Reactor modeling and simulation for the copper-chlorine thermochemical solar hydrogen generation process

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ABSTRACT

Reactor Modeling and Simulation for the Copper-Chlorine Thermochemical Solar Hydrogen Generation Process

by

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Interest in hydrogen as a clean fuel has surged in the recent past as concerns over the costs of fossil fuels to the economy and environment have become paramount. As hydrogen burns only to produce water and can be used in efficient fuel cells, it has a great opportunity to be the replacement for carbon-based fuels in the twenty-first century. Hydrogen is an attractive fuel because it is renewable as an energy resource and it is also flexible as an energy carrier.

Quantities of hydrogen gas on earth are limited, so it must be chemically derived from some other sources. Thermochemical water-splitting cycles coupled to a solar heat source to drive the thermal reactions are considered a feasible and possibly advantageous method of generating hydrogen without greenhouse gas emissions. In this study, the copper-chlorine (Cu-Cl) cycle has been studied as a promising cycle which can produce hydrogen at a lower temperature than the other cycles. The cycle is closed since all materials are recycled with the exception of water which is split into hydrogen and oxygen. The process involves three main separate reactions: two thermal steps driven by heat and an electrochemical step driven by electric energy. Argonne National Laboratory
(ANL) has recently initiated exploratory research to develop a Cu-Cl cycle that operates at 550°C.

Conceptual design of receiver/reactor system is introduced in this study based on the CuCl cycle including detailed drawings showing the arrangement of the receiver and how it couples to provide the necessary heat to the reactors. Intensive study has been done on different types of chemical reactors, since they are generally the most important unit operations in the system. Based on the copper chlorine cycle the performance of the reactors was simulated. MATLAB numerical analysis package was used to solve the partial differential equations. The result gives information on the reactor design such as the relations between the changes of the solids reactants radius with time and length of the reactor. Finally, the piping system has been sized and the pumping requirements have been specified.
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CHAPTER 1

INTRODUCTION

Hydrogen, first on the periodic table of the elements, is the least complex and most abundant element in the universe. Using hydrogen as fuel can fundamentally change our relationship with the natural environment. As a nearly ideal energy carrier, hydrogen will play a critical role in a new, decentralized energy infrastructure that can provide power to vehicles, homes, and industries. Hydrogen boasts many important advantages over other fuels: it is non-toxic, renewable, clean to use, and packs much more energy per pound. Hydrogen is also the fuel of choice for energy-efficient fuel cells. Hydrogen, which exists as a gas under normal atmospheric conditions, is odorless, colorless, and tasteless. It can be transported safely.

To appreciate the various benefits of hydrogen as an energy carrier, it is important to understand the shortcomings of fuels we depend upon today. Conventional petroleum-based fuels like gasoline or diesel, as well as natural gas and coal, all contain carbon. When these fuels are burned, their carbon recombines with oxygen from the air to form carbon dioxide (CO$_2$), the primary greenhouse gas that causes global warming. To stabilize atmospheric CO$_2$ concentrations at levels that avoid irreversible climate changes, it will be necessary to reduce carbon emissions from fuel combustion several fold within this century [1-2].

The main processes for hydrogen production are:
- Steam-methane reforming (SMR) process
- Catalytic decomposition of natural gas process
- Partial oxidation of heavy oil process
- Coal gasification process
- Water electrolysis process
- Thermochemical water splitting process
- Photochemical process
- Electrochemical process
- Biological process

The first four processes are based on fossil fuels. SMR, coal gasification and water electrolysis are the most important industrial processes for hydrogen production today. As far as the long term is concerned, electrolysis and thermochemical water splitting cycles seem to be the two possible routes which do not involve hydrocarbons. These processes need large amounts of energy (heat or electricity), which can be delivered by solar energy. As hydrogen generation through direct thermolysis process encountered with high temperature (around 2500°C), thermochemical water splitting is one of the best process to generate hydrogen gas at relatively low temperature (less than 1000°C).

Various thermochemical cycles have been successfully tested and evaluated including their chemistry. Of the identified thermochemical processes, the sulfur family of processes, including sulfur-iodine (S-I) and hybrid-sulfur, appear to have the highest efficiencies and hence to be the most promising. The sulfur-iodine cycle proposed by the General Atomics (GA) Company is one such cycle developed for large-scale hydrogen production. The calcium-bromine cycle, also known as the UT-3 cycle, invented by the
University of Tokyo, gained considerable attention in addition to the GA proposed S-I cycle.

Various studies on thermochemical processes have been reported in the literature (Huang and Raisi [3]; Ozturk, Hammache and Bilgen [4]; Roth and Knoche [5]; Norman, Mysels, Sharp and Williamson [6]; Bilgen and Bilgen [7]). But only GA has described and analyzed the S-I thermochemical process with flowsheet and simulation results [8]. The UT-3 cycle has also been studied and analyzed by Sakurai, Miyake, Tsutsumi and Yoshida [9]; Aihara, Umida, Tsutsumi and Yoshida [10]; Tadokoro, Yamaguchi, Sakai, Kaneyama, Yoshida, Aochi, Nobue, Aihara, Amir, Kondo and Sato [11]. The chemistry of these cycles has been studied extensively. The efficiency of hydrogen generation, for a stand alone plant, is predicted to be 36%-40%, depending upon the efficiency of the membrane separation processes. Higher overall efficiencies, 45%-49%, are predicted for a plant that co-generates both hydrogen and electricity. It is not evident from the published reports if these numbers are based on steady-state operation or if they take into account the additional inefficiencies associated with the transient operation. The Cu-Cl cycle has been studied and analyzed experimentally at Argonne National Laboratory (ANL) [12-13]. Though all the chemistry equations of this cycle have been approved and validated, it is not fully flowsheeted yet. The overall efficiency of this cycle is 41% based on thermodynamics.

ANL is developing low temperature cycles designed for producing hydrogen at 500-550°C. For this temperature region the copper-chlorine (Cu-Cl) cycle is the most promising cycle.
1.1 Basics of the Solar Thermochemical Water Splitting Cycles

Solar energy on the Earth being an intermittent source, its utilization for thermochemical applications requires specific design and conception, and a suitable coupling for a proper operation of chemical processes. In the earlier studies, this aspect has been considered and the flowsheets have been developed to suit the intermittent characteristics of the heat source. In general, the following operation may be devised.

- The thermochemical process is run intermittently, in which case the high temperature solar energy is used directly in the process.
- The thermochemical process can be devised to run in a cyclic manner, consisting of day and night operations. During day operation, the high temperature solar heat is used to produce some intermediate chemicals, which are stored. These stored chemicals are used during night operation.
- The thermochemical process is run continuously. The high temperature solar energy is used directly during sunshine hours and also stored in a thermal storage system. The thermal energy is supplied to the process during night operation from the thermal storage system.

From the chemical engineering point of view, the first system is not preferred, since intermittent operation of a chemical process will result in start-up and shutdown problems. The second option is used in several solar-thermochemical process coupling studies (Bilgen and Bilgen [7]). The third option is the ideal case for the operation of a chemical process. It represents a straightforward option if the high temperature solar energy can be stored at the desired temperature level.
Thermochemical production of hydrogen involves the separation of water into hydrogen and oxygen through chemical reactions at high temperatures. Ideally, water can be separated directly (thermolysis); however this process requires temperatures in excess of 2500°C.

$$\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \quad > 2500^\circ\text{C}$$

Because these temperatures are impractical, the thermochemical water-splitting cycles achieve the same result (i.e., separation of water into hydrogen and oxygen) at lower temperatures. A thermochemical water-splitting cycle is a series of chemical reactions that sum to the decomposition of water. To be useful, each reaction must be spontaneous and clean. Chemicals are chosen to create a closed loop where water can be fed to the process, oxygen and hydrogen gas are collected, and all other reactants are regenerated and recycled.

