is carried by the larger diameter bubbles. Another aspect enhancing mass transfer is the motion of the bubbles which was observed to be in a spiral motion therefore more mass is transferred across the interface. Since there is a difference
in concentration of gas and liquid, diffusive mass transfer occurs across the interfacial boundaries of the gas bubbles and due to the motion of the bubbles, mass transfer also occurs due to convection.

After determining the factors enhancing mass transfer across the interface of bubbles, it was determined that they can be expressed through dimensionless numbers such as Sherwood, Reynolds, Eotvos, aspect ratio and height to diameter ratio. These were obtained using MATLAB and applying the analysis presented in Chapter 4.

Prior to determining the exponents \( m_1, m_2, m_3 \) and \( m_4 \) in Eq. (4.15), scatter plots were generated using MATLAB to observe the relationship between \( Sh \) and \( Re \), \( Sh \) and \( Eo \), \( Sh \) and \( d/D \) and \( Sh \) and \( H/D \). The relationship between the PI terms for a flow rate of 0.5L/s is shown in Figures 7.1 – 7.4. Figure 7.1 shows the relationship between \( Sh \) and \( Re \). It is observed that a correlation exists between the terms, with \( Sh \) increasing as \( Re \) increases. In determining the goodness of fit, an \( R^2 \) value of 0.91 was obtained which indicates a good correlation between the points.

A scatter plot for to show the relationship between \( Sh \) and \( Eo \) was then generated and it is shown in Figure 7.2 and a correlation between the points is observed. Once again, it is noted that \( Sh \) increases as \( Eo \) increases therefore it is expected that \( Eo \) influences mass transfer. In this instance, a \( R^2 \) value of 0.88 was returned which also indicates a good correlation between the points.
Figure 7.1 – Plot of $Sh$ vs. $Re$ for gas input flow rate of 0.5L/s

Figure 7.2 – Plot of $Sh$ vs. $Eo$ for an input gat flow rate of 0.5 L/s
Subsequently, a scatter plot to investigate the relationship between Sh and aspect ratio was generated and it can be seen in Figure 7.3. From figure, it can be noted that there is no correlation between the points and therefore it is probable that the influence of the aspect ratio on mass transfer is negligible compared to the other terms in the correlation. Also, a goodness of fit of 0.001 was obtained which indicates no correlation between the points.

![Figure 7.3 – Plot of Sh vs. aspect ratio for input gas flow rate of 0.5 L/s](image)

Finally, a scatter plot to observe the correlation between Sh and height to diameter ratio was generated, which can be seen in Figure 7.4. A fit of the curve was then generated to obtain determine whether a correlation between the points exists. The goodness of fit returned an $R^2$ value of 0.77, which indicates a good correlation between the data points. It is noted from the figure that Sh decreases with increasing H/D however
this is expected since the height, H, is constant and varying parameter is the diameter of
the bubble, D. Therefore, a higher diameter means a lower H/D, which corresponds to a
higher Sh. It is also important to note that the best fit was obtained with an equation of the
form \( y = mx^b \), which is the form of the obtained correlation between the factors affecting
mass transfer and the amount of mass transfer.

A similar approach was followed in obtaining information regarding data at a flow
rate of 1 L/s. Figures 7.5 – 7.8 show the scatter plots of Sh vs. Re, Eo, aspect ratio and
height to diameter ratio. Similar to the results obtained for a flow rate of 0.5 L/s, a
correlation is observed in the plotted data of Sh vs. Re, Sh vs. Eo, and Sh vs. H/D.
Figure 7.5 – Plot of Sh vs. Re for input nitrogen gas flow rate of 1 L/s

Figure 7.6 – Plot of Sherwood number vs. Eotvos number for nitrogen gas input of 1 L/s
The $R^2$ values obtained as a result of the fit are 0.79, 0.73 and 0.76, respectively, which suggests a good correlation between the points. Also, a $R^2$ value of 0.04 is obtained for the fit of $Sh$ vs. $d/D$, which indicates that there is no correlation between the points. Once again, the best fit was obtained with an equation of the form $y = mx^b$, which is the form of the obtained correlation to be optimized.

![Figure 7.7 – Plot of Sherwood number vs. aspect ratio for nitrogen gas input flow rate of 1 L/s](image)

Results obtained for a flow rate of 1.5 L/s are displayed in Figures 7.9 – 7.12. In Figure 7.9 it is noted that there exists a correlation between the points for Re lower than 100 however, in calculating the goodness of fit all data was used and an $R^2$ value of 0.82 was obtained, which indicates a good correlation between the points.
Figure 7.8 – Plot of Sherwood number vs. H/D for nitrogen gas input flow rate of 1 L/s

Figure 7.9 – Plot of Sherwood number vs. Reynolds number for nitrogen gas input flow rate of 1.5 L/s
When plotting $\text{Sh}$ vs. $\text{Eo}$ and $\text{Sh}$ vs. $\text{H/D}$, a correlation between the points is noted and the returned $R^2$ values are 0.83 and 0.76, respectively. Observing Figure 7.11, it is apparent that no correlation exists between the $\text{Sh}$ and $\text{d/D}$, which is confirmed by the returned $R^2$ value of 0.1.

![Figure 7.10 – Plot of Sherwood number vs. Eotvos number for nitrogen gas input flow rate of 1.5 L/s](image)

Lastly, the data for 2 L/s was plotted in Figures 7.13 – 7.16. Similar to results obtained for 1.5 L/s, the plot of $\text{Sh}$ vs. $\text{Re}$ exhibits discrepancies at $\text{Res}$ higher than 100. However, a correlation is still noticed between the points and the goodness of fit returned an $R^2$ value of 0.86, which shows a good correlation between the points. The returned $R^2$ values for plots of $\text{Sh}$ vs. $\text{Eo}$ and $\text{Sh}$ vs. $\text{H/D}$ are 0.71 and 0.74 which shows an acceptable
correlation between the points. Once again, no correlation is observed between the point in Figure 7.15 and the returned $R^2$ value is 0.1.

Figure 7.11 – Plot of Sherwood number vs. aspect ratio for nitrogen gas input flow rate of 1.5 L/s

Figure 7.12 – Plot of Sherwood number vs. H/D for nitrogen gas input flow rate of 1.5 L/s
Figure 7.13 – Plot of Sherwood number vs. Reynolds number for nitrogen gas input flow rate of 2 L/s

Figure 7.14 – Plot of Sherwood number vs. Eotvos number for nitrogen gas input flow rate of 2 L/s
Figure 7.15 – Plot of Sherwood number vs. aspect ratio for nitrogen gas input flow rate of 2 L/s

Figure 7.16 – Plot of Sherwood number vs. H/D for nitrogen gas input flow rate of 2 L/s
Since it was determined that a correlation exists between \( \text{Sh} \) and other terms in the correlation and in order to finalize the correlation the exponents \( m_1, m_2, m_3 \) and \( m_4 \) have to be determined. Hence, MATLAB Optimization toolbox was employed to optimize exponents \( m_1, m_2, m_3, \) and \( m_4 \). Multifunction Genetic Algorithm (GA) was utilized and exponents were obtained as given in Eq. (7-1). The multifunction GA was used since the objective is to determine the exponents such that the correlation is applicable to all ranges of flow rates. Since four different flow rates were investigated in this thesis, it follows that four different objective functions were minimized. The exponents to be determined were constrained to an interval of 0 to 1 to be consistent with literature [21-31]. Also, not constraining the exponents between the two chosen values caused the algorithm to diverge for most of the runs. Convergence was achieved after 218 generations with a Pareto spread of 0.046 and average Pareto distance of 0.0016. The obtained exponents \( m_1, m_2, m_3 \) and \( m_4 \) are as shown in Eq. (7-1) below:

\[
\text{Sh} = \text{Re}^{0.6267} \text{Eo}^{0.4659} \left( \frac{d}{D} \right)^0 \left( \frac{H}{D} \right)^{0.5754}
\]  

