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Thermo-chemical Cycle of Cu-Cl

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ABSTRACT

Thermo-chemical water spitting with a copper-chloride (Cu-Cl) cycle is a promising process that could be linked with nuclear reactor to decomposed water into its constituents. Oxygen and hydrogen through intermediate copper and chlorine compound hydrogen is used for that heat generation and oxygen are beneficial for the environment. It specially focuses on simulation, thermochemical data, advanced materials safety reliability and economics of the cu-cl cycle. Aspen plus simulations of various system configurations are performed to improve the cycle efficiency. In addition, simulations based on exergo-economic and exergy-cost-mass (EXCEM) methods for system design are presented. Modelling of the linkage between nuclear and hydrogen plants demonstrates how the Cu-Cl cycle would be integrated with an SCWR (Super Critical Water Reactor; Canada's Generation IV reactor).
Keywords : Electrodes, Chlorine, Copper.

I. INTRODUCTION

The hybrid copper-chlorine (Cu-Cl) cycle is one of the most promising thermochemical cycles for hydrogen production using nuclear molar heat. The advantage of the hybrid CuCl cycle relative to other cycles is the relatively lower temperature heat (550°C) source required. Several types of nuclear reactors can be used as a heat source. Examples are the supercritical water reactor being developed in Canada, CANDU Mark 2, the lead cooled reactor, or the high temperature gas reactor. Solar heat can be provided using the commercially proven tower technology All these provide heat near or above 600°C, the maximum temperature required for the cycle. The lower temperature should mitigate some of the demands on the materials of construction.

The copper-chlorine cycle consists of the three major reactions shown in Table 1 The electrolysis reaction (l) in which cupric chloride ($CuCl_2$) is produced at the anode and H_2 at the cathode is carried out electrochemically. The $CuCl_2$(a) from (1) is hydrolyzed to copper oxychloride (Cu_2OCI_2) according to the hydrolysis reaction (2) Molten cuprous chloride (CUCI) is then produced from the decomposition reaction (3)

Table 1. Reactions in the Copper-Chlorine Cycle

Reaction	*Conditions*
(1)CuCl(a)+HCl(a)+2H₂O →CuCl₂ 2H₂O(a)+½H₂(g)	*100°C, 24bar*
(2)2CUCl₂(s)+H₂O(g)→Cu₂OCl₂(s)+2HCl(g)	*400°C, 1 bar*
(3) Cu₂OCl₂(s) →½ O₂(g)+2CuCl(s)	*540'C, 1 bar*

All reactions have been experimentally demonstrated the early experiments indicated technical challenges the hydrolysis (2) and electrolysis reactions (1) The two thermal reactions, the hydrolysis of $CuCl_2$ (2), and the decomposition of Cu_2OCl_2 (3) have been proven at Argonne National Laboratory. In bench scale experiments, all of the oxygen was recovered at 530°C from reaction (3). The electrolytic reaction (1) was demonstrated at the Atomic Energy of Canada, Ltd (AECL) at Chalk River recently Meeting performance (500 mA/cm^2 at 0.5V) and cost target (\$2500/m^2) is the primary challenge for the electrolysis reaction

We consider the hydrolysis reaction to be the most challenging reaction because of two factors (i) a competing reaction of $CuCl_2$ and (ii) the need for excess water .

The competing reaction is the thermal decomposition of $CuCl_2$:

$2CuCl_2(s) \leftarrow \rightarrow 2CuCl\ (s) + Cl_2(g).$

Because CuCl is a product of the subsequent reaction, this competing reaction is not a showstopper, provided the chlorine can be scavenged and the amount of chlorine formed is minimal. We believe that this competing reaction can be minimized by the choice of operating conditions and the reactor design.

A sensitivity study and the experimental results indicate that the steam must be in excess for high yields of the desired Cu_2OCl_2 and HCI The excess steam increases capital costs significantly because of the larger number of vessels required

In the first sub-section, a conceptual process design for the cycle is presented. It consists of two sections: (1) the electrolyzer and crystallizer, and (2) the hydrolyzer and oxychloride decomposition reactors. In order to determine the potential of the Cu-Cl cycle, an Aspen Plus flowsheet was developed using this process design and the eycle's efficiency was calculated. The energy and mass balances, the heat exchanger duties and shaft work were calculated and heat Recovery was optimized with pinch analysis. Because there are no performance data for the electrolyzer needed in the Cu-Cl cycle, we used the same performance targets as those for the hybrid sulfur cycle. The hydrogen production cost was estimated using the hydrogen analysis (H2A) methodology (1) Capital costs and operating costs for the thermal processes were estimated using capcost software

II. METHODS

Most thermochemical cycles require process heat at high temperatures, exceeding 850°C-900°C. However, existing nuclear power plants typically operate at 250°C-500°C. Recently, Atomic Energy of Canada Limited and Argonne National Laboratory in the U.S.have been developing low-temperature thermochemical cycles designed to accommodate heat sources around 500°C-550°C. Such cycles can be more readily integrated with nuclear reactors. For this temperature range, the copper-chlorine (Cu-CI) cycle is one of the most promising. Several Cu-CI cycles have been examined in the laboratory and various alternative configurations identified. Proof-of-principle experiments that demonstrate the feasibility of the processes have been undertaken and a preliminary assessment of the cycle efficiency has demonstrated its potential.