Recent studies conducted through the Nuclear Energy Research Initiative (NERI) have identified more than 100 thermochemical water-splitting cycles. A few of the most promising cycles have been selected for further research and development, based on the simplicity of the cycle, the efficiency of the process, and the ability to separate a pure hydrogen product. Among them the sulfur-iodine cycle (S-I) and hybrid-sulfur cycle appear to have the highest efficiencies and hence to be the most promising [figure 1.1].
The S-I cycle uses iodine (I\textsubscript{2}) and sulfur dioxide (SO\textsubscript{2}) as chemical components to split water. First, water reacts with I\textsubscript{2} and SO\textsubscript{2} to form hydrogen iodide (HI) and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}).

\[
I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4
\]

Then the HI and H\textsubscript{2}SO\textsubscript{4} are separated from each other. The I\textsubscript{2} and SO\textsubscript{2} are then recovered from the HI and H\textsubscript{2}SO\textsubscript{4} and recycled, and hydrogen and oxygen gases are collected.

\[
H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2}O_2
\]

\[
2HI \rightarrow H_2 + I_2
\]

The reaction that requires the highest heat input is the thermal decomposition of H\textsubscript{2}SO\textsubscript{4}, typically in the range of 850°C. High temperatures are necessary to produce large quantities of hydrogen in a cost-effective manner, because the efficiency of the process decreases rapidly with decreasing the temperature. Another leading candidate is the
hybrid-sulfur process. This process uses the same high-temperature step as the S-I process but replaces the lower-temperature chemical reactions with an electrolytic cell.

\[
\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2 \quad \text{Electrolysis: 80°C}
\]

The power requirements for this electrochemical step are much less than direct electrolysis of water. The process adds the complication of an electrolysis step but reduces the complexity of the chemical plant. Other thermochemical cycles that use other chemical systems may also be feasible for large-scale cost-effective hydrogen production. For example, the calcium-bromine (Ca-Br) cycle (extensively studied in Japan) is a promising thermochemical process. The chemical steps of this cycle can be seen as follow:

\[
\begin{align*}
\text{CaBr}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) & \rightarrow \text{CaO}(\text{s}) + 2\text{HBr}(\text{g}) & 750 \text{ C} \\
\text{CaO}(\text{s}) + \text{Br}_2(\text{g}) & \rightarrow \text{CaBr}_2(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) & 600 \text{ C} \\
\text{Fe}_3\text{O}_4(\text{s}) + 8\text{HBr}(\text{g}) & \rightarrow 3\text{FeBr}_2(\text{s}) + 4\text{H}_2\text{O}(\text{g}) + \text{Br}_2(\text{g}) & 300 \text{ C} \\
3\text{FeBr}_2(\text{s}) + 4\text{H}_2\text{O}(\text{g}) & \rightarrow \text{Fe}_3\text{O}_4(\text{s}) + 6\text{HBr} + \text{H}_2(\text{g}) & 600 \text{ C}
\end{align*}
\]

The advantage of the Ca-Br cycle is that it requires lower temperature (~750°C) than that of the sulfur-Iodine cycle. However, unlike the S-I and sulfur-hybrid cycles, which contain only gases and liquids, the Ca-Br cycle contains solids.

1.2 Solar Energy to Generate Hydrogen Gas

Solar thermal power is one of the main candidates to provide a major share of renewable clean energy needed in the future. Solar radiation is the largest renewable energy resources on earth. Approximately 1% of the world’s desert area utilized by solar thermal power plants would be sufficient to generate the world’s entire electricity
demand [1-2]. Solar thermochemical hydrogen generation is mainly based on the use of concentrated solar radiation as the energy source of high-temperature process heat for driving an endothermic chemical transformation. All concentrating solar thermal power technologies rely on four basic elements: concentrator, receiver, transport-storage, and power conversion. The concentrator captures and concentrates solar radiation, which is then delivered to the receiver. The receiver absorbs the concentrated sunlight, transferring its heat energy to a working fluid. The transport-storage system passes the fluid from the receiver to the power conversion system; in some solar-thermal plants a portion of the thermal energy is stored for later use [15]. There are three solar thermal power systems currently being developed all over the world: parabolic troughs, power towers, and dish/engine systems.

1.2.1 Parabolic Trough

The parabolic trough or solar farm (Fig. 1.2) consists of long parallel rows of identical concentrator modules, typically using trough-shaped glass mirrors. Tracking the sun from East to West by rotation on one axis, the trough collector concentrates the direct solar radiation onto an absorber pipe located along its focal line. A heat transfer medium, typically oil, at temperatures up to 400°C, is circulated through the pipes. The hot oil converts water to steam driving the steam turbine generator of a conventional power block [16].
1.2.2 Solar Central Receiver or Power Tower

The solar central receiver or power tower (Fig. 1.3) is surrounded by a large array of two-axis tracking mirrors, termed heliostats, reflecting direct solar radiation onto a fixed receiver located on the top of the tower. Within the receiver, a fluid – water, air, liquid metal and molten salt have been tested – transfers the absorbed solar heat to the power block where it is used to heat a steam generator. Advanced high temperature power tower concepts are now under investigation, which heat pressurized air up over 1000°C in order to feed it into the gas turbines of modern combined cycles [16].
1.2.3 Solar Dish/Engine Systems

Dish/Engine systems use an array of parabolic dish-shaped mirrors (stretched membrane or flat glass facets) to focus solar energy onto a receiver located at the focal point of the dish (Fig. 1.4). Fluid in the receiver is heated to 1000°C and used to generate electricity in a small engine attached to the receiver. Engines currently under consideration include Stirling and Brayton cycle engines. Several prototype dish/engine systems, ranging in size from 7 to 25 kW, have been deployed in various locations in the U.S. and abroad. High optical efficiency and low startup losses make dish/engine systems the most efficient (29.4% record solar to electricity conversion) of all solar technologies. In addition, the modular design of dish/engine systems make them a good match for both remote power needs in the kilowatt range as well as hybrid end-of-the-line grid-connected utility applications in the megawatt range [16].

Figure 1.4 Solar Concentrated Dish Generator
The capability of these collection systems to concentrate solar energy is described in terms of their mean flux concentration ratio. The solar flux concentration ratio typically obtained is at the level of 100, 1000, and 10,000 suns for trough, tower, and dish systems, respectively [17]. Higher concentration ratios imply lower heat losses from smaller areas and, consequently, higher attainable temperatures at the receiver. To some extent, the flux concentration can be further augmented with the help of non-imaging secondary concentrators, e.g., compound parabolic concentrators (CPC), when positioned in tandem with the primary parabolic concentrating systems. Towers and troughs are best suited for large, grid-connected power projects in the 30-200 MW_e size, whereas, dish/engine systems are modular and can be used in single dish applications or grouped in dish farms to create larger multi-megawatt projects. Parabolic trough plants are the most mature solar power technology available today and the technology most likely to be used for near-term deployments. Power towers, with low cost and efficient thermal storage, promise to offer dispatchable, high capacity factor in the near future. The modular nature of dishes will allow them to be used in smaller, high-value applications. Towers and dishes offer the opportunity to achieve higher solar-to-electric efficiencies and lower cost than parabolic trough plants, but uncertainty remains as to whether these technologies can achieve the necessary capital cost reductions and availability improvements. Parabolic troughs are currently a proven technology primarily waiting for an opportunity to be developed. Power towers require the workability and maintainability of the molten-salt technology to be demonstrated and the development of low cost heliostats. Dish/engine systems require the development of at least one commercial engine and the development of a low cost concentrator [16].
In this study the conceptual design of receiver/reactor system is introduced based on the CuCl cycle including detailed drawings showing the arrangement of the receiver and how it couples to provide the necessary heat to the reactors. Also, the low-temperature (550°C) copper-chlorine cycle has been studied and analyzed for hydrogen generation. In addition, modeling and simulation have been done to predict the behavior of the thermochemical reactors.
CHAPTER 2

PROCESS ANALYSIS OF THE COPPER-CHLORINE CYCLE

For quite some time hydrogen has been hailed as a potential, pollution free energy source. As a consequence there have been considerable advances in the research and development devoted to hydrogen production. Among the generation methods investigated, water electrolysis is the only industrially established clean hydrogen production technology available at present. High temperature water electrolysis involves the separation of water into hydrogen and oxygen through direct thermolysis at high temperatures (in excess of 2500°C) [8].

At this high temperature only 10% of the water is decomposed. In addition, a means of preventing the hydrogen and oxygen from recombining upon cooling must be provided or no net production would result [8]. In order to avoid hydrogen generation at high temperature, low temperature thermochemical processes are preferred over water electrolysis to produce hydrogen gas. As the thermochemical process is highly endothermic there is an opportunity to supply this heat from concentrated solar radiation.

2.1 The Copper Chlorine Cycle

Copper-chlorine (Cu-Cl) cycle is a good alternative for hydrogen gas generation at low temperature in which chemicals are combined with water and heated to cause chemical reactions that produce hydrogen (and oxygen) at 550°C, a temperature
compatible with current power plant technologies. The chemicals are not consumed, and are recycled. Argonne National Laboratory’s Chemical Engineering Division is currently working on this cycle. The cycle is referred as Argonne Low Temperature Cycle-1 (ALTC-1). This cycle is considered promising over other cycles for the following reasons [13]:

- The maximum cycle temperature (<550°C) allows the use of multiple and proven heat sources
- The intermediate chemicals are relatively safe, inexpensive and abundant
- All reactions have been proven in the laboratory and no significant side reactions have been observed.

One potential disadvantage with ALTC-1 cycle is that one of the reactions is electrochemical, which imposes a significant energy cost. However, the experimental data suggest that the electrolytic step can be performed at voltages significantly lower than in direct water electrolysis.