(7-1)

It is observed that after optimization \( m_3 = 0 \) which implies that the term \( d/D \) does not influence the correlation. This is expected since it was determined from Figures 7.3, 7.7, 7.11 and 7.15 that there is no apparent correlation between \( \text{Sh} \) and the aspect ratio. From Eq. (7-1), it can also be deduced that the terms with the highest influence on mass transfer are \( \text{Re} \) and the height to diameter ratio. This is to be expected since mass transfer is due to the motion of bubbles through liquid and \( \text{Re} \) describes the motion and the longer the bubbles travel through the liquid the more mass is being transferred across the boundary.
Once the model was obtained, the performance must be evaluated. In order to evaluate the performance of the model, the mean relative error $\eta$ is defined as:

$$\eta = \sum_{i=1}^{n} \left| \frac{M - P}{M} \right| / n \times 100\%$$  \hspace{1cm} (7-2)

where $M$ represents the measured data, $P$ the predicted data, and $n$ the total number of data points. The performance of the predictive model for all flow rates is summarized in Table 7.1.

<table>
<thead>
<tr>
<th>Flow Rate (L/s)</th>
<th>Number of Data Points</th>
<th>Mean Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>379</td>
<td>3.82</td>
</tr>
<tr>
<td>1</td>
<td>689</td>
<td>5.62</td>
</tr>
<tr>
<td>1.5</td>
<td>1002</td>
<td>6.46</td>
</tr>
<tr>
<td>2</td>
<td>1391</td>
<td>7.75</td>
</tr>
</tbody>
</table>

From Table 7.1 it is noted that the mean relative error is the lowest for lower flow rates. This is predictable since it was noted that the correlation between $Sh$ and the other PI terms was exhibiting discrepancies at higher flow rates therefore increasing the expected error. This could be attributed to the larger count of bubbles and the introduced uncertainty associated with them. However, a mean relative error of less than 10% is demonstrated in all flow rates, which results in a good performance of the model.

The model was then validated and Figures 7.17 - 7.20 show its performance at 0.5L/s, 1L/s, 1.5L/s and 2L/s, respectively. Fifty data points for each flow rate were chosen at random to test the model and it can be seen that the response is within the error bounds for most instances for all tested flow rates.
Figure 7.17 – Performance of the obtained model for a nitrogen gas input flow rate of 0.5 L/s

Figure 7.18 – Performance of the obtained model for a nitrogen gas input flow rate of 1 L/s
Figure 7.19 – Performance of the obtained model for a nitrogen gas input flow rate of 1.5 L/s

Figure 7.20 – Performance of the model for a nitrogen gas input flow rate of 2 L/s
As it can be seen in Figures 7.17 through 7.20, the performance of the model is within the error bounds for the majority of the data indicating a good correlation between points. Also, Table 7.1 also suggest a good correlation between the data points as the error is below 10%. Additionally, the correlation is in agreement with other similar correlations found in literature [22-27]. This experimental data and correlation provide useful information for better understanding of diffusive mass transfer through bubbles, particularly for applications related to hydrogen production. Based on the obtained correlation, it is possible to calculate the amount of liquid carried by the bubbles to the surface of the liquid. This information is useful for designing of water electrolysis equipment and to determine the concentration change of aqueous HCl in the electrolysis step of the thermochemical Cu-Cl cycle for hydrogen production.

7.2 Mass Transfer Quantification

The results pertaining to the quantification of liquid carried by bubbles in gas-liquid flows are presented in this section. The approach for quantification was presented in Section 4.3.2. Eq. (4-17) is employed to obtain \( h_{\text{mass}} \) where \( \text{Sh} \) is given by Eq. (7-1). In the next step of the analysis the surface area, \( A_s \), of each bubble was calculated using Eq. (4-19). Once the surface area of each bubble and \( h_{\text{mass}} \) were obtained, they were substituted in Eq. (4-16) to obtain the rate of mass convection due to bubble motion through liquid. All calculations were performed using MATLAB and the results pertaining to different flow rates are tabulated in Table 7.2.
It is important to note that the results in Table 7.2 refer to the amount of liquid carried to the surface within one minute. Also, the quantity of liquid carried to the surface for a flow rate of 0.5, 1, 1.5 and 2 L/s corresponds to 379, 689, 1002 and 1391 generated bubbles, respectively. Since more bubbles are generated for higher flow rates, it was expected that more liquid would be carried to the surface which is validated in the calculations shown in Table 7.2.

Table 7.2 – Mass transfer quantification results

<table>
<thead>
<tr>
<th>Flow rate (L/s)</th>
<th>m (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.94x10^{-4}</td>
</tr>
<tr>
<td>1</td>
<td>7.39x10^{-3}</td>
</tr>
<tr>
<td>1.5</td>
<td>1.20x10^{-2}</td>
</tr>
<tr>
<td>2</td>
<td>1.88x10^{-2}</td>
</tr>
</tbody>
</table>

These results provide useful information regarding the amount of mass carried to the surface in bubbly flows such as those encountered in hydrogen production through water electrolysis and electrolysis reactor in the thermochemical Cu-Cl cycle for hydrogen production. Since the amount of liquid to the surface was calculated, a design recommendation for mass transfer minimization is presented in the next section.

7.3 Electrolysis Design Recommendations

Based on the experimental results and obtained correlation, design recommendations for mass transfer minimization in water electrolysis and electrolysis step of the thermochemical Cu-Cl cycle can be made.
From Eq. (4-16), it can be noted that in order to minimize the quantity of liquid carried out by bubbles, the mass transfer coefficient and surface area of bubbles should be minimized. For the mass transfer coefficient to be minimized Sh should be minimized therefore, it is necessary to explore the parameters affecting mass transfer in Eq. (7-1). As expected, it is necessary to minimize Reynolds number, Eotvos number and the height to diameter ratio.

Reynolds number is affected by parameters such as velocity of the bubble and its diameter. The velocity of the bubble is affected by parameters such as its diameter and its aspect ratio therefore the diameter of the bubble should be optimized for minimum Reynolds number. Likewise, Eo is a function of diameter and it follows that decreasing bubble’s diameter would decrease Eo. The last parameter to be optimized for minimizing mass transfer is the height of the vessel. It is noted that minimizing the distance travelled by the bubble through liquid would minimize the last term in Eq. (7-1) and therefore minimize mass transfer.

Another recommendation consists of designing a condenser, which would condense the liquid carried to the surface. The condenser can be designed based on the liquid quantification method presented in Section 4.3.2. However, this would introduce more components to the process and cost would be increased.
7.4 Uncertainties in Experimental Measurements and Results

An uncertainty analysis of the experimental results, apparatus and measuring techniques is investigated by considering the device accuracy, bias and precision error. The uncertainty, $U$, of the experimental results associated with Eq. (7-1) is determined by:

$$U_i = \sqrt{B_i^2 + P_i^2}$$

(7-3)

where $B$ and $P$ represent the bias and precision error, respectively. As shown in Table 7.3, the measuring devices used in the experiments have a relatively high accuracy and low bias error associated with their operation.