The Cu-Cl cycle consists of a set of reactions to achieve the overall splitting of water into its constituents, hydrogen and oxygen. The overall net reaction is

$H_2O\ (g) + H_2(g) + 1/2O_2(g).$

The Cu-Cl cycle uses a series of intermediate copper and chloride compounds. These chemical reactions form a closed internal loop that recycles all chemicals on a continuous basis, without emitting any greenhouse gases.

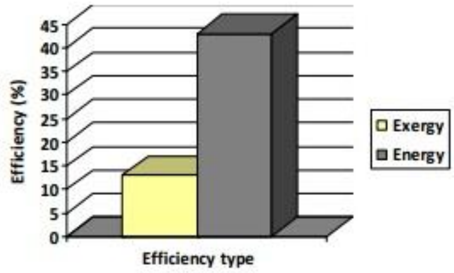
The Cu-Cl cycle has been shown [1-9] to be a potentially attractive option for generating hydrogen from nuclear energy. Compared with other hydrogen production options, the thermochemical Cu-Cl cycle is expected to have a higher efficiency, to produce hydrogen at a lower cost, and to have a smaller impact on the environment by reducing airborne emissions, solid wastes and energy requirements.

It can be observed in Fig. 1 that only water and nuclear-derived heat enter the Cu-Cl cycle and only H_2 and O_2 are produced, while greenhouse gas emissions are avoided. In the first step of the cycle (S1), steam at 400°C and solid copper chloride ($CuCl_2$) at 400°C from the dryer enter the fluidized bed, where an endothermic chemical reaction occurs that yields hydrochloric gas (HCI) and Cu,OCI_2. The hydrochloric gas is compressed and the Cu_2OCl_2 is transferred to another process step after its temperature is increased to the oxygen production reaction temperature of 500°C. In the second (oxygen production) step (S2) an endothermic chemical reaction takes place in which Cu_2OCl_2 is heated and O_2 and copper monochloride (CuCl) are produced. Liquid copper monochloride is solidified by cooling it to 20°C, after which it enters the third (copper production) step (S3) together with the solid copper chloride from the fifth step (S5). In the third step, solid copper chloride and water interact endothermically at 20°C. The water act as a catalyst in this reaction, and does not react with the other elements or compounds. The third reaction involves an electrolysis step, which makes it the most expensive step depending on the price of electricity. In this reaction, solid copper and a copper chloride-water solution are produced. A mixture of copper chloride and water is transferred to the dryer (S4), and solid copper enters the fifth step after its temperature is increased to that step's operating temperature. In the fifth (hydrogen production) step, hydrochloric gas and copper enter and are converted to hydrogen gas (H_2) and solid copper chloride (CuCl) in a steady-state reaction at 450°C.

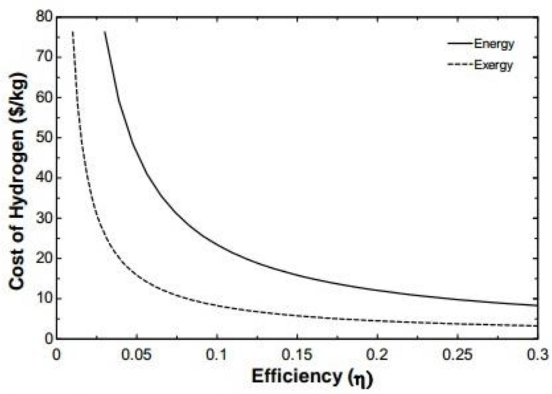
III. RESULTS AND DISCUSSION

Energy and exergy efficiencies of the Cu-Cl cycle are shown in Fig. 2. The energy efficiencyis 0.43 while exergy efficiency is 0.13. The variation of the cost of hydrogen produced withrespect to the efficiencies of the Cu-Cl cycle is shown in Fig. 3. This graph is obtained usingEq. (6). The cost of hydrogen decreases by improving the energy or exergy efficiency of thecycle. This is because as efficiencies increase, the destruction cost, which represents thecost that been lost by exergy destruction, decreases.