The Cu-Cl thermochemical cycle was first proposed by Carty et al. and was designated H-6 in a Gas Research Institute (GRI) report [12]. In that study, H-6 consisted of four reactions, three thermal and one electrochemical. ANL’s preliminary study indicated that two additional reactions should be added to the original H-6 cycle. So the proposed ALTC-1 cycle consists of six reactions. Reaction-1 is the hydrogen generation reaction and Reaction-6 is oxygen generation reaction [12]. The other reactions close the cycle. The reactions involved in ALTC-1 cycle are given in the following table:
Table 2.1 Reactions Involved in Cu-Cl Cycle

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reaction</th>
<th>T °C</th>
<th>ΔG kcal/mol</th>
<th>ΔH kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2Cu(s) + 2HCl(g) → 2CuCl(s) + H₂(g)</td>
<td>450</td>
<td>3.85</td>
<td>-13.50</td>
</tr>
<tr>
<td>2.</td>
<td>4CuCl(s) + 4Cl^−(aq) → 4CuCl₂^−(aq)</td>
<td>30</td>
<td>8.27</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Electrochemical step</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>4CuCl₂^−(aq) → 2CuCl₂(aq) + 2Cu(s) + 4Cl^−(aq)</td>
<td>30</td>
<td>14.50</td>
<td>2.93</td>
</tr>
<tr>
<td></td>
<td>Electrochemical step</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>2CuCl₂(aq) → 2CuCl₂(s)</td>
<td>100</td>
<td>6.0</td>
<td>19.90</td>
</tr>
<tr>
<td></td>
<td>Drying Step</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>2CuCl₂(s) + H₂O(g) → CuO(s) + CuCl₂(s) + 2HCl(g)</td>
<td>400</td>
<td>9.50</td>
<td>28.00</td>
</tr>
<tr>
<td>6.</td>
<td>CuO(s) + CuCl₂(s) → 2CuCl(l) + 1/2O₂(g)</td>
<td>550</td>
<td>-1.93</td>
<td>31.00</td>
</tr>
</tbody>
</table>

The first step in cycle development is to determine its thermodynamic feasibility. The free energies ΔG and the enthalpies ΔH for the reactions shown in the above table were obtained by using HSC Chemistry 5.11 which contains a thermodynamic database. At the temperature indicated in the table, based on cycle stoichiometry to produce 1 mol of hydrogen, the free energy change of each reaction step is ± 10 kcal, except for the electrochemical step, which has ΔG of 14.50 kcal/mol at 30°C. The current research of this cycle at ANL concludes that all of these reactions are viable on thermodynamic basis using the values of the free energies.
According to Carty [12], who proposed this cycle in a Gas Research Institute (GRI) report in 1981, reactions whose free energy change lies within ±10 kcal for a given temperature are considered likely candidates for a cyclic process. Small positive free energy changes are acceptable if nonequilibrium reactor configurations can be utilized, such as continuous product removal, reactants in excess, and where there are a smaller number of product gases than reactant gases. Reactions with a positive free energy change of 10 to 25 kcal/mol can generally be accomplished electrochemically.

2.2 Study of the Reaction Kinetics of Cu-Cl Cycle

2.2.1 H₂ Production (Reaction-1)

\[ 2\text{HCl (g)} + 2\text{Cu(s)} \rightarrow 2\text{CuCl (s)} + \text{H}_2 (g) \]

The reaction between HCl and Cu is a heterogeneous exothermic reaction. It has been suggested that the reaction proceeds rapidly at 230°C, the temperature at which 93% of HCl is decomposed and the Gibbs free energy change is -3.95 kcal/mol. However, no hydrogen is detected at this temperature. Hydrogen starts to be produced in significant amounts at temperature above 350°C. The kinetics of the reaction are accelerated at temperatures higher than 430°C, the temperature at which CuCl melts, facilitating the interaction between HCl and Cu [13].

For a batch process, a reaction tank in which Cu powder/granules are fed with a continuous bleed of HCl gas could be utilized. However, a continuous process reactor can be used in this step. Process heat from a solar concentrator is used to heat the mixture to the reaction temperature. The copper could be introduced at room temperature and
heated to the desired reaction temperature, or it could be preheated before placing it in the reactor. Obviously, preheating will reduce the overall length of this reactor [18].

2.2.2 Copper Production by Electrolysis

Reaction-2: 4CuCl(s) + 4Cl- → 4CuCl' (aq)

Reaction-3: 4CuCl' (aq) → 2CuCl2 (aq) + 2Cu(s) + 4Cl'

CuCl is very sparingly soluble in water but soluble in HCl. The electrochemical disproportionation of CuCl is therefore being conducted at room temperature in an HCl aqueous solution.

2.2.3 Recovery of CuCl2(s) from the Aqueous Solution Containing CuCl2 and HCl

Reaction-4: 2CuCl2 (aq) → 2CuCl2(s)

The output from the electrolyzer will be an aqueous solution containing CuCl2 and HCl. This step involves recovery of the CuCl2(s) from the solution for the subsequent oxygen production step. This step also involves addition of sufficient thermal energy to remove (by vaporization) the water and HCl in order to recover the solid CuCl2. Process heat from the solar panel should be used to preheat the solution to 110°C before the mixture is forced through settling chamber [18].

2.2.4 Oxygen Production Step

Reaction-5: 2CuCl2(s) +H2O(g) → CuO(s) +CuCl2(s) + 2HCl(g)

Reaction-6: CuO(s) + CuCl2(s) → 2CuCl (l) +1/2O2(g)

The first step of this two-step process involves steam oxidation of CuCl2 at 400°C. The second step involves additional heating of the reaction byproduct to 550°C where the
CuO(s)+CuCl$_2$(s) react to form CuCl(l) and O$_2$(g). Process heat from the solar heat source is used to provide the thermal energy needed to carry out these reactions.

The net heat input to the Cu-Cl thermochemical cycle is to be provided by the solar panels. Of the chemical reactions, the oxygen production step has the highest temperature requirement, 550°C.
CHAPTER 3

CONCEPTUAL DESIGN OF THE RECEIVER/REACTOR SYSTEM

3.1 Receiver/Reactor Concepts

There are three very basic types of receiver/reactor designs that may be useful for solar thermochemical applications.

- Tube Receiver/Reactor
- Direct Receiver/Reactor
- Indirect Receiver/Reactor

Tube Receiver/Reactor has tubular reactor elements which are directly heated by the solar energy in the receiver. Direct Receiver/reactor absorbs sunlight directly on the reactor catalyst. Indirect Receiver/Reactor uses an intermediate heat transfer fluid between the receiver and the reactor [19]. Indirect Receiver/Reactor has been selected as a possible design consideration. Since the indirect receiver works by using a fluid that acts as an intermediate heat carrier from the receiver to the reactor, this allows the receiver and the reactor to be designed independently from one another [19]. The advantage of using the indirect Receiver/Reactor over the other two types is that this type of configuration is set up such that the receiver can be decoupled from the reactor, allowing for the two to be placed in different locations. This type of configurations is being considered for several reasons:
• The copper-chlorine cycle has corrosive chemicals that could be damaging if there is damage to the system or a leak in the system.
• If the chemicals need to be maintained or replaced it is simpler and safer to do it at ground level
• Maintenance of the reactor itself would be simpler

3.2 Preliminary Design for the Receiver/Reactor System

Based on the copper chlorine cycle, conceptual design of the indirect Receiver/Reactor system has been developed. Figure 3.1 illustrates a preliminary design for the entire system. It can be seen from the block diagram that the system is closed. The solar dish will collect the solar radiation and concentrate it on the receiver which will heat up the heat transfer fluid. Many fluids are possible, but for practical purposes they are limited to molten salts and metals. The hot fluid will then pumped through a flexible pipe to the heat exchanger. The function of the heat exchanger is to heat up the gas (H2O) to 500 C which is the first reaction’s temperature. The hot gas (H2O) will enter the first reactor and react with the solid (2CuCl), the chemical equation of the reaction is:

\[ 2\text{CuCl}_2(s) + \text{H}_2\text{O}(g) \rightarrow 2\text{CuCl}(s) + 2\text{HCl}(g) + \text{O}_2(g). \]

The cold fluid leaving the heat exchanger will be circulated back to the receiver.
After the first reaction is done the hot gas (2HCl) coming out of the first reactor as a product will be introduced to the second reactor where the reaction temperature needed is 450 C. The chemical equation for the second reactor is:

$$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(s) + H_2(g)$$

After reactions one and two are done, the solid products will leave the reactors by gravity going to the third reactor where the electrochemical step will take place. The solids products (2CuCl) will be pumped to the third reactor as slurry after mixing them with liquid (4Cl) which is coming from the third reactor. The chemical reaction equation for the third reactor is:

$$4CuCl_2(s) + 4Cl(l) \rightarrow 2CuCl_2(aq) + 2Cu + 2Cl(l)$$

As seen from this equation the product (2CuCl2) is coming out of the third reactor as an aqueous component. To keep this component in a solid form a dryer will be utilized to dry it before let go to the first reactor. Two different pumps will be used in the system, the first one is to circulate the molten salt, and the second is to move the solids particles.
as a slurry. The function of the molten salt pump is to deliver the fluid from the receiver to the heat exchanger, since the receiver will be up with the dish and the heat exchanger will be on the ground. There will be a sensor mounted near the receiver to collect the intensity of the sun’s radiation, and send a signal to the VFD (Variable Frequency Drive) which will be connected to the pump to control the amount of the fluid that will be delivered to the heat exchanger.