### Table 7.3 – Gas-liquid mass transfer device accuracy and precision

<table>
<thead>
<tr>
<th>Variable</th>
<th>Measurement device</th>
<th>Accuracy</th>
<th>Device range</th>
<th>Reference value</th>
<th>Relative bias error</th>
<th>Relative precision error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>Omega Rotameter</td>
<td>± 0.15</td>
<td>0 to 60 L/min</td>
<td>6 L/min</td>
<td>0.025</td>
<td>5.7x10^{-9}</td>
</tr>
<tr>
<td>[HCl]</td>
<td>Eppendorf Research plus pipette</td>
<td>± 2 µl</td>
<td>100 to 1000 µl</td>
<td>500 µl</td>
<td>0.004</td>
<td>-</td>
</tr>
<tr>
<td>$t$</td>
<td>Fisher Scientific traceable stopwatch</td>
<td>-</td>
<td>300 s</td>
<td>5 s</td>
<td>-</td>
<td>0.011</td>
</tr>
<tr>
<td>$A$</td>
<td>FlowSense 2ME Camera</td>
<td>-</td>
<td>1600x300 pixels</td>
<td>-</td>
<td>0.001</td>
<td>0.054</td>
</tr>
</tbody>
</table>
Consistent operating conditions are maintained during the uncertainty analysis, and the relative bias error is taken as the ratio of bias error to the corresponding reference value and the limit is calculated as follows:

\[ B_{S_h}^2 = \left( \frac{\partial S_h}{\partial D_{eq}} \right)^2 B_{eq}^2 + \left( \frac{\partial S_h}{\partial H} \right)^2 B_H^2 + \left( \frac{\partial S_h}{\partial V} \right)^2 B_V^2 + \left( \frac{\partial S_h}{\partial \sigma} \right)^2 B_\sigma^2 + \left( \frac{\partial S_h}{\partial \mu} \right)^2 B_\mu^2 + \left( \frac{\partial S_h}{\partial g} \right)^2 B_g^2 + \left( \frac{\partial S_h}{\partial \rho} \right)^2 B_\rho^2 \]

(7-4)

The precision error is double the standard deviation of the results [30]. A sample of 50 measurements at equilibrium conditions is considered for the precision error calculations. The propagation of precision error is determined as follows:

\[ P_{S_h}^2 = \left( \frac{\partial S_h}{\partial D_{eq}} \right)^2 P_{eq}^2 + \left( \frac{\partial S_h}{\partial H} \right)^2 P_H^2 + \left( \frac{\partial S_h}{\partial V} \right)^2 P_V^2 + \left( \frac{\partial S_h}{\partial \sigma} \right)^2 P_\sigma^2 + \left( \frac{\partial S_h}{\partial \mu} \right)^2 P_\mu^2 + \left( \frac{\partial S_h}{\partial g} \right)^2 P_g^2 + \left( \frac{\partial S_h}{\partial \rho} \right)^2 P_\rho^2 \]

(7-5)

In order to minimize error, the velocity information was extracted through combining a correlation algorithm and measuring displacement between two successive images via a dedicated particle-tracking algorithm. The setup was designed based on Refs. [84-86] so that the uncertainty associated with the experiment is minimized. The experimental error introduced due to the equipment and analysis as well as the deviation is shown in Table 7.4. It is observed that the highest error is due to calibration of the camera. In order to minimize this error, a calibration technique suggested in [69] was employed and compared with the calibration technique presented in DynamicStudio software.
A MATLAB code (see Appendix) is used to obtain the partial derivatives in Eqs. 7-4 and 7-5 and calculate the uncertainty associated with experimental results. The partial derivatives are given by Eqs. (7-6) through (7-12).

Table 7.4 – Uncertainties associated with camera

<table>
<thead>
<tr>
<th>Source of Error</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration</td>
<td>0.019</td>
</tr>
<tr>
<td>Residual</td>
<td>0.01</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.011</td>
</tr>
<tr>
<td>Vessel distortion</td>
<td>0.005</td>
</tr>
<tr>
<td>Analysis</td>
<td>0.009</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.054</strong></td>
</tr>
</tbody>
</table>

\[
\frac{\partial S_h}{\partial D_{eq}} = 0.6267 V \rho \left( \frac{H}{D} \right)^{0.5754} \left( \frac{D_{eq} \rho}{\sigma} \right)^{0.4659} \mu \left( \frac{D_{eq} \rho}{\mu} \right)^{0.3733} + 0.9318 D_{eq} \rho \left( \frac{H}{D} \right)^{0.5754} \left( \frac{D_{eq} \rho}{\mu} \right)^{0.6267} \left( \frac{D_{eq} \rho}{\sigma} \right)^{0.5341}
\]

(7-6)

\[
\frac{\partial S_h}{\partial H} = 0.5754 V \rho \left( \frac{D_{eq} \rho}{\mu} \right)^{0.6267} \left( \frac{D_{eq} \rho}{\sigma} \right)^{0.4659} \left( \frac{H}{D} \right)^{0.4246} D
\]

(7-7)

\[
\frac{\partial S_h}{\partial V} = 0.6267 D_{eq} \rho \left( \frac{H}{D} \right)^{0.5754} \left( \frac{D_{eq} \rho}{\sigma} \right)^{0.4659} \mu \left( \frac{D_{eq} \rho}{\mu} \right)^{0.3733}
\]

(7-8)
\[
\frac{\partial S_h}{\partial \sigma} = - \frac{0.4659D_{eq}^2g\rho (\frac{H}{D})^{0.5754} \left( \frac{D_{eq}V\rho}{\mu} \right)^{0.6267}}{\sigma^2 \left( \frac{D_{eq}^2g\rho}{\sigma} \right)^{0.5341}} 
\]

(7-9)

\[
\frac{\partial S_h}{\partial \mu} = - \frac{0.6267D_{eq} V\rho (\frac{H}{D})^{0.5754} \left( \frac{D_{eq}^2g\rho}{\sigma} \right)^{0.4659}}{\mu^2 \left( \frac{D_{eq}V\rho}{\mu} \right)^{0.3733}} 
\]

(7-10)

\[
\frac{\partial S_h}{\partial g} = \frac{0.4659D_{eq}^2g\rho (\frac{H}{D})^{0.5754} \left( \frac{D_{eq}V\rho}{\mu} \right)^{0.6267}}{\sigma \left( \frac{D_{eq}^2g\rho}{\sigma} \right)^{0.5341}} 
\]

(7-11)

\[
\frac{\partial S_h}{\partial D_{eq}} = \frac{0.6267D_{eq} V\rho (\frac{H}{D})^{0.5754} \left( \frac{D_{eq}^2g\rho}{\sigma} \right)^{0.4659}}{\mu \left( \frac{D_{eq}V\rho}{\mu} \right)^{0.3733}} + \frac{0.4659D_{eq}^2g\rho (\frac{H}{D})^{0.5754} \left( \frac{D_{eq}V\rho}{\mu} \right)^{0.6267}}{\sigma \left( \frac{D_{eq}^2g\rho}{\sigma} \right)^{0.5341}} 
\]

