Life Cycle Assessment for Thermolysis and Electrolysis Integration in the Copper-Chlorine Cycle of Hydrogen Production

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Abstract: Production, transformation, and use of energy are the main causes of many environmental problems including acid precipitation, ozone depletion, and climate change. Therefore, there is a global push for sustainable energy alternatives. One promising paradigm of a clean energy system is the hydrogen economy. However, current methods of hydrogen production are often unsustainable as they are based primarily on fossil fuels such as natural gas or coal, which release CO_2 into the atmosphere. Promising alternatives for sustainable hydrogen production are thermochemical cycles. In thermochemical cycles for hydrogen production, the overall water splitting into hydrogen and oxygen is achieved through a series of reactions. This paper discusses various designs for integration of the molten salt reactor and electrochemical cell in a thermochemical copper-chlorine (Cu-Cl) cycle. A life cycle assessment is used to aid in the selection process of the best design for integration. This is done based on a point system within an impact category, where the design with the lowest points is taken to be the most feasible and hence chosen for integration of the cycle.

Key-Words: clean energy technologies, thermochemical copper-chlorine cycle, electrolysis, hydrogen production, life cycle assessment

1 Introduction

Environmental problems such as acid rain, ozone depletion and climate change are caused by energy conversion of fossil fuels and their use. These problems have motivated global efforts to develop sustainable alternatives. Hydrogen can be a clean energy carrier and thus contribute to mitigating climate change.

In recent years, the copper-chlorine (Cu-Cl) cycle has attracted increasing interest of engineers and scientists due to its lower temperature input (i.e. below 550 °C) than most other thermochemical cycles, which are usually above 650 °C [1-3]. The Cu-Cl cycle splits water into hydrogen and oxygen through intermediate copper and chlorine compounds during a series of chemical reactions.

The Cu-Cl thermochemical water decomposition cycle generally involves at least four distinct steps:

- Hydrogen production at 25-90 °C (electrolysis):

$$2CuCl + 2HCl(g) \rightarrow 2CuCl_2(aq) + H_2(g) \quad (1)$$

- Drying at 60-200 °C:

$$2CuCl_2\,(aq) \rightarrow 2\,CuCl_2\,(s)\ \text{(physical)} \quad (2)$$

- Recycling at 350-450 °C (hydrolysis):

$$2CuCl_2 + H_2O(g) \rightarrow Cu_2OCl_2 + 2HCl(g) \quad (3)$$

- Oxygen production at 550 °C (thermolysis):

$$Cu_2OCl_2 \rightarrow 2CuCl + \tfrac{1}{2}\,O_2(g) \quad (4)$$

The chemical reactions in Eqs. 1-4 form a closed loop, re-cycle all chemicals internally on a continuous basis, and only consume water. The overall inputs and outputs of the cycle as well as the inputs and outputs of each reactor with their temperature requirements are shown in Fig. 1. It can be seen that greenhouse gases are not emitted to the atmosphere via the cycle.

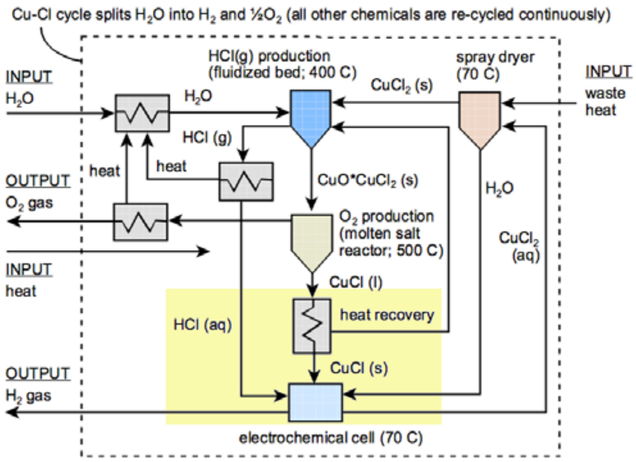

Figure 1. Configuration of Cu-Cl cycle showing input and output requirements

The cycle faces a challenge in integrating the different reactors within the cycle to form a closed loop that recycles the materials on a continuous basis, and addressing this challenge is the focus of the present paper. The objective is to use a life cycle assessment to aid in the selection process of the best design for integration of the molten salt reactor and electrochemical cell, by contrasting various designs for integration. The various designs considered for the integration of the thermolysis/electrolysis steps are considered and presented in Section 2. Section 3 discusses the design selection processes based on a life cycle assessment whereas Section 4 presents conclusions.