3.3 Consideration of Working Fluids for Heat Transport

There would have to be a method to transfer the heat collected from the receiver to the reactor. For this a flexible tube that will carry a working fluid from the top of the receiver to the bottom and up again would be required. While there are several possibilities for heat transfer fluids such as pressurized water, boiling water and sodium vapor, at this moment generalized fluids called molten salts are being considered.

Several different molten salts have been tested for use as a heat transfer fluid. Each has different freezing points, densities, viscosity, thermal conductivities and heat capacities and these properties need to be considered when the final choice for a heat transfer fluid is chosen. Even different compositions of mole percent in one type of molten salt can have different effects on properties. Table 3.1 lists four different types of nitrate salts against the high temperature synthetic oil called Therminol VP-1 [20].
The nitrate salts have low melting points but their boiling points seem to top around 600°C which makes use in cycles exceeding that temperature implausible. Also, nitrate salts tend to be unstable above 600°C. The salts listed that have high boiling temperature also have high melting temperatures which can be challenging to maintain especially in a small system like a SAIC dish. This seems to be the case for fluoride salts. Carbonate salts also have high end temperatures but are corrosive and have high melting points. Problems such as solidification can become a major issue in the design process. Pressurized air, helium and lead-bismuth are also some other possibilities for heat transfer fluids. Lead – bismuth has a relatively low melting point, but solidification is also a major issue for lead – bismuth. Air and helium both have poor heat transfer
properties and at elevated temperatures are pressurized and can pose some design problems also.

Sodium/potassium (NaK) is another option, but not recommended. Although it has good heat transfer characteristics and stays liquid at subfreezing temperatures, it reactivity, corrosion rates, safety, and material processing requirements makes it a poor choice.

Table 3.2 lists some properties found on various types of molten salts.

<table>
<thead>
<tr>
<th>Material</th>
<th>T&lt;sub&gt;mel&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;boil&lt;/sub&gt; (°C)</th>
<th>ρ (kg/m&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>c&lt;sub&gt;p&lt;/sub&gt; (kJ/kg °C)</th>
<th>ρc&lt;sub&gt;p&lt;/sub&gt; (kJ/m&lt;sup&gt;3&lt;/sup&gt; °C)</th>
<th>k (W/m°C)</th>
<th>νx10&lt;sup&gt;6&lt;/sup&gt; (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li&lt;sub&gt;2&lt;/sub&gt;BeF&lt;sub&gt;4&lt;/sub&gt; (Flibe)</td>
<td>459</td>
<td>1,430</td>
<td>1,940</td>
<td>2.34</td>
<td>4,540</td>
<td>1.0</td>
<td>2.9(m²/s)</td>
</tr>
<tr>
<td>NaF-ZrF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>500</td>
<td>1,290</td>
<td>3,140</td>
<td>1.17</td>
<td>3,670</td>
<td>2.1</td>
<td>0.53(m²/s)</td>
</tr>
<tr>
<td>LiF-NaF-ZrF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>460</td>
<td>?</td>
<td>2706</td>
<td>1.47</td>
<td>3,978</td>
<td>2.1</td>
<td>1.64(m²/s)</td>
</tr>
<tr>
<td>Helium (7.5 MPa)</td>
<td>—</td>
<td>—</td>
<td>3.8</td>
<td>5.2</td>
<td>20</td>
<td>0.29</td>
<td>11.0(m²/s)</td>
</tr>
<tr>
<td>LiF-NaF-KF</td>
<td>454</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solar Salt NaNO&lt;sub&gt;3&lt;/sub&gt;-KNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>220</td>
<td>600</td>
<td>1899</td>
<td>1.495</td>
<td></td>
<td></td>
<td>3.26(cP)</td>
</tr>
<tr>
<td>Hitec NaNO&lt;sub&gt;3&lt;/sub&gt;-KNO&lt;sub&gt;3&lt;/sub&gt;-NaNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>142</td>
<td>535</td>
<td>1640</td>
<td>1.56</td>
<td></td>
<td></td>
<td>3.16(cP)</td>
</tr>
<tr>
<td>Calcium Nitrate Salt NaNO&lt;sub&gt;3&lt;/sub&gt;-KNO&lt;sub&gt;3&lt;/sub&gt;-Ca(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>120</td>
<td>500</td>
<td>1992</td>
<td>1.447</td>
<td></td>
<td></td>
<td>6.37(cP)</td>
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<tr>
<td>LiNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>120</td>
<td>550</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiF-BeF&lt;sub&gt;2&lt;/sub&gt;-ThF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>500</td>
<td>3347</td>
<td>1.36</td>
<td></td>
<td></td>
<td></td>
<td>8.11(cP)</td>
</tr>
</tbody>
</table>
3.4 Thermochemical Reactors

3.4.1 Reactor Configurations

It was found that thermochemical reactors have diverse sizes, shapes, and modes and conditions of operation based on the nature of the reaction system and its behavior as a function of temperature, pressure, and catalyst properties. The reactor which is the heart of the chemical process must be a reliable mechanical system that supports heat transfer and chemical processes. The reactor's energy conversion performance is also an important attribute of the reactor design. Thus, the reactor must be designed such that the temperature of the gas entering the reactor is matched to the rate of the chemical reaction being affected in the reactor. Furthermore, the reactor must be designed so the desired reaction proceeds when the sun is available; one cannot afford spending large periods of time heating a reactor to the reaction temperature. The goal of the reactor is to maximize the portion of energy driving the chemical reaction. Table 3.3 lists many of the parameters controlling the reactor performance. The parameters have been grouped into the various physio-chemical processes taking place in the reactants or on their surfaces: chemical reaction, etc. Some of these parameters, like the reaction's activation energy and its thermal properties are all intrinsic to the chemical system [21]. Other parameters, such as reactor geometry, method of feeding the reactants, size and form of the reactants, flow patterns of fluids flowing in the reactor, reactor materials, and the product recovery system can be treated as design variables. Our role is to select these parameters and estimate the reactor performance.
Table 3.3 Processes and Parameters Influencing the Reactor Performance

<table>
<thead>
<tr>
<th>Process</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical reaction</td>
<td>Kinetics of reaction</td>
</tr>
<tr>
<td></td>
<td>Enthalpy of reaction</td>
</tr>
<tr>
<td></td>
<td>Form of reactants</td>
</tr>
<tr>
<td></td>
<td>Endothermic or Exothermic</td>
</tr>
<tr>
<td>Conduction</td>
<td>Thermal conductivity of materials</td>
</tr>
<tr>
<td></td>
<td>Reactant size and feed condition</td>
</tr>
<tr>
<td></td>
<td>Reactor geometry</td>
</tr>
<tr>
<td>Convection</td>
<td>Mass flow rates of gases</td>
</tr>
<tr>
<td></td>
<td>Window design</td>
</tr>
<tr>
<td></td>
<td>Chemical equilibrium</td>
</tr>
<tr>
<td></td>
<td>Product recovery method</td>
</tr>
<tr>
<td></td>
<td>Heat capacity of gases</td>
</tr>
<tr>
<td></td>
<td>Contact time with reactor and reactant surfaces</td>
</tr>
<tr>
<td>Heating</td>
<td>Heat capacity of materials in reactor</td>
</tr>
<tr>
<td></td>
<td>Reactant feed condition</td>
</tr>
</tbody>
</table>

Chemical reactors may be operated in batch, semibatch, or continuous modes. More details about those modes will be considered in the following discussion.
• Batch

When a reactor is operated in a batch mode, the reactants are charged, and the vessel is closed and brought to the desired temperature and pressure. These conditions are maintained for the time needed to achieve the desired conversion and selectivity, that is, the required quantity and quality of product. At the end of the reaction cycle, the entire mass is discharged and another cycle is begun. The complete cycle includes charging, heat-up, reaction (cook) time, cool-down, and discharge.

• Semibatch

In this type of reactor operation, one or more reactants are in the batch mode, while the coreactant is fed and withdrawn continuously. For example, a batch of liquid is exposed to a continuously fed and withdrawn gas phase.

• Continuous

In a chemical reactor designed for continuous operation, there is continuous addition and withdrawal of reactants and products from the reactor system. The reaction time is the actual residence time of the molecules within the reactor. There are two extremes of residence or exposure time. If all molecules have the same reaction exposure time, the reactor is a plug- or piston-flow reactor (PFR); that is, reactant-product species move through the reactor as would a piston or plug, with no (zero) mixing in the direction of flow. If, however, the mixing is perfect (infinite) in the direction of flow, the reactor is a continuously fed stirred-tank reactor (CSTR). For this type of reactor, concentrations and temperature are uniform throughout the vessel due to vigor of agitation, and the residence times are distributed around the mean value. In contrast, in the piston-flow reactor,
concentrations and temperature are distributed nonuniformly between reactor inlet and outlet, and residence time is unique.