(7-12)

Eqs. (7-6) through (7-12) are then substituted into Eq. (7-4) and (7-5) to determine the uncertainty propagated due to bias and precision limits. This step is performed using MATLAB and the uncertainty for different flow rates is tabulated in Table 7.5.
Table 7.5 – Uncertainties for gas-liquid flows

<table>
<thead>
<tr>
<th>Flow rate (L/s)</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.0382</td>
</tr>
<tr>
<td>1</td>
<td>0.0383</td>
</tr>
<tr>
<td>1.5</td>
<td>0.0414</td>
</tr>
<tr>
<td>2</td>
<td>0.0434</td>
</tr>
</tbody>
</table>

7.5 Dissolution Rate Optimization

In order to optimize a system’s dissolution rate, it is important to recognize that a chemical reaction has kinetic and thermodynamic aspects. Kinetics refers to the energy input required to move the reaction from a state of stability whereas to that of converting itself to a state of products, therefore kinetics is related to reactivity. The reactivity of the reactants (i.e. the activation energy required for the reaction to take place) is expressed through a rate constant, k. Therefore, reaction kinetics gives information regarding the rates of reaction and how fast equilibrium is reached however, it does not provide information about the equilibrium conditions. Hence, reaction thermodynamics is employed.

Unlike reaction kinetics, the most stable state of a thermodynamic reaction is in the form of products therefore, thermodynamics provides us with information regarding the spontaneity of reaction without the need of added energy. The quantity used to give information regarding the stability of the products relative to that of reactants is Gibbs free energy, which is described in next section.
Since thermodynamics gives information regarding the equilibrium conditions of solid CuCl dissolving in aqueous HCl and reaction kinetics gives information regarding the rate of reaction, it is important to determine both thermodynamic and kinetic limit for optimum dissolution.

### 7.6 Reaction Thermodynamics

In general, thermodynamics refers to the different forms of energy that are converted every time a reaction occurs which are written in terms of Gibbs free energy such that:

\[ \Delta G = \Delta H - T\Delta S \]  

where \( \Delta H \) is reaction enthalpy, \( \Delta S \) is the entropy and \( T \) is temperature. When \( \Delta G \) is positive, the reaction takes energy from the environment and it is said to be nonspontaneous whereas a negative \( \Delta H \) indicates release of energy usually in the form of temperature and the reaction is spontaneous which is the case of CuCl dissolving in HCl as shown in Chapter 6.

As previously stated, reaction thermodynamics indicates the solubility of CuCl in HCl (i.e. reaction equilibrium) without considering the rate of reaction. It can be noted in Figure 7.22 that the increase of the HCl concentration in the ternary system favours the dissolution of CuCl at different temperatures. As a result, a model describing the solubility of CuCl in HCl as a function of temperature and reaction’s activation energy was developed using the strategy presented in Chapter 6.
In order to obtain the predictive model given by Eq. (6-35) which, relates the solubility of CuCl to the activation energy, temperature and concentration of HCl, experimental data was obtained from literature [36-38]. The behavior of CuCl in a binary system was first investigated and presented in Figure 7.23. It can be noted that the solubility of CuCl in water at low temperatures is negligible; however, the reaction is favoured with increasing temperature. Eq. (6-34) gives the mathematical model relating solubility to temperature. This was obtained after fitting the experimental data with an $R^2$ value of 0.9972 and RMSE of 0.000204, which indicates a good correlation between the data points.

![Figure 7.21 – CuCl solubility in the ternary system for temperatures of 10, 25, and 80°C](image-url)
Figure 7.22 - Molar ratios of $S_{\text{CuCl}}$ and $S_{\text{HCl}}$ for temperatures of 0, 25, and 100°C

Figure 7.23 - Comparison of experimental data and model predictions for dissolution of CuCl in H$_2$O
Experimental data for the ternary system at 0°C, 10°C, 20°C, 25°C, 30°C, 40°C, 60°C, 80°C and 100°C was then investigated to determine a mathematical model relating solubility of CuCl to the factors favouring solubility without investigating the rate of reaction. The data for 0°C, 30°C, 60°C, and 100°C is plotted in Figures 7.24 - 7.27, respectively. From the figures, it can be noted that the data follows a power curve given by Eq. (6-29) with a and b at different temperatures tabulated in Table 7.6. From Table 7.6 it can also be noted that the $R^2$ values are between 0.9933 and 0.9997, which indicates a very good correlation between the data points.

Table 7.6 – Coefficients of power curves and corresponding error for various temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>a</th>
<th>b</th>
<th>R² value</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.733</td>
<td>2.003</td>
<td>0.9995</td>
<td>1.85x10⁻⁴</td>
</tr>
<tr>
<td>10</td>
<td>1.560</td>
<td>1.900</td>
<td>0.9998</td>
<td>1.15x10⁻⁴</td>
</tr>
<tr>
<td>20</td>
<td>1.257</td>
<td>1.760</td>
<td>0.9933</td>
<td>8.11x10⁻⁴</td>
</tr>
<tr>
<td>25</td>
<td>1.221</td>
<td>1.721</td>
<td>0.9996</td>
<td>1.98x10⁻⁴</td>
</tr>
<tr>
<td>30</td>
<td>1.119</td>
<td>1.657</td>
<td>0.9997</td>
<td>1.99x10⁻⁴</td>
</tr>
<tr>
<td>40</td>
<td>1.006</td>
<td>1.565</td>
<td>0.9996</td>
<td>2.47x10⁻⁴</td>
</tr>
<tr>
<td>60</td>
<td>1.347</td>
<td>1.578</td>
<td>0.9937</td>
<td>1.3x10⁻⁴</td>
</tr>
<tr>
<td>80</td>
<td>0.742</td>
<td>1.278</td>
<td>0.9991</td>
<td>5.12x10⁻⁴</td>
</tr>
<tr>
<td>100</td>
<td>0.674</td>
<td>1.174</td>
<td>0.9989</td>
<td>6.54x10⁻⁴</td>
</tr>
</tbody>
</table>

The next step in obtaining the predictive model given by Eq. (6-35) was to determine a relationship between the obtained coefficients in Eq. (6-29) and temperature (i.e. activation energy). After optimization using non-linear least square estimate a relationship for coefficients a and b was determined which is given by Eq. (6-32) and (6-33), respectively.
Figure 7.24 - Comparison of experimental data and model predictions at 0°C

Figure 7.25 - Comparison of experimental data and model predictions at 30°C
Figure 7.26 - Comparison of experimental data and model predictions at 60°C

Figure 7.27 - Comparison of experimental data and model predictions at 100°C
Table 7.7 – Mean relative error of the reaction thermodynamics model

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Number of data points</th>
<th>Mean Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14</td>
<td>1.23</td>
</tr>
<tr>
<td>10</td>
<td>14</td>
<td>1.15</td>
</tr>
<tr>
<td>20</td>
<td>14</td>
<td>1.07</td>
</tr>
<tr>
<td>25</td>
<td>14</td>
<td>1.01</td>
</tr>
<tr>
<td>30</td>
<td>14</td>
<td>0.96</td>
</tr>
<tr>
<td>40</td>
<td>14</td>
<td>0.85</td>
</tr>
<tr>
<td>60</td>
<td>14</td>
<td>0.56</td>
</tr>
<tr>
<td>80</td>
<td>14</td>
<td>0.35</td>
</tr>
<tr>
<td>100</td>
<td>14</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Figure 7.28 - Comparison of experimental data and model predictions at 10, 20, 40 and 80°C

In order to evaluate the performance of the model, the mean relative error $\eta$ is used as shown in Eq. (7-2). The binary model’s accuracy is 0.01% whereas the performance of
the ternary model at all temperatures is summarized in Table 7.7. Figure 7.28 shows the predictive performance of the ternary model at 10, 20, 40 and 80°C.