2 Design Requirements of Thermolysis to Electrolysis Loop

The chemicals downstream from the electrochemical cell are solid cuprous chloride (CuCl), hydrochloric acid (HCl) of different molarities (M) and water. Prior to entering the electrochemical cell, the CuCl is dissolved in HCl forming a ternary system. Hence, a dissolution cell is included in the design to obtain an aqueous CuCl-HCl-H_2O system. Molten CuCl exiting from the molten salt reactor is quenched in a water quench cell to recover heat. Since the solubility of CuCl is negligible in water at room temperature, it solidifies to form a slurry. To design the quench cell, the flow rate of molten CuCl from the molten salt reactor is determined and the slurry temperature calculated. Based on these findings, the volume of the quench cell and amount of water required are analyzed. Different designs are considered for the transport of CuCl from the quench cell to the dissolution cell.

2.1 Design 1: Sieve, Pump, and Conveyer

The CuCl passes through a sieve to separate the solid CuCl from water. The water is re-cycled back into the quench cell via a pump whereas the CuCl is weighed and transported via a conveyer into the dissolution cell filled with a 6M HCl solution. The dissolution system consists of three cells: one into which the materials are transported, one that is undergoing dissolution after the desired amount of materials enter, and a third in which dissolution is completed from which the ternary system is transported to the electrolytic cell. The CuCl may quickly oxidize in the presence of air, so it is necessary to encase the conveyer into a nitrogen-filled environment during movement. This increases significantly the cost of the transport system; hence a new design is considered below.

2.2 Design 2: Sifter and Pump

In this design, gravity is used to transport the materials from the molten CuCl reactor to the electrochemical cell. The quench cell is placed at a calculated height and the CuCl-water slurry is allowed to flow through a sifter equipped with an outlet port for the solids and one for the liquid. The CuCl is moved to the outlet of the sifter due to induced vibrations and it is allowed to fall directly into the dissolution cell filled with aqueous HCl. The top of the sifter is equipped with a hood containing a nitrogen filled environment to prevent CuCl oxidation. After separation of solids, the desired amount of liquid solution is pumped into the dissolution cell and the rest is pumped back into the quench cell. Although this is a relatively simple design, it is advantageous from a space saving perspective. But the height requirement is a constraint that cannot be readily met.

2.3 Design 3: Slurry Pump and Sensors

In this design, a slurry pump is used to pump the CuCl-H_2O slurry to the dissolution cell. This design is promising since it requires a reduced number of components and the concern of CuCl oxidization in the atmosphere is avoided. The quench cell is equipped with a pump delivering water into the cell and a slurry pump to move the product from the quench cell and into the dissolution cell on a continuous basis. The ratio of CuCl to water is carefully monitored with a flow control system and a concentration sensor. Once the desired amount of slurry is reached, aqueous HCl is added to the slurry in the dissolution cell and the ternary system is allowed to reach equilibrium. Since a slurry pump usually does not operate well at high temperatures, a higher amount of cold water is added to the quench cell and then extracted from the dissolution cell. Also, careful selection of the slurry pump is needed to avoid malfunctioning due to the highly corrosive CuCl-H_2O slurry.

3 Design Selection Based on Life Cycle Assessment

The life cycle assessment (LCA) process typically entails gathering information of the designed system from raw materials extraction through to its end of life [4]. Here, LCA was used as a decision making tool in order to choose between the three alternative transport designs for establishing the linkage between the thermolysis and electrolysis stages outlined above.

Tasks before beginning the LCA process include the following:

- Inventory assessment
- Characterization of factors

The LCA was streamlined for the purpose of the preliminary design analysis and thus did not take the complete ‘cradle to grave’ approach. Manufacturing process data for each of the designs were limited. Despite this, the perspective of the assessment is maintained since the focus is primarily on the consumption of resources to operate each of the designs.