3.4.2 Selection of the reactors

The choice of the reactor is determined by reaction characteristics. The reactor environment with respect to temperature is likewise determined and may be isothermal, adiabatic, or the intermediate case (partial heat removal or addition). A decision must be made as to what reactor type, mode of operation, and environment should be employed. In our case the copper chlorine cycle was selected for this analysis. Figure 3.2 illustrates the flowsheet for the cycle and its different phases. As shown in the figure, the cycle contains three main steps. Each step will take place in a separate reactor. The three reactors will be contained together in a closed system. In the copper chlorine cycle the chemical reactions occur in the presence of more than one phase and are referred to as heterogeneous.

The first step of the cycle occurs between a solid (2Cu) and a gas (2HCl); a continuous reactor would be used here. The same kind of reactor would be used with step number three where a liquid (H2O) and a solid (2CuCl2) will react. The problem is step number two where the electrochemical step is needed; this step is still under investigation by Argonne National Labs.
3.5 Moving Solids

Reactions involving solid particles can be challenging in the reactor design, since there are problems with moving the solid particles. One of the major issues of the copper chlorine cycle is the transportation of solid materials between the reactors. Several suggestions were mentioned in the industry regarding this topic, which are the gravity method, the Belt Conveyor method, the Screw Augers method, and the Fluidization method.

The first approach is simply based on the idea of gravity, seen in Figure 3.3, which the solid material is being transferred easily from reactor 3 to reactors 1 and 2 by the effect of gravity, but the major problem here is how the solid can be transferred vertically or in other words from reactors 1 and 2 to reactor 3 (Figure 3.3).
Figure 3.3 Moving Solids between the Reactors in the Receiver/Reactor system

The solution for this problem can be illustrated in Figure 3.4, where a vertical belt conveyor can be used to carry out the particles of the solid and move them to the reactor at the top, another belt conveyor will be used to move the solids horizontally (Figure 3.4).

Screw augers and pulverizing of the solids in preparation for transport are routine processes in industry. A modified paddle dryer design approach was introduced by Argonne National Labs to develop a continuous chemical reactor for the hydrogen production step in the copper chlorine cycle.
Figure 3.4 Illustration of the Transportation of Solid Vertically between the Reactors

An illustration of a conventional paddle dryer is shown in Figure 3.5. In this case, the feed and output forms are both powders. A potential design modification to the conventional paddle dryer is shown in Figure 3.6. In this case, a separation header has been added at the end of the reactor to separate out the H₂ gas and the CuCl (l) salt that result.
A screen conveyer is used to collect any unreacted copper and return it to the start of the process. Process heat from the solar reactor is used to heat the mixture to the reaction temperature. The copper could be introduced at room temperature and heated to the desired reaction temperature, or it could be preheated before placing it in the reactor. Preheating the copper will reduce the overall length of the reactor. [18]

Figure 3.6 Potential Modified Paddle Dryer Design for Carrying Out H₂ Production Step
Finally, the fluidization method, fluidization is the operation by which fine solids are transformed into a fluidlike state through contact with a gas or liquid. This method of contacting has a number of unusual characteristics [22]. A dense-phase gas fluidized bed looks very much like a boiling liquid and in many ways exhibits liquidlike behavior. This is shown in Fig. 3.7. For example, a large, light object is easily pushed into a bed, and on release it will pop up and float on the surface.

![Figure 3.7 Liquidlike Behavior of Gas Fluidized Beds](image)

The upper surface of the bed remains horizontal when the container is tipped, and when two beds are connected their levels equalize. Also, the difference in pressure between any two points in a bed is roughly approximated by the static head of bed between these points. The bed also has liquid-like flow properties. Solids will gush in a jet from a hole in the side of a container and they can be made to flow like a liquid from vessel to vessel.
CHAPTER 4

REACTOR MODELING AND SIMULATION

Nomenclature

$C_{go}$ Initial molar concentration of gas reactant [mol cm$^{-3}$]

$C_g$ Concentration of gas reactant [mol cm$^{-3}$]

$C_{pg}$ Average heat capacity of gaseous substances [cal mol$^{-1}$ C$^{-1}$]

$C_{ps}$ Average heat capacity of solid substances [cal cm$^{-3}$ C$^{-1}$]

$C_{so}$ Initial molar density of solid reactant [mol cm$^{-3}$]

$C_s$ Molar density of solid reactant [mol cm$^{-3}$]

$D_e$ Effective diffusion coefficient in product layer [cm$^2$ s$^{-1}$]

$f$ Conversion of gas reactant [-]

$G_0$ Initial molar velocity of gas [mol s$^{-1}$ cm$^{-2}$]

$G$ Molar specific velocity of gas [mol s$^{-1}$ cm$^{-2}$]

$h_w$ Film coefficient of heat transfer [cal cm$^{-2}$ s$^{-1}$ C$^{-1}$]

$\Delta H_R$ Heat of reaction [cal mol$^{-1}$]

$K_c$ Effective heat conductivity of solid [cal cm$^{-1}$ s$^{-1}$ C$^{-1}$]

$kr$ Overall reaction rate constant [cm s$^{-1}$]

$ks$ Reaction rate constant based on unit surface [cm$^4$ mol$^{-1}$ s$^{-1}$]

$l$ Non dimensional length $L/Lo$ [-]

$ls$ Length of reaction zone [cm]

$Lo$ Total length of solid reactant [cm]

$L$ Distance from the inlet of reactor [cm]

$P$ Reaction Pressure [atm]

$r$ Non dimensional radius $[(R-Ro)/(Rw-Ro)]$ [-]

$Ro$ Inner radius [cm]

$Rw$ Outer radius [cm]

$R$ Distance from the center of hole to reaction surface [cm]

$t_o$ Resident time of reactant in reactor [s]

$t$ Reaction time [s]

$To$ Inlet temp of gas reactant [C]

$Tg$ Temp of gas reactant [C]
In reactor design we want to know what size and type of reactor and method of operation are best for a given job. Since this may require that the conditions in the reactor vary with position as well as time, this question can only be answered by a proper integration of the rate equation for the operation. This may pose difficulties because the temperature and composition of the reacting fluid may vary from point to point within the reactor, depending on the endothermic or exothermic character of the reaction, and depending on the rate of heat addition or removal from the system. In addition, the actual geometry of the reactor will determine the path of the fluid through the vessel and fix the gross mixing patterns which help to dilute rich feed and redistribute material and heat. In effect, then, many factors must be accounted for in predicting the performance of a reactor. How best to treat these factors is the main problem of reactor design.

The starting point for all design is the material balance expressed for any reactant (or product). Thus, as illustrated in Fig. 4.1, we have

\[ \frac{m_n}{m_g} \]

where

- \( m_n \) is the molar mass of the solid reactant,
- \( m_g \) is the molar mass of the gas reactant.

The non-dimensional variables used in the rate equation are:

- \( \theta_g \) = Non-dimensional temperature of gas \( T_g/\theta_0 \) [-]
- \( \theta_s \) = Non-dimensional temperature of solid \( T_s/\theta_0 \) [-]
- \( \rho_{g0} \) = Inlet molar density of gas \( \rho_{g0} \) [mol cm\(^{-3}\)]
- \( \rho_g \) = Molar density of gas \( \rho_g \) [mol cm\(^{-3}\)]
- \( \tau \) = Non-dimensional time \( t/\theta_0 \) [-]
- \( \phi \) = Non-dimensional concentration of gas \( C_g/C_{g0} \) [-]
\[
\left( \text{rate of reactant flow into element of volume} \right) = \left( \text{rate of reactant flow out of element of volume} \right) + \left( \text{rate of reactant loss due to chemical reaction within the element of volume} \right) + \left( \text{rate of accumulation of reactant in element of volume} \right)
\]

(4.1)

Where the composition within the reactor is uniform (independent of position), the accounting may be made over the whole reactor. Where the composition is not uniform, it must be made over a differential element of volume and then integrated across the whole reactor for the appropriate flow and concentration conditions. For the various reactor types this equation simplifies one way or another, and the resultant expression when integrated gives the basic performance equation for that type of unit.

Figure 4.1 Material Balance for an Element of Volume of the Reactor

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In nonisothermal operations energy balances must be used in conjunction with material balances. Thus, as illustrated in Fig. (4.2) we have

\[
\text{rate of heat flow into element of volume} = \text{rate of heat flow out of element of volume} + \text{rate of disappearance of heat by reaction within the element of volume} + \text{rate of accumulation of heat within element of volume} \tag{4.2}
\]

Again, depending on circumstances, this accounting may be made either about a differential element of reactor or about the reactor as a whole.

The material balance of Eq. (4.1) and the energy balance of Eq. (4.2) are tied together by their third terms because the heat effect is produced by the reaction itself.

Since Equations 4.1 and 4.2 are the starting points for all design, we consider their integration for our situation.
When we can predict the response of the reacting system to changes in operating conditions (how rates and equilibrium conversion change with temperature and pressure), when we are able to compare yields for alternative designs (adiabatic versus isothermal operations, single versus multiple reactor units, flow versus batch system), and when we can estimate the economics of these various alternatives, then and only then will we feel sure that we can arrive at the design well fitted for the purpose at hand. Unfortunately, real situations are rarely simple.