A model for reaction thermodynamics was obtained however, the model does not give full information about the dissolution of CuCl in HCl; it provides information about the equilibrium of the reaction. In order to have a solid understanding of dissolution of CuCl in HCl it is necessary to investigate reaction kinetics which is presented in next subsection.

7.7 Reaction Kinetics

Reaction kinetics studies the rates of chemical processes investigating the speed of reaction in different experimental conditions such as varied temperatures, pressures, concentrations and presence of catalysis. Mathematical models are then constructed to describe the characteristics of the chemical reaction in terms of its transition states and reaction mechanisms.

The dissolution of solid CuCl particle in aqueous HCl is described as an elementary reaction the chemical species react directly to form products. As discussed in Section 6.4, this process is given by:

$$\text{CuCl}_{(s)} \rightleftharpoons \text{Cu}^{\text{cplx}}_{(aq)} + \text{Cl}^{\text{cplx}}_{(aq)}, k_r$$

(7-14)

where $k_r$ is the reaction constant.

The rate constant $k_r$ describes how fast a chemical reaction reaches equilibrium; that is how fast the reactants are turned into products due to activation energy enabling the
reaction to move forward. Without activation energy, the reaction would not take place as shown in previous section (i.e. CuCl does not dissolve in a binary system at low temperature and the dissolution rate increases with the increase in concentration of HCl).

The rate reaction $k$ and the kinetic energy required for activation of reaction tell us how fast this reaction will reach equilibrium (i.e. how fast reactants are fully converted to products).

Therefore, the integrated rate law of a first-order reaction is:

$$\ln[\text{CuCl}]_t = -k_r t + \ln[\text{CuCl}]_0$$

Eq. (7-15) can be rearranged as follows:

$$\ln\left(\frac{[\text{CuCl}]_t}{[\text{CuCl}]_0}\right) = -k_r t$$

(7-16)

Solving Eq. (7-16) results in:

$$[\text{CuCl}]_t = [\text{CuCl}]_0 e^{-k_r t}$$

(7-17)

where $[\text{CuCl}]_0$ is initial concentration of CuCl, $[\text{CuCl}]_t$ is the concentration of CuCl at time $t$, $k_r$ is the rate constant and $t$ is elapsed time.

This analysis is applied in this section however, the change in area of the solid CuCl particle is examined, rather the concentration. The particles are examined using the methodology presented in Chapter 5. Solid CuCl particles of the same mass (i.e. 7mg) were dropped in quiescent HCl solution and the change in area was recorded. Figures 7.29 - 7.31 illustrate the change in area for particles dissolving in 6M, 9M and 12M HCl.
solution, respectively, where $M$ is the molarity of the solution. It is important to note that although the particles have the same mass, the projected area recorded by the camera is different due to the irregular shape of the particles.

![Graph](image)

Figure 7.29 – Dissolution of CuCl particle in a 6M HCl quiescent solution

It is observed in Figure 7.29 that the particle’s area decreases exponentially and the equation of the line is:

$$A_{6M} = 9.874 \times e^{-0.00031t}$$  \hspace{1cm} (7-18)

where $A_{6M}$ represents the surface area, and $t$ is the time. This representation returned an R-squared value of 0.974, which indicates a good correlation between the variables. Also, it can be estimated that a change in area of approximately 3.5 mm$^2$ would take about 1,500 seconds.
By the same procedure, a model for particle dissolution in 9M HCl quiescent solution is obtained (see Figure 7.30) which is of the following form:

\[ A_{9M} = 12.97e^{-0.0057t} \]  

(7-19)

where \( A_{9M} \) represents the surface area of particle dissolving in 9M HCl, and \( t \) is the time. This representation returned an R-squared value of 0.9801, which indicates a good correlation between the variables. Also, it can be estimated that a decrease in area from 12.6 mm\(^2\) to 4.86 mm\(^2\) would take about 1,500 seconds.
Lastly, from Figure 7.31 it can be noted that the solid particle’s area change follows an exponential decrease given by:

\[ A_{12M} = 9.706e^{-0.00083t} \]  \hspace{1cm} (7-20)

where \( A_{12M} \) represents the surface area, and \( t \) is the time. This representation returned an R-squared value of 0.9811, which indicates a good correlation between the variables. Also, a change in area from 9.62 mm\(^2\) to 3.43 mm\(^2\) took about 1,100 seconds.

A relationship between the exponents as a function of concentration of HCl is needed. Through a semi-mechanistic approach based on non-linear least square method, a relationship for the exponents was determined as follows:

\[ k_{r,q} = -8.696 \cdot 10^{-5}[HCl] + 0.00021 \]  \hspace{1cm} (7-21)
where \( k_{r,q} \) describes the dissolution rate in quiescent HCl solution.

Also, it is to be noted that constants 9.874, 12.97 and 9.706 in Eq. (7-18), (7-19) and (7-20), respectively, are the initial projected areas of the CuCl particles. Therefore, an expression for expressing the change in area of CuCl particles in quiescent HCl solution is given by:

\[
A_{t,q} = A_0 e^{-k_{r,q} t}
\]  
(7-22)

where \( A_{t,q} \) is the projected area changing as a function of time \( t \) in quiescent solution, \( A_0 \) is the initial area and \( k_{r,q} \) is given by Eq. (7-21).

Similarly, the data pertaining to the dissolution rate of solid CuCl in 6M, 9M and 12M aqueous HCl in the presence of nitrogen as the mixing agent is observed in Figures 7.32 – 7.34.

Figure 7.32 – Dissolution of CuCl particle in a 6M HCl solution with mixing
An exponential dissolution rate is again observed in Figure 7.32 and the equation is given by:

\[ A_{6M} = 11.87e^{-0.00074t} \]  
(7-23)

This returned an R-squared value of 0.9938, which indicates a good correlation between the points. From Figure 7.32, it is estimated that a change in the area of the particle of approximately 4 mm\(^2\) would take about 700 seconds. Therefore, when nitrogen bubbles are introduced as a mixing agent, the time to dissolve a particle with the same area is halved.

Similarly, a model for particle dissolution in 9M HCl solution (see Figure 7.33) is obtained which is of the following form:

\[ A_{9M} = 6.809e^{-0.00098t} \]  
(7-24)

where \(A_{9M}\) represents the surface area of particle dissolving in 9M HCl, and \(t\) is the time. This representation returned an R-squared value of 0.9762, which indicates a good correlation between the points. Also, it can be estimated that a decrease in area from 6.94 mm\(^2\) to 3.59 mm\(^2\) takes about 750 seconds.

Finally, Figure 7.34 pertains to dissolution of solid CuCl particle in 12M HCl and the change in projected area is given by:

\[ A_{12M} = 13.77e^{-0.0012t} \]  
(7-25)

This returned an R-squared value of 0.9438, which indicates a good correlation between the points. From Figure 7.34, it is estimated that a change in projected area of the
particle from 13.1 mm$^2$ to 6.21 mm$^2$ takes about 560 seconds. Therefore, when nitrogen bubbles are introduced as a mixing agent, the time to dissolve particles is halved.