This assessment focuses on:

- Installation and use
    - Consumables required for installation as well as operation.
- Maintenance and upgrades
    - Product cleaning and component replacement
- Transport
- End of life actions
    - Reuse, recycle, compost
    - Incineration or landfilling

The assessment intentionally excludes the following factors: spatial variations, local environment uniqueness, dynamics of environment, linearity of impacts and weighting. The spatial variation factor refers to the environmental impact of naturally occurring processes based on site location and, thus, average results are considered. Local environment uniqueness identifies that impacts are as adverse in environments at different locations around the world. The dynamics of environment are excluded so that impacts are considered equally adverse during different times of day and different seasons. The linearity of weighting assumption implies that any impact identified between two designs is assumed to be linearly adverse and that any relevant thresholds are not considered.

Since this is phase 1 of the integration, we use this LCA on the process in order to reduce impacts or risks of impacts to employees and the environment by preventing pollution where it is generated. The risk is highest in this step because it involves the transport of corrosive materials. This process evaluation entails developing a sequential flow of the chemicals, while identifying consumptions of materials as well as energy and water. The assessment is performed in an online platform known as Sustainable Minds ® (SM). A system bill of materials is produced using the software’s SM 2013 database for materials use, and end of life stages.

The SM platform works with a single score system that allows the comparison of the various cases against a reference case. Therefore, the user selects a reference case based on preference and all subsequent cases are evaluated based on that case to validate whether the design improves the system. SM employs the procedure of constructing a system bill of materials, considering the impacts based on materials identified, characterization of the impacts, normalization of the impact scores, and finally a weighting stage considering the impact significance. The scores of each category are shown in Table 1. The SM impact characterization stage uses a method known as Tool for Reduction and Assessment of Chemical and other Environmental Impacts (TRACI) developed by the US EPA and relies on environmental data for North America built into the SM 2013 database. At the end of the assessment, SM provides a single score in the units of millipoints (mPt) that represent the annual environmental load divided to the share of each resident of the nation. Once a design is selected, the design parameters can be identified based on their relationships with stressors as shown in Table 2.

Table 1. SM 2013 impact and weighting factors using TRACI impact categories and normalization

IC	NF	Unit	WF
Ecological damage			
Acidification	90.9	kg SO_2 eq (sulphur dioxide) /year /capita	0.036
Ecotoxicity	11000	CTUe /year /capita	0.084
Eutrophication	21.6	kg Neq (nitrogen) /year /capita	0.072
Global Warming	24200	kg CO_2 eq (carbon dioxide) /year /capita	0.349
Ozone depletion	0.161	kg CFC-11 eq /year /capita	0.024
Human health damage			
Carcinogens	5.07 (10^{-5})	CTUh /year /capita	0.096
Non-Carcinogens	1.05 (10^{-3})	CTUh /year /capita	0.060
Respiratory effects	24.3	kg PM2.5 eq (fine particulates) /year /capita	0.108
Smog	1390	kg O_3 eq (ozone) /year /capita	0.048
Resource depletion			
Fossil fuel depletion	17300	MJ surplus /year /capita	0.121
IC – Impact Category; NF – Normalization Factor; WF – Weighting Factor			

The slurry transport mechanism changes from dense slurry to dilute slurry with mechanical separation due to two major considerations, which are safety and the requirement for proper concentration control.

Initially, the water-CuCl slurry was to be pumped at a high concentration, dictated by the requirements of the electrolysis stage. However, this would leave the peristaltic pump and tubing in a vulnerable state since the minimal water content could pose a threat of pipe rupture. Furthermore, it would use less electricity to pump a dilute version of the water-CuCl slurry. There are a number of variables that impact the life of the tubing used in a peristaltic pump such as the tubing material and its chemical resistance, dimensions such as wall thickness and inner diameter, system pressure, number of occlusions, pump head diameter, and roller parameters. Thus, the dilute slurry transport design is able to pump more CuCl quickly while maintaining the tubing life.

Table 2. Stressor-impact chains developed for design involving slurry transport

Stressor	Impacts
Size of quenched CuCl particles	- Quench cell outlet (ID) - Tubing size (Transfer and Pump Tubing ID) - Concentration of slurry
Temperature of CuCl particles and water	- Quench cell capacity and height (to create temperature gradient) - Transfer tubing material - Pump tubing material and wall thickness
Pressure of Quench tank	- Quench cell capacity - Tubing size (Transfer and Pump Tubing material and wall thickness) - Slurry Pump (inlet pressure must be kept low)
Flow rate of molten CuCl into Quench tank	- Quench cell capacity (for heat transfer and achieving desired concentration slurry) - Threshold of permissible HCl and impurities to prevent volatile reaction
Recycling of water	- Threshold of permissible HCl and impurities to prevent volatile reaction - Flow rate of water taken from other parts of the cycle - Temperature of water and requirement of intermediary cooling