4.1 Simulation of the Reactors Performance

The aim of this simulation is to predict the performance of the reactor using a honeycomb shaped solid reactant. Figure 4.3 illustrates the honeycomb-shaped solid reactants and the reactor [23]. The simulation has been done based on the first and the
second step of the copper chlorine cycle (see table 2.1) where both solid and gas are involved in the reactions. These reactions are also called the oxygen generation step and the hydrogen generation step. Last step which involves an electrochemical reaction is still under investigation, the simulation for this step will be done as soon as we specify the suitable reactor for the job.

First the following assumptions are made in the model:

- The reaction proceeds topochemically as shown by dotted lines (fig. 4.3) and follows the shrinking core model [24].
- The temperature distribution in the radial direction is negligible.
- The honeycomb shaped reactor is a bundle of independent tabular sections (illustrated by dot-dash lines in fig. 4.3).
- Turbulent heat transfer between the gas reactant and the inside wall of solid reactant occurs.
- Heat transfer in the axial direction takes place by conduction for solid and by convection for gas.

Figure 4.3 Model of Honeycomb Shaped Solid Reactants
Based on these assumptions, the mass and heat balance of both gas and solid reactants are expressed in the following dimensionless form:

- Mass balance for gas reactant

\[
\frac{\partial \phi}{\partial \tau} + K_1 \frac{\partial \phi}{\partial l} = (K_2 \gamma) \phi
\]  

(4.3)

Where:

\[
K_1 = \frac{G_0 t_0}{L_0 \rho e_0}
\]

\[
K_2 = \frac{2t_0 k_s C_{so}}{R_0}
\]

\[
\gamma = \frac{k_r}{k_s C_{so}} = \frac{1}{k_s C_{so}} \times \left[ \frac{R \ln(R / R_0)}{D_e} + \frac{R_0}{R k_s C_{so}} \right]^{-1}
\]

- Mass balance for solid reactant

\[
\frac{\partial r}{\partial \tau} = \frac{K_3}{r + R_0 / (R_w - R_0)} \times \gamma \times \phi
\]  

(4.4)

Where:

\[
K_3 = \frac{\beta R_0 t_0 C_{so} k_s}{(R_w - R_0)^2}
\]

- Heat balance for gas reactant

\[
\frac{\partial \theta_g}{\partial l} = K_4 (\theta_g - \theta_s)
\]  

(4.5)

Where:
\[ K_4 = \frac{2h_w L_o}{R_0 G C_{ps}} \]

- Heat balance for solid reactant

\[
\frac{\partial \theta_s}{\partial \tau} = K_5 (\theta_s - \theta_g) + K_6 \frac{\partial^2 \theta_s}{\partial l^2} - K_7 \gamma \times \phi \tag{4.6}
\]

Where:

\[
K_5 = -\frac{8R_0 h_w t_0}{(R^2_w - R^2_o)C_{ps}}
\]

\[
K_6 = \frac{k_f t_0}{C_{ps} L_o^2}
\]

\[
K_7 = -\frac{8R_0 \Delta H R t_0 C_{go} k_f C_{so}}{(R^2_w - R^2_o)T_0 C_{ps}}
\]

- Boundary and Initial conditions are given by

\[
\theta_g = 1, \theta_s = 1, \phi = 0 \text{ for } \tau = 0 (l \geq 0) \\
\theta_g = 1, \theta_s = 1, \phi = 0 \text{ for } l = 0 (\tau > 0)
\]

After specifying all the required equations, and calculating all the constants, the next step will be solving these partial differential equations by the means of computer. MATLAB numerical analysis package has been used to solve the PDEs. The results gave information on the reactor design. Table 4.1 summarizes the data used in this study.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{pg}$</td>
<td>8.5</td>
<td>cal mol$^{-1}$C$^{-1}$</td>
</tr>
<tr>
<td>$C_{ps}$</td>
<td>0.31</td>
<td>cal cm$^{-3}$ C$^{-1}$</td>
</tr>
<tr>
<td>$C_{so}$</td>
<td>$3.36 \times 10^{-3}$</td>
<td>mol cm$^{-3}$</td>
</tr>
<tr>
<td>$D_e$</td>
<td>$8.0 \times 10^{-3}$</td>
<td>cm$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$L_o$</td>
<td>600.0</td>
<td>cm</td>
</tr>
<tr>
<td>$\Delta H_R$</td>
<td>$-8.26 \times 10^{-3}$</td>
<td>cal mol$^{-1}$</td>
</tr>
<tr>
<td>$K_c$</td>
<td>$1.80 \times 10^{-3}$</td>
<td>cal cm$^{-1}$ s$^{-1}$ C$^{-1}$</td>
</tr>
<tr>
<td>$k_s$</td>
<td>308</td>
<td>cm$^4$ mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$h_w$</td>
<td>$3.11 \times 10^{-3}$</td>
<td>cm$^4$ mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$T_o$</td>
<td>500</td>
<td>C</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.0/8.0</td>
<td>--</td>
</tr>
<tr>
<td>$P$</td>
<td>20.0</td>
<td>atm</td>
</tr>
</tbody>
</table>
4.2 Simulation Results for the first step (Hydrogen generation step)

First, the hydrogen generation step is analyzed, and later in this chapter the second step (Oxygen generation step) is simulated. The MATLAB code that simulates the first step can be seen in Appendix A-1. The plots of the results are given below:

![Nondimensional Radius](image.png)

**Figure 4.4 Non Dimensional Radius as a Function of Time and Length**

Figure 4.4 illustrates the relation between the non dimensional radius, the time, and the length of the reactor. As seen from the figure and as expected the radius of solid is decreasing as the time is increasing, the value of the radius goes to zero at $\tau = 1.37$. Another figure showing a 2-D illustration for this situation has been made, the 2-D relation can be seen in figure 4.5 as follows:
As seen from fig. 4.5, $r = 0$ at $\tau = 1.37$.

From the definition of $\tau$, 

$$\tau = \frac{t}{to} \quad \text{where} \quad t = \text{reaction time}$$

$$to = 3600 \text{ s}$$

$$t = 4932 \text{ sec} = 82.2 \text{ min}$$

This means that the reaction will be completed within the time (in minutes) of 82.
Figure 4.6 illustrates the change of the gas concentration as a function of time and length. As seen from the figure, when the time increases the concentration of the gas increases, this means that the generation of the hydrogen is increasing with time. The nondimensional temperature of gas and solid as a Function of distance and time can be seen in figures 4.7 and 4.8.
Figure 4.7 Non Dimensional Temperature of Gas as a Function of Length and Time

Figure 4.8 Non Dimensional Temperature of Solid as a Function of Length and Time
4.3 Simulation Results for the second step (Oxygen reaction)

The MATLAB code that simulates the second step can be seen in Appendix A-2, the plots of the results is given below:

![Graph of Nondimensional Radius as a Function of Time and Length](image)

Figure 4.9 Non Dimensional Radius as a Function of Time and Length
Figure 4.10 Non Dimensional Radius as a Function of Time

As seen from fig. 4.10, \( r = 0 \) at \( \tau = 1.68 \),

From the definition of \( \tau \),

\[
\tau = \frac{t}{to} \quad \text{where} \quad t = \text{reaction time}
\]

\( to = 3600 \text{ s} \)

\( t = 6048 \text{ sec} = 100.8 \text{ min} \)

This means that the reaction will be completed within the time (in minutes) of 109.
Figure 4.11 illustrates the change of the gas concentration as function of time and length. As seen from the figure that when the time increases the concentration of the gas increases, this means that the generation of the hydrogen is increasing with time. The non dimensional temperature of gas and solid as a Function of distance and time can be seen in figures 4.12 and 4.13. As seen from the figures that the temperatures of the solid and gas are increased with time, and that because the reaction is endothermic.
Figure 4.12 Non Dimensional Temperature of Solid as a Function of Length and Time

Figure 4.13 Non Dimensional Temperature of Gas as a Function of Length and Time
The effect of the initial molar density of the solid reactant, $C_{so}$, on the radius of solid and when the solid is finished has been studied. According to the definition of the reaction rate $\gamma$, it is inversely proportional to $C_{so}$. The variation of the solid radius $r$ as a function of time for three different values of $\gamma$ at length $l = 0.5$ is shown in figure (4.14) which can be obtained by running the Matlab code in appendix A-3. Figure (4.14) shows that the reaction rate $\gamma$ is greatly affecting the time at which the reaction terminates and, as a result, when the solid reactant is going to vanish. It can be concluded from this parametric study, therefore, that when the initial molar density of the solid reactant, $C_{so}$ increases, the time needed for the radius of the solid becomes zero noticeable increases. It is advisable, therefore, to use in practical applications solid reactants with high molar density to decrease the frequency at which staff changes the reactor body.