Figure 7.33 – Dissolution of CuCl particle in a 9M HCl solution with mixing

Figure 7.34 – Dissolution of CuCl particle in a 12M HCl solution with mixing
Similar to the procedure described for particles dissolving in quiescent solution, it is necessary to obtain a relationship describing the exponents in terms of HCl concentration. The same semi-mechanistic model described above was applied to determine a relationship as follows:

\[ k_{r,m} = 7.671 \times 10^{-5} [\text{HCl}] + 0.00029 \]  \hspace{1cm} (7-26)

Also, constants 11.87, 6.81 and 13.77 in Eq. (7-23) to (7-25) in the presence of mixing is obtained as follows:

\[ A_{t,m} = A_0 e^{-k_{r,m}t} \]  \hspace{1cm} (7-27)

where \( A_{t,m} \) is the area changing with time \( t \) in the presence of mixing, \( A_0 \) is the initial projected area of the particle and \( k_{r,m} \) is given by Eq. (7-26).

In order to evaluate the performance of the model, Eq. (7-2) was employed to calculate the mean relative error \( \eta \). The performance of the model at different HCl concentrations, with and without mixing is summarized in Table 7.8.

**Table 7.8 – Mean relative error of the reaction kinetics predictive model**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Molarity (M)</th>
<th>Number of Data Points</th>
<th>Mean Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid-Solid</td>
<td>6</td>
<td>4</td>
<td>2.71</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>5</td>
<td>12.68</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>5</td>
<td>28.39</td>
</tr>
<tr>
<td>Gas-Liquid-Solid</td>
<td>6</td>
<td>4</td>
<td>4.87</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>5</td>
<td>4.64</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>5</td>
<td>6.49</td>
</tr>
</tbody>
</table>
Figure 7.35 – Dissolution of CuCl particle in a 6M HCl quiescent solution

Figures 7.35 and 7.36 shows the performance of the predictive model for quiescent solution and non-quiescent solution, respectively. From figures, it is noted that the performance of the model is within the error bounds. For a better accuracy of the model more data points will be used in future studies.

Figure 7.36 – Dissolution of CuCl particle in a 9M HCl solution with mixing
Based on the above results, it is noted that since the temperature is constant, the concentration of HCl is what drives the reaction to move forward, therefore providing the activation energy for the reaction kinetics. However, the reaction kinetics is limited by thermodynamics in that once the solution is saturated, reaction kinetics will not take place. The limit is given by Eq. (6-35), which in future studies, will be combined with Eq. (7-22) and (7-27) to obtain a sound mathematical model.

7.8 Particle Dynamics

The main forces acting on a falling particle are gravitational, buoyant (i.e. force opposing gravitational force) and drag (i.e. force that appears whenever there is motion of the particle relative to fluid) as shown in Eq. (6-36). For a particle at rest, the gravitational force and buoyant force are equal and opposite whereas for a particle in motion a drag force, which is a function of particle’s velocity, opposes gravitational force. The particle’s velocity increases until gravitational force and drag force are equal, at which point there is no further change in particle’s velocity and this velocity is referred to as terminal velocity. A falling particle’s terminal velocity is affected by parameters altering drag; therefore the terminal velocity is most notably dependent upon particle size, particle’s shape (i.e. sphericity) and its density. Also, drag is affected by fluid parameters such as viscosity and density of the fluid.

The behavior of single spherical particles in an infinite fluid can be described by Stokes, transitional and Newtonian settling models. However these models have limitations in practical applications since the walls of the vessel and other particles can
also affect particle’s velocity. Therefore, it is important to consider the interaction of particles in the fluid, or the interaction of the particles with the container walls in practical applications such as the copper-chlorine cycle. For this reason, hindered settling velocity was considered in the analysis of particle dynamics for improved dissolution in this thesis. Subsequently, a semi-analytic is used in this research to perform meaningful hindered settling calculations, as presented in Chapter 6.

The first step in the analysis is to calculate Reₘ using Eq. (6-40) and particle’s instantaneous velocity as recorded by the camera. Reₘ gives information about the flow of particles, whether laminar or turbulent so the proper analysis can be carried on. From Table 7.9, it is noted that Reₘ > 1 therefore Stoke’s law for calculating drag is not suitable and hence, Newtonian law was used for this analysis [87]. Consequently, Eq. (6-41) and (6-42) were employed in calculating terminal velocity. Once Reₘ, particle’s terminal velocity and sphericity were calculated, the hindered settling velocity of the particle was obtained from Figure 6.5. The data is tabulated in Table 7.9.

From Table 7.9 it can be observed that the hindered settling velocity ranges from about 0.27 to 0.63 m/s for the tested particles. Therefore, for all the particles to be suspended, the flow velocity must be much greater than the upper range of the hindered settling velocity. A design recommendation for integration purposes based on the above findings will be discussed in the next section.
In this section, a method for integration of the electrolysis reactor and oxygen reactor in the thermochemical Cu-Cl cycle is presented. From results presented in Chapters 6 and 7, it can be concluded that higher the concentration of aqueous HCl and the temperature of operation, the faster the dissolution of solid CuCl. Hence, it is recommended for the integration to be performed at higher temperatures.
From Eq. (6-34) and Figure 7.23, it can be concluded that CuCl dissolves in water at higher temperatures. In this case, one possibility for integration would be to first quench the CuCl overflowing out of oxygen reactor to obtain a CuCl-water slurry. This process has been studied by the research group at UOIT for heat recovery purposes, such that the molten CuCl quenched in water generates steam needed in the hydrolysis reactor. Since CuCl’s solubility increases with increased HCl concentration and temperature, the CuCl-water slurry will then be mixed with high concentration (i.e. 12M) aqueous HCl for further dissolution. For better efficiency of the electrolysis, the solution’s temperature should be monitored such that it is kept at an optimum. Since the temperature of the CuCl water slurry is dependent on the heat transfer of the quenching process, the variable that can be optimized would be the temperature of HCl such that the desired ternary solution temperature is obtained for improved efficiency of electrolysis. Also, as described in Section 7.2, the concentration of HCl could be decreasing due to HCl vapor loss from gas-liquid phase flow. Therefore, calculating the mass transfer in the multiphase system using the proposed Eq. (7-1) will monitor the concentration of HCl such that the amount of HCl carried out during integration can be obtained.

From the proposed Eq. (7-22) it can be noted that the reaction kinetics is improved with increasing HCl concentration. From Eq. (6-35) it is concluded that the reaction thermodynamics is improved with increasing HCl concentration and temperature in a ternary system. Therefore, an alternative design approach could be the quenching of solid CuCl in a solution of HCl and water. For improved dissolution, the quenched particles will be suspended by introducing a counterflow with a velocity obtained using the method presented in Section 6.5. Similar to the previous recommendation, the temperature and
concentration of HCl will be monitored in this procedure for improved efficiency of electrolysis and optimum integration of the cycle. Although this method for integration presents more viable due to the improved dissolution and less steps for achieving the desired solution, the drawback is that the heat cannot be recovered and provided to the hydrolysis reactor, as presented in the previous recommendation. This is due to HCl being present in the steam produced as a result of quenching; therefore, a cost and efficiency analysis for both suggested methods of integration is necessary prior to integrating and the most viable method for improved efficiency and minimized cost should be implemented.