A concentration control mechanism is added to the design since there is additional water being transported and it needs to be separated. It is most advantageous to perform this separation of the water-CuCl slurry mechanically and this is accomplished by a screw-separator assembly. The screw-separator assembly consists of a collection vessel with a fine sieve at the bottom that can contain the water-CuCl slurry as it arrives from the peristaltic pump without permitting the CuCl solids to pass. Once the vessel reaches the threshold to operate and the CuCl solids settle at the bottom, the screw-separator is actuated by an electrical DC electrical stepper motor to slowly push the settled CuCl solids towards the dissolution cell. When the screw-separator is retracted, the remaining water should be able to be filled either in an intermediate reservoir or pumped back to the quench vessel since it is by definition low temperature clean water. The DC stepper motor does not require special energy access and provides accurate measurement of the CuCl solids that are transported into the dissolution cell.

One of the areas that will be focused on further are requirements of the electrolysis stage. The rate of dissolution of CuCl in presence of HCl must be determined for the flow rate of this cycle, which is currently approximated at 25 mL/min of the water-CuCl slurry based on stoichiometric calculations of the reactions involved in the cycle.

The proposed experimental design is utilized to test the dissolution rate of CuCl in 8 M, 10 M, and 12 M HCl. The solubility of CuCl in HCl as ploted in Fig. 2 based on experimental data of Kale et al. [5] and extrapolated for higher concentrations. The solubility curve in Fig. 2 shows that, at 8 M HCl, the CuCl solubility is approximately 2.85 mol/L, while the CuCl solubility at 10 M HCl is 4.38 mol/L and at 12 M HCl is 6.23 mol/L. Since the 8 M HCl exhibits the lowest solubility, this trend is employed yielding approximately 30 g of CuCl. The purpose is to find the time required for the CuCl particles to be dissolved in an HCl solution and to simulate the conditions of the dissolution cell.

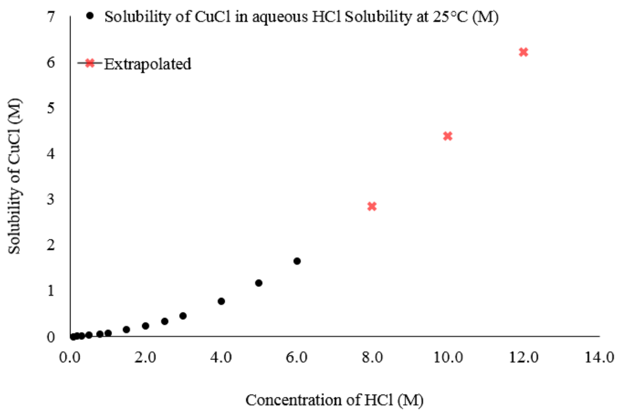

Figure 2. Solubility curve for CuCl in aqueous HCl at 25 °C

Figures 3-5 present the results of each design measured in the impact functional unit discussed in this assessment. The SM single score of 62 mPts/year is achieved by the sifter and conveyor transport design. This is the highest score in the assessment and so it is treated as the reference case in this LCA.

Figure 4 shows the results for the dense slurry transport which has a total of 28 mPts/year. This is considered a 55% improvement to the reference case. If one takes the difference between the single score of the reference case and the dense slurry transport, a result of +34 mPts is observed. The ratio of this difference and the reference case single score yields the performance improvement. An identical approach can be employed to determine the performance improvement of the final case which is the dilute slurry transport and mechanical separation. As seen in Fig. 5, the final case has a SM single score of 19 mPts/year which is approximately a 70% improvement.