![Graph showing the variation of r versus t for three different values of Gamma](image)

Figure 4.14 The Variation of $r$ versus $t$ for Three Different Values of Gamma
4.4 Piping Design and pump selection for the receiver/reactor system

The distribution of fluids by pipes is essential to our system, the fluids encountered are gases and liquids. From the standpoint of overall design of the system, molten salt and gases are of greatest importance. This discussion deals with the fundamental of designing a piping system for our system, and that of course will be based on the copper chlorine cycle.

4.4.1 Fluid Flow Basics

The steady flow of a fluid in a pipe is governed by the first law of thermodynamics, which leads to the equation (4.23)

\[
\frac{P_1}{\rho_1} + \frac{V_1^2}{2g_c} + \frac{g z_1}{g} = \frac{P_2}{\rho_2} + \frac{V_2^2}{2g_c} + \frac{g z_2}{g} + w + \frac{g}{g_c} l_f
\]

Where:
- \( P \) = static pressure, N/m^2
- \( \rho \) = mass density at a cross section, kg/m^3
- \( V \) = average velocity at a cross section, m/s
- \( g \) = local acceleration of gravity, m/s^2
- \( g_c \) = constant = 32.17 (lbm-ft)/(lbf-sec^2) = 1.0 (kg-m)/(N-s^2)
- \( z \) = elevation, ft or m
- \( w \) = work, (ft-lbf)/lbm or J/kg
- \( l_f \) = lost head, ft or m

Each term of equation (4.23) has the units of energy per unit mass, or specific energy.

The last term on the right in equation (4.23) is the internal conversional of energy due to friction. The first three terms on each side of the equality are the pressure energy, kinetic energy, and potential energy, respectively. A sign convention has been selected such that work done on the fluid is negative.
Another governing relation for steady flow in a pipe is the conservation of mass. For one-dimensional flow along a single pipe the mass rate of flow at any two cross section 1 and 2 is given by

\[ \dot{m} = \rho_1 \bar{V}_1 A_1 = \rho_2 \bar{V}_2 A_2 \]

Where:
- \( \dot{m} \) = mass flow rate, lbm/sec or kg/s
- \( A \) = cross sectional area normal to the flow, ft\(^2\) or m\(^2\)

4.4.2 Lost Head

For incompressible flow in pipes the lost head is expressed as

\[ l_f = f \frac{L \bar{V}^2}{D \ 2g} \]

Where:
- \( f \) = Moody friction factor
- \( L \) = length of pipe, ft or m
- \( D \) = diameter of the pipe, ft or m
- \( \bar{V} \) = average velocity in the pipe, ft/sec or m/s
- \( g \) = acceleration due to gravity, ft/sec\(^2\)

the lost head has the units of feet or meters of the fluid flowing. The Reynolds number is defined as

\[ \text{Re} = \frac{\rho \bar{V} D}{\mu} \]

Where:
- \( \rho \) = mass density of the flowing fluid, kg/m\(^3\)
- \( \mu \) = dynamic viscosity, (N-s)/m\(^2\)

Figure 4.15 shows a tow pipe molten salt system which will be used in the receiver/reactor system. The main aim of this study is to size the piping system and specify the pumping requirements.
Based on reference [25], the maximum velocity can be assumed to be 5 ft/sec and the maximum head loss is about 7 ft per 100 ft in the main run. By using figure 10-22 from reference [25] we select pipe sizes as follows. The equivalent length of fittings has been calculated. As the various sections are sized it is helpful to create Table 4.2. The lost head for the two parallel circuits that begin at 3 and end at 7 may now be determined from the data in the table:
### Table 4.2 Sizing of Pipes for the Molten Salt System

<table>
<thead>
<tr>
<th>Pipe Section No.</th>
<th>Flow Rate, gpm</th>
<th>Size, in.</th>
<th>Fluid Velocity ft/sec</th>
<th>Lost Head Per/100 ft ft/100 ft</th>
<th>Pipe Length ft</th>
<th>Fittings EQUIV. Length, ft</th>
<th>Total Length, ft</th>
<th>Total Lost Head, ft</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-1</td>
<td>32</td>
<td>2</td>
<td>4.0</td>
<td>2.6</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>2-3</td>
<td>32</td>
<td>2</td>
<td>4.0</td>
<td>2.6</td>
<td>75</td>
<td>30</td>
<td>105</td>
<td>2.7</td>
</tr>
<tr>
<td>3-4</td>
<td>16</td>
<td>1</td>
<td>3.8</td>
<td>6.5</td>
<td>10</td>
<td>5</td>
<td>15</td>
<td>1.0</td>
</tr>
<tr>
<td>4-5</td>
<td>16</td>
<td>1</td>
<td>3.8</td>
<td>6.5</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>1.0</td>
</tr>
<tr>
<td>6-7</td>
<td>16</td>
<td>1</td>
<td>3.8</td>
<td>6.5</td>
<td>15</td>
<td>20</td>
<td>35</td>
<td>2.2</td>
</tr>
<tr>
<td>3-7</td>
<td>16</td>
<td>1</td>
<td>3.8</td>
<td>6.5</td>
<td>10</td>
<td>35</td>
<td>45</td>
<td>2.9</td>
</tr>
<tr>
<td>Recev.</td>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14.0</td>
</tr>
<tr>
<td>Ex. (1)</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td>Ex. (2)</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.0</td>
</tr>
</tbody>
</table>

\[
H_{E(2)} = l_{34} + l_{45} + l_{E(2)} + l_{67} + l_{71} \\
= 1.0 + 1.0 + 10.0 + 2.2 + 0.5 \\
= 14.7 \text{ ft}
\]

\[
H_{E(1)} = l_{35} + l_{E(1)} \\
= 2.9 + 10 \\
= 12.9 \text{ ft}
\]

Now the required pump head may be estimated by adding the parallel circuit to section 7-1, the receiver, and section 2-3:

\[
H_p = l_{71} + l_{rec} + l_{23} + l_{37} + l_{E(1)} \\
= 0.5 + 14.0 + 2.7 + 2.9 + 10 \\
= 30.1 \text{ ft}
\]

*The pump may then be specified to produce 32 gpm at about 30 ft of head.*
CHAPTER 5

CONCLUSION AND SUGGESTIONS

The preliminary design of a receiver/reactor plant for the low temperature production of hydrogen using the CuCl thermochemical cycle was described. Based on the conceptual design of the whole process, the performance of the reactors where solid and gas are involved in the reactions were simulated using experimental data. The relationship between the reactor length verses gas concentration and the relation between the reactor length verses gas and solid temperatures were obtained. Also, as expected the simulation showed that the solid reactants shrink with time. Based on these results, the amount of solids consumed in the reactor can be specified. In addition, the molten salt system has been sized, and the pumping requirements have also been specified.

Here some of the concluding remarks and suggestions have been pointed out for future work.

- Thermodynamic feasibility of the reactions involved in the Cu-Cl cycle has been determined using HSC Chemistry 5.11.
- Experimental work has to be done on the copper chlorine cycle to find all the data needed for the reactor simulation.
- This kind of work should be done for all the other reactions to find the optimum size configuration of reactor for the performance of all reactions.
Then, the feasibility of the thermochemical cycle with solid reactants must be carefully discussed on the basis of a complete flowsheet.

- Process heat will be supplied from a concentrated solar heat source which will be mainly needed for the steps where O$_2$ and HCl are generated.

- Though one of the reactions is electrochemical, the CuCl cycle poses advantages over the S-I cycle because of its operating temperature (550°C).

- Though the simulation model presented for this reactor is preliminary, it will be very helpful for producing insights for future improvement of this reactor.

- The cost analysis of Cu-Cl cycle has not been done. But it is very necessary to conduct cost analysis and estimation for the economic feasibility of the cycle.

- The solar input must be matched to the chemical process such that high thermal efficiency is obtained, but not at the expense of sacrificing the operability of the combined plant.

- The matching must be done in a way that promotes operational stability of the chemical process.