7.10 Uncertainties in Experimental Measurements and Results

The 95% confidence uncertainty associated with the experimental result, A, in Eq. (7-27) is calculated using Eq. (7-3). The steps in calculating the uncertainty are explained in detail in Section 7.3 and are applied to this analysis as follows:

\[ P_A^2 = \left( \frac{\partial A}{\partial A_0} \right)^2 P_{A_0}^2 + \left( \frac{\partial A}{\partial [HCl]} \right)^2 P_{[HCl]}^2 + \left( \frac{\partial A}{\partial t} \right)^2 P_t^2 \]  \hspace{1cm} (7-28)

\[ B_A^2 = \left( \frac{\partial A}{\partial A_0} \right)^2 B_{A_0}^2 + \left( \frac{\partial A}{\partial [HCl]} \right)^2 B_{[HCl]}^2 + \left( \frac{\partial A}{\partial t} \right)^2 B_t^2 \]  \hspace{1cm} (7-29)

The precision and bias errors used in Eq. (7-28) and (7-29) are obtained from manufacturer’s manuals and are presented in Table 7.10. Once the precision and bias errors are defined, the partial derivatives with respect to the variables are computed.
The partial derivatives with respect to the variables in Eq. (7-28) are obtained using the MATLAB code presented in Appendix so that the partial derivative with respect to initial area, HCl concentration and time is given by Eq. (7-30), (7-31) and (7-32), respectively.

\[
\frac{\partial A}{\partial A_0} = e^{-(7.671 \cdot 10^{-5} \cdot [\text{HCl}] + 2.9 \cdot 10^{-4})t} \quad (7-30)
\]

\[
\frac{\partial A}{\partial [\text{HCl}]} = -7.671 \cdot 10^{-5} \cdot A_0 \cdot e^{-(7.671 \cdot 10^{-5} \cdot [\text{HCl}] + 2.9 \cdot 10^{-4})t} \quad (7-31)
\]

\[
\frac{\partial A}{\partial t} = -A_0 \left(7.671 \cdot 10^{-5} \cdot [\text{HCl}] + 2.9 \cdot 10^{-4}\right) e^{-(7.671 \cdot 10^{-5} \cdot [\text{HCl}] + 2.9 \cdot 10^{-4})t} \quad (7-32)
\]

Table 7.10 – Device accuracy and precision for liquid solid mass transfer

<table>
<thead>
<tr>
<th>Variable</th>
<th>Measurement device</th>
<th>Accuracy</th>
<th>Device range</th>
<th>Reference value</th>
<th>Relative bias error</th>
<th>Relative precision error</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>Omega Rotameter</td>
<td>± 0.15</td>
<td>0 to 60 L/min</td>
<td>6 L/min</td>
<td>0.025</td>
<td>5.7 \times 10^{-9}</td>
</tr>
<tr>
<td>[HCl]</td>
<td>Eppendorf Research plus pipette</td>
<td>± 2 µl</td>
<td>100 to 1000 µl</td>
<td>500 µl</td>
<td>0.004</td>
<td>-</td>
</tr>
<tr>
<td>t</td>
<td>Fisher Scientific traceable stopwatch</td>
<td>-</td>
<td>300 s</td>
<td>5 s</td>
<td>-</td>
<td>0.011</td>
</tr>
<tr>
<td>A</td>
<td>FlowSense 2ME Camera</td>
<td>-</td>
<td>1600x300 pixels</td>
<td>-</td>
<td>0.001</td>
<td>0.054</td>
</tr>
</tbody>
</table>
The partial derivatives obtained are then used in the MATLAB code to calculate the uncertainty associated with experimental results using Eq. (7-3). The uncertainty is tabulated in Table 7.11.

Table 7.11 – Uncertainties in liquid-solid systems

<table>
<thead>
<tr>
<th>Phase</th>
<th>Molarity (M)</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid-Solid</td>
<td>6</td>
<td>0.0536</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.0539</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.0539</td>
</tr>
<tr>
<td>Gas-Liquid-Solid</td>
<td>6</td>
<td>0.0631</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.0640</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.0636</td>
</tr>
</tbody>
</table>
Chapter 8

Conclusions and Recommendations

“I am turned into a sort of machine for observing facts and grinding out conclusions.”

CHARLES DARWIN

8.1 Summary of Main Contributions

This research has made several original contributions to multiphase flows, particularly gas-liquid and liquid-solid flows and applications to the thermochemical Cu-Cl cycle for hydrogen production.

The contributions to gas-liquid flows are listed as follows:

• performed an analysis on heat transfer due to bubble motion and determined that heat transfer is negligible;
• performed experiments to determine mass transfer in bubbles due to diffusion and convection as a result of bubble motion, size and shape;
• obtained correlation for mass transfer in gas-liquid flows in terms of flow characteristics, bubble shape and distance traveled by bubbles;

The original contributions to dissolution are listed as follows:
• performed kinetics experiments to determine the dissolution rate of solid CuCl particles in quiescent and turbulent HCl of different concentrations;

• obtained models for dissolution of solid CuCl in quiescent and turbulent HCl of different molarities for integration of the thermochemical Cu-Cl cycle for hydrogen production;

• developed a new correlation for the solubility of CuCl in binary (i.e. CuCl-H$_2$O) and ternary (i.e. CuCl-HCl-H$_2$O) systems;

• developed a dissolution process for integration of electrolysis with upstream reactors in the thermochemical Cu-Cl cycle for hydrogen production.

8.2 Summary of Main Findings

This research achieved a number of main findings as a result of experimental work and analyses performed on the multiphase flows. Some of the findings pertain to the gas-liquid phase whereas others pertain to liquid-solid interactions as follows.

Findings for gas-liquid:

• from experimental and analytical work, it was found that there is negligible heat transfer due to the motion of the bubbles;

• from the experimental data and the new correlation, it was found that the factors most influencing the mass transfer are flow characteristics (given by Reynolds number), bubble shape (given by Eotvos number) and ratio of the diameter of the bubble to the distance travelled by the bubble;
• amount of moisture carried to the surface of liquid by the ascending bubbles as calculated based on the obtained correlation.

Findings for dissolution:

• solubility of CuCl in HCl follows a power model and it is a function of temperature and Gibbs free energy;
• dissolution rate of CuCl in HCl decreases exponentially and it is accelerated by high concentrations of HCl and turbulence;
• since the dissolution rate is accelerated by turbulence, the velocity of a flow in the opposite direction of the falling CuCl particles to suspend the particles has been found. This aids in the integration of the electrolysis process with upstream reactors in the thermochemical Cu-Cl cycle for hydrogen production.