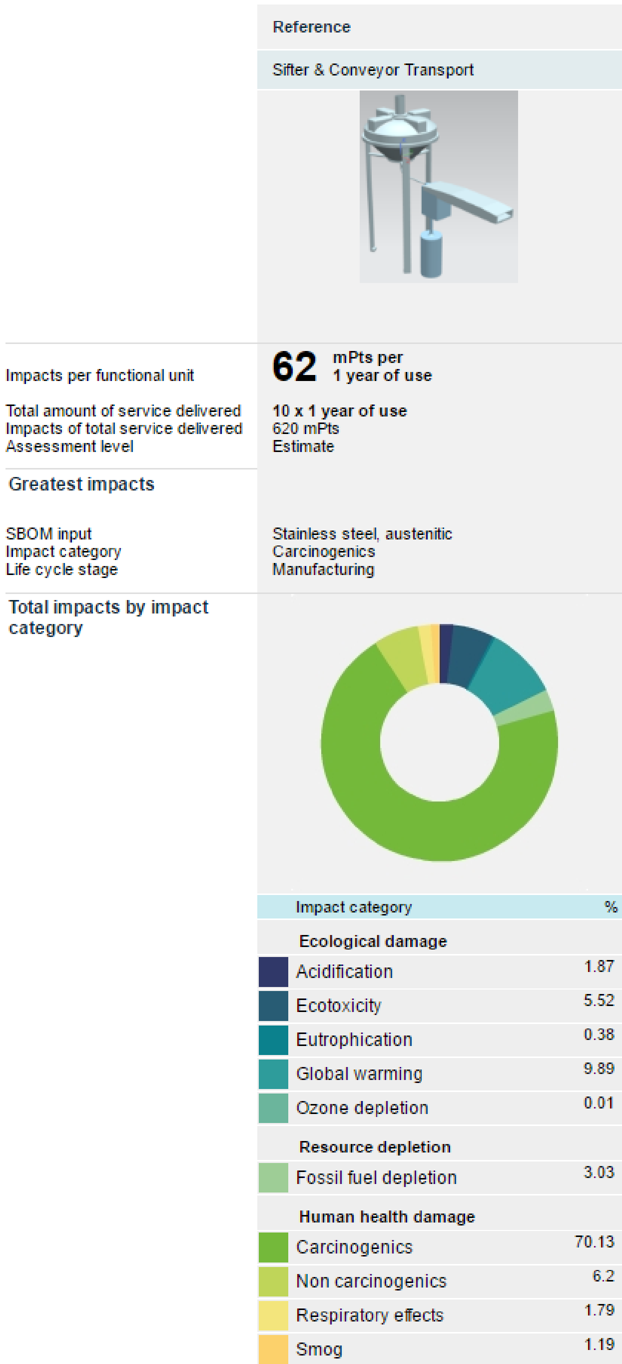

Figure 3. SM single score for the reference case

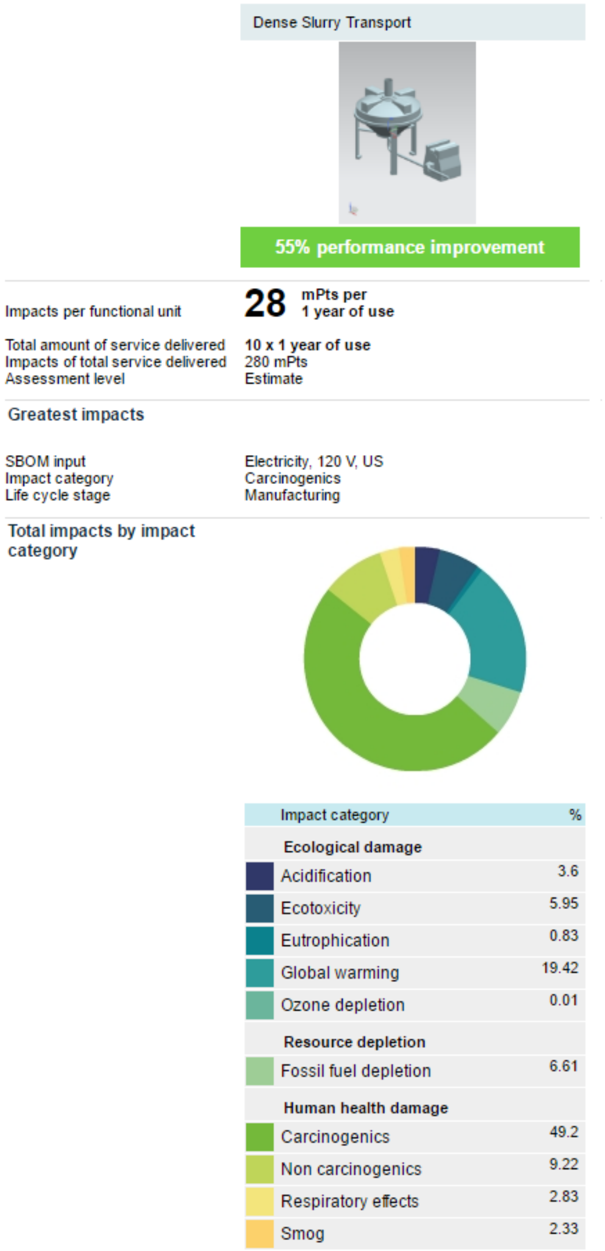

Figure 4. SM single score for the dense slurry transport design

An interesting point relates to the impact category score within each design's performance. The impact category scores refer to the categories identified by TRACI such as acidification, ecotoxicity, eutrophication, global warming, ozone depletion, fossil fuel depletion, carcinogens, non-carcinogens, respiratory effects, and smog. These are a subset of the single scores determined by the SM platform. This is an important distinction because, despite the fact that the reference case has a lower impact on global warming, it is still the least environmentally friendly alternative due to its gross score being much higher than those for the other two cases. Thus, the 19.16% for global warming is attributed to the 19 mPts/year for the final case, whereas the 9.89% for global warming is attributed to the 62 mPts/year for the reference case. Thus, the reference case has a higher dependence on resources.