- Significant research should continue to fully characterize cycles to realistically estimate cost and efficiency, demonstrate the feasibility of the processes to produce significant amounts of hydrogen, and understand tradeoffs between different thermochemical cycles.
function pdex4
clear
cle
% Constants from the model
******************************************************************************
******************************************************************************
global k gamma Ro Rw
k = [9.114*10^2 10.61 -6.843 58.541 -1.032*10^1 5.806 5.335*10^-5];
gamma = 0.12
% Ro and Rw are in [cm]
Ro=0.125
Rw=0.225
******************************************************************************
******************************************************************************

m = 0;
% x and t represent l and tau
% x is the distance over which you want a the spatial solution
% t is the time over which you would like to have the solution
x = [0:0.01:1];
t = [0:0.01:1.349];

sol = pdepe(m,@pdex4pde,@pdex4ic,@pdex4bc,x,t);
% u1 stands for phi
% u2 stands for r
% u3 stands for theta_g
% u4 stands for theta_s
% u=[phi r theta_g theta_s];
u1 = sol(:,:,1);
u2 = sol(:,:,2);
u3 = sol(:,:,3);
u4 = sol(:,:,4);
size(u2)
function [c,f,s] = pdex4pde(x,t,u,DuDx)

% u = [phi r theta_g theta_s];
global k gamma Ro Rw

c = [1; 1; 0; 1];

f = [-k(1);0;-1;0].*u+[0;0;0;k(6)].* DuDx;

s = [k(2)*gamma*u(1);
      k(3)*gamma*u(1)/(u(2)+Ro/(Rw-Ro));

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\[ k(4)*(u(4)-u(3)); \\
- k(5)*(u(4)-u(3))-k(7)*\gamma*u(1) \]

\%---------------------------------------------------------------------
function u0 = pdex4ic(x);
\% u=[\phi r \theta_g \theta_s];
global k gamma Ro Rw
\% Below is the initial conditions
\% These are basically the values for x>0 and t=0
u0 = [1; 1; 1; 1];

\%---------------------------------------------------------------------
function [pl,ql,pr,qr] = pdex4bc(xl,ul,xr,ur,t)
global k gamma Ro Rw
\% u=[\phi r \theta_g \theta_s];
\% These are the boundary values
\% Left hand boundary values
\% Boundary values at x=1
pl = [ul(1)-1; ul(2)-1; ul(3)-1; ul(4)-1];
\%
\% ql = [0; 0; 0; 0]; % ql and qr must be zero
\%
\% Right hand boundary value
\% Boundary values at x=0
pr = [ur(1)-1; ur(2)-0; ur(3)-1.03; ur(4)-1.03];
\%
\% qr = [0; 0; 0; 0]; % ql and qr must be zero
function pdex4
    clear
    clc
    % Constants from the model
    % Constants from the model
    *******************************************************************
    % Constants from the model
    % Constants from the model
    *******************************************************************
    global k gamma Ro Rw
    k = [9.114*10^2 10.61 -6.843 58.541 -1.032*10^1 5.806 5.335*10^-5];
    gamma = 0.12
    % Ro and Rw are in [cm]
    Ro=0.125
    Rw=0.225
    *******************************************************************
    % Constants from the model
    % Constants from the model
    *******************************************************************
    m = 0;
    % X  and t represent l and tau
    % X  is the distance over which you want a the spatial solution
    % t is the time over which you would like to have the solution
    x = [0:0.01:1];
    t = [0:0.01:1.675];
    sol = pdepe(m,@pdex4pde,@pdex4ic,@pdex4bc,x,t);
    % u1 stands for phi
    % u2 stands for r
    % u3 stands for theta_g
    % u4 stands for theta_s
    % u=[phi r theta_g theta_s];
    u1 = sol(:,:,1);
    u2 = sol(:,:,2);
    u3 = sol(:,:,3);
    u4 = sol(:,:,4);
    size(u2)

    figure
    surf(x,t,u1)
    title('Nondimesional Gas Concentration');
    zlabel('\phi(x,t)')
    xlabel('Distance x')
    ylabel('Time t')
figure
surf(x,t,u2)
title('Nondimensional Radius');
xlabel('Distance x')
ylabel('Time t')

size(t)
size(u2)
figure
plot(t,u2(:,51)), grid
xlabel('Time t'), ylabel('r')
title('r versus t for l=0.5')

figure
surf(x,t,u3)
title('Nondimensional Gas Temperature');
xlabel('Distance x')
ylabel('Time t')

figure
surf(x,t,u4)
title('Nondimensional Solid Temperature');
xlabel('Distance x')
ylabel('Time t')

%----------------------------------------------------------
function [c,f,s] = pde4pde(x,t,u,DuDx)
% u=[phi r theta_g theta_s];
global k gamma Ro Rw

c = [1; 1; 0; 1];
f = [-k(1);0;-1;0].*u+[0;0;0;k(6)].*DuDx;

s=[k(2)*gamma*u(1);
   k(3)*gamma*u(1)/(u(2)+Ro/(Rw-Ro));
   k(4)*(u(4)-u(3));
   k(5)*(u(4)-u(3))-k(7)*gamma*u(1)];
%----------------------------------------------------------
function u0 = pde4ic(x);
% u=[phi r theta_g theta_s];
global k gamma Ro Rw
% Below is the initial conditions
% These are basically the values for x>0 and t=0

\[ u_0 = \begin{bmatrix} 1; 1; 1; 1 \end{bmatrix}; \]

function [pl,ql,pr,qr] = pdex4bc(xl,ul,xr,ur,t)
global k gamma Ro Rw
\% u = [\phi \ r \ \theta_g \ \theta_s];

% These are the boundary values

% Left hand boundary values
% Boundary values at x=1
pl = [ul(1)-1; ul(2)-1; ul(3)-1; ul(4)-1];

% Right hand boundary value
% Boundary values at x=0
pr = [ur(1)-1; ur(2)-0; ur(3)-1.03; ur(4)-1.03];

% qr = [0; 0; 0; 0]; % ql and qr must be zero

A-3 Parametric_study.m

function pdex41
clear
clc
% Constants from the problem

% C
% global k gamma Ro Rw
k = [9.114*10^2 10.61 -6.843 58.541 -1.032*10^1 5.806 5.335*10^-5];
for i = 1:3
gamma = input('Input gamma = 0.05 then 0.09 then 0.12 ')
end
Ro = 0.125
Rw = 0.225

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m = 0;
x = [0:0.01:1];
t = [0:0.01:1.5];
sol = pdepe(m,@pdex41pde,@pdex41ic,@pdex41bc,x,t);

% u1 stands for phi
% u2 stands for r
% u3 stands for theta_g
% u4 stands for theta_s
% u=[phi r theta_g theta_s];
ul = sol(:,:,1);
u2 = sol(:,:,2);
u3 = sol(:,:,3);
u4 = sol(:,:,4);
size(u2)

%figure
%surf(x,t,ul)
%title('Nondimesional Gas Concentration');
%ylabel('\phi(x,t)')
%xlabel('Distance x')
%ylabel('Time t')

%figure
%surf(x,t,u2)
%title('Nondimensional Radius');
%ylabel('r(x,t)')
%xlabel('Distance x')
%ylabel('Time t')
%uu(:,i)=u2(:,51);

%figure
%plot(t,u2(:,51)), grid
%xlabel('Time t'), ylabel('r')
%AXIS([0 1.4 0 1])
%title('r versus t for l=0.5')

%figure
%plot(x,u2(51,:)), grid
%xlabel('Length L'), ylabel('r')
%title('r versus L for t=0.5')
```matlab
%figure
%surf(x,t,u3)
%title('Nondimensional Gas Temperature');
%zlabel('theta_g(x,t)')
%xlabel('Distance x')
%ylabel('Time t')

%figure
%surf(x,t,u4)
%title('Nondimensional Solid Temperature');
%zlabel('\theta_s (x,t)')
%xlabel('Distance x')
%ylabel('Time t')
end

figure
plot(t,uu(:,l),'*',t,uu(:,2),'.-',t,uu(:,3),'o'), grid
xlabel('Time t'), ylabel('r')
AXIS([0 1.5 0 1])
title('Effect of initial molar solid density on r for l=0.5 m')
gtext('Gamma = 0.05'),gtext('Gamma = 0.09'),gtext('Gamma = 0.12')

%--------------------------------------------------------------
function [c,f,s] = pdex41pde(x,t,u,DuDx)
% u=[phi r theta_g theta_s];
global k gamma Ro Rw

c = [1; 1; 0; 1];

f = [-k(l);0;-l;0].*u+[0;0;0;k(6)].* DuDx;

s=[k(2)*gamma*u(1);
  k(3)*gamma*u(1)/(u(2)+Ro/(Rw-Ro));
  k(4)*(u(4)-u(3));
  k(5)*(u(4)-u(3))-k(7)*gamma*u(l)];

%--------------------------------------------------------------
function u0 = pdex41ic(x);
% u=[phi r theta_g theta_s];
global k gamma Ro Rw
u0 = [1; 1; 1; 1];

%--------------------------------------------------------------
function [pl,ql,pr,qr] = pdex41bc(xl,ul,xr,ur,t)
global k gamma Ro Rw
% u=[phi r theta_g theta_s];
```
% These are the boundary values

% Left hand boundary values
% Boundary values at x=1 (l=1 in the paper)
pl = [ul(1)-1; ul(2)-1; ul(3)-1; ul(4)-1];
% pl above is arranged as follows:
% ul(1) which is phi = value(x=0,t)
% ==> You write it pl=[ul(1)-value(x=0,t),etc...]
%
ql = [0; 0; 0; 0]; % ql and qr must be zero

% Right hand boundary value
% Boundary values at x=0
pr = [ur(1)-1; ur(2)-0; ur(3)-1.03; ur(4)-1.03];
% pr above is arranged similar to ul
%
qr = [0; 0; 0; 0]; % ql and qr must be zero
%end
REFERENCES


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VITA

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Thesis Title:
Reactor Modeling and Simulation for the Copper-Chlorine Thermochemical
Solar Hydrogen Generation Process

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