8.3 Conclusions

This thesis has developed new relationships between the flow dynamics and mass transfer kinetics of multiphase flows involving inert gas bubbles and the amount of water vapour entrained by the gas. Experimental data were obtained for the change of bubble humidity and velocity to simulate the bubbles rising in a quiescent liquid. A new correlation was developed to relate the bubble dynamics and water vapour generation rate with Reynolds and Sherwood numbers, particularly involving the amount of mass transfer across the interfacial boundary. The experimental data and model can provide a better understanding of the gas bubble dynamics and water vapour generation kinetics related to hydrogen production [88].
The process integration is examined for the oxygen production and electrolytic hydrogen production steps of the copper-chlorine (Cu-Cl) thermochemical hydrogen production cycle. It is found that the dissolution of CuCl is significantly influenced by the temperature and concentration of the solution in the CuCl–HCl–H₂O ternary system. Also, the dissolution of the solid CuCl could be implemented in an aqueous HCl solution, as this can significantly reduce the temperature requirement of otherwise dissolving CuCl in water. Alternatively, molten CuCl exiting the oxygen reactor could be quenched in water to obtain a binary slurry which would then be combined with a binary aqueous HCl solution. Through non-dimensionalization of the two binary systems (i.e. CuCl-H₂O and HCl-H₂O), a semi-empirical model is proposed for the solubility prediction. The model is found to perform well at temperature and concentration ranges of interest, for both binary and ternary systems [89].

This thesis has presented new experimental data on the particle dynamics and dissolution associated with copper chloride dissolution in hydrochloric acid. These transport processes have importance to the thermochemical copper-chlorine cycle of hydrogen production. Correlations were developed to provide new insight into the velocity of the particles and concentration of the solution with respect to a change in mass due to dissolution of the particle. Using these results, an optimum mixing technique for improved efficiency can be achieved. The thermochemical Cu-Cl cycle has the ability to produce large amounts of hydrogen without releasing greenhouse gases to the atmosphere. Shortcomings regarding the integration of the first and last steps of the cycle were discussed and a method to overcome the shortcomings for efficiency improvement have been presented in this thesis [90].
8.4 Recommendations for Future Research

This thesis provided useful information pertaining to mass transfer in multiphase flows, more specifically in gas-liquid flows and liquid-solid interactions. The results of the experiments and analysis enable the integration of the oxygen reactor with the electrolysis step of the thermochemical Cu-Cl cycle for hydrogen production. Further recommendations for future work are presented in this section.

In this thesis, a correlation for mass transfer in bubbly flows was obtained based on experimental results. However, one of the limitations of the analysis is that it does not take into account temperature. Since temperature is a factor affecting mass transfer as the diffusivity increases with increasing temperature, it should be considered in future investigations. Therefore, it is suggested that the experimental setup is redesigned to enable the investigation of how temperature affects mass transfer across a bubble interface. For this experiment, the vertical column should be insulated to prevent heat transfer to the surroundings while also able to allow visualization in order to obtain data pertaining to bubble size and velocity.

Additionally, various assumptions regarding bubble shape could be omitted if images are captured from 3 dimensions (i.e. x, y and z directions). This would require the use of two additional camera systems. The setup consists of arranging mirrors around the vertical at angles such that images of the bubbles would also be captured in the mirrors. By placing the mirror at an appropriate angle, it would be possible to determine the distortion and obtain the actual shape of the bubbles.
In this thesis, the dissolution rate of solid CuCl in aqueous HCl was investigated experimentally and models for dissolution in terms of HCl concentration in a quiescent solution, as well as in the presence of gas for mixing, were presented. The experiments related to the data presented in this thesis were performed at room temperature. Since the dissolution is enhanced at a higher temperature, it is suggested to develop a model for reaction kinetics in terms of temperature as well as concentration. In order to achieve this goal, experiments should be performed at different temperatures ranging from 10 to 100°C.

Furthermore, the analysis of particle kinetics could be improved if the actual shape of the particle of CuCl was known. In order to determine the shape of the particle, images should be captured from x, y and z directions as described in the suggested improvements for gas-liquid systems. Alternatively, CuCl particles of predetermined shapes such as spheres should be dissolved for a more accurate dissolution rate. In this case, the analysis would be performed in terms of volume rather than projected area. Therefore the change in mass over time could be determined. Also, determining whether the shape or size of particles has a greater influence on settling velocity would be beneficial for integration therefore additional experiments should be performed. Additionally, it is suggested to couple the reaction kinetics model with the thermodynamic model so that a reaction kinetics model with the thermodynamic limit can be obtained.
References


[73] Palmer, S.L., Papangelakis, V.G. Modeling cuprous chloride solubility in the CuCl-HCl-H₂O ternary system from 298K to 363K. ORF Workshop on Clean Hydrogen Production with Water Splitting Technologies, Chalk River, ON, Canada, April 22nd, 2013.


Appendix

In this appendix, a sample MATLAB code used to calculate the uncertainties associated with experimental results is presented. The code presented was used to calculate the uncertainties in liquid-solid systems. The inputs were modified when applied to the data for experiments in gas-liquid systems.

```
clear all; close all; clc; format short;

Time_12M_LS = [13 301 748 920 1101]';
Area_12M_LS = [9.62 7.38 5.61 4.72 3.43]';
Time_9M_LS = [3 241 616 1046 1508]';
Area_9M_LS = [12.6 11.2 9.58 7.36 4.86]';
Time_6M_LS = [6 506 1006 1506]';
Area_6M_LS = [9.98 8.36 6.93 6.48]';

Time_12M_GLS = [11 234 363 483 569]';
Area_12M_GLS = [13.1 11.3 9.23 7.62 6.21]';
Time_9M_GLS = [1 149 366 555 746]';
Area_9M_GLS = [6.94 5.83 4.54 3.79 3.59]';
Time_6M_GLS = [82 178 448 681]';
Area_6M_GLS = [11.3 10.2 8.58 7.15]';

t = Time_12M_LS(1,1);
A = Area_12M_LS(1,1);
HCl = 12;

Variables = 'A HCl t';
Eq = 'A*exp((-7.671*10^-5)*HCl+0.00029)*t';
Conversion = 1;

string.Eq = ' for f';

% Variable          Bias
Precision
%----------------------------------------------------------------------

Variable_Values = [A 0.001 0.054; t 1 0.011; HCl 0.004 1];
```
index = 0;
string.old = [];
for i = 1:length(Variables)
    if ~isspace(Variables(i)) && i ~= length(Variables)
        string.new = sprintf('%c',Variables(i));
        string.old = strcat(string.old,string.new);
    elseif i == length(Variables)
        index = index + 1;
        string.new = sprintf('%c',Variables(i));
        string.old = strcat(string.old,string.new);
        Symbolic_Variables(index) = sym(string.old);
        string.old = [];
    else
        index = index + 1;
        Symbolic_Variables(index) = sym(string.old);
        string.old = [];
    end
end

%% Finding Partial Derivatives
% Display Initial Equation
string.Initial_Eq = sprintf('Initial Equation%s:
\n\n\n',string.Eq,char(Eq));
disp(string.Initial_Eq)

% Calculate and Display Partials
for i = 1:length(Symbolic_Variables)
    string.Partial = sprintf('Partial wrt %s:',char(Symbolic_Variables(i)));
    Partial(i) = diff(Eq,Symbolic_Variables(i));
    if Partial(i) ~= 0
        disp(string.Partial)
        disp(Partial(i))
    end
end

%% Compute Uncertainty
uncertainty = 0;
for i = 1:length(Symbolic_Variables)
    uncertainty_b = (eval(Partial(i))*Variable_Values(i,2))^2 + uncertainty;
end
for i = 1:length(Symbolic_Variables)
    uncertainty_p = (eval(Partial(i))*Variable_Values(i,3))^2 + uncertainty;
end
uncertainty = sqrt(uncertainty_p+uncertainty_b)*Conversion;

%% Display Answer
string.Answer = sprintf('The uncertainty is %.4f\text{\,s}', uncertainty, string.Eq);
disp(string.Answer)