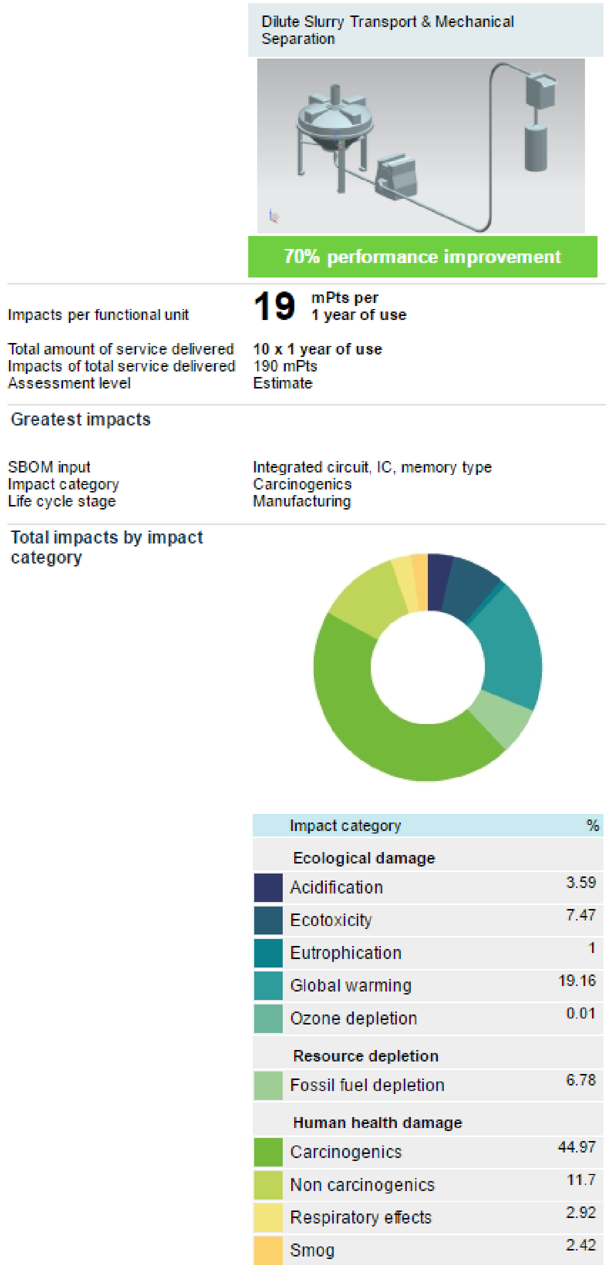

Figure 5. SM single score for the final case of the dilute slurry transport design

4 Conclusions

The thermochemical copper-chlorine cycle for hydrogen production is a promising alternative to other energy solutions as it splits water into hydrogen and oxygen via intermediate chemicals that are re-cycled continuously without emissions to the environment. One challenge of this cycle is the transport of highly corrosive and oxidizing materials between reactors to form a closed cycle. This paper explores various designs for integration of the molten salt reactor with the electrochemical cell within the Cu-Cl cycle for hydrogen production. Three designs have considered and a life cycle assessment is used in the selection process of the best candidate for integration. The design with the lowest impact is chosen for integration and is currently being constructed by the research team.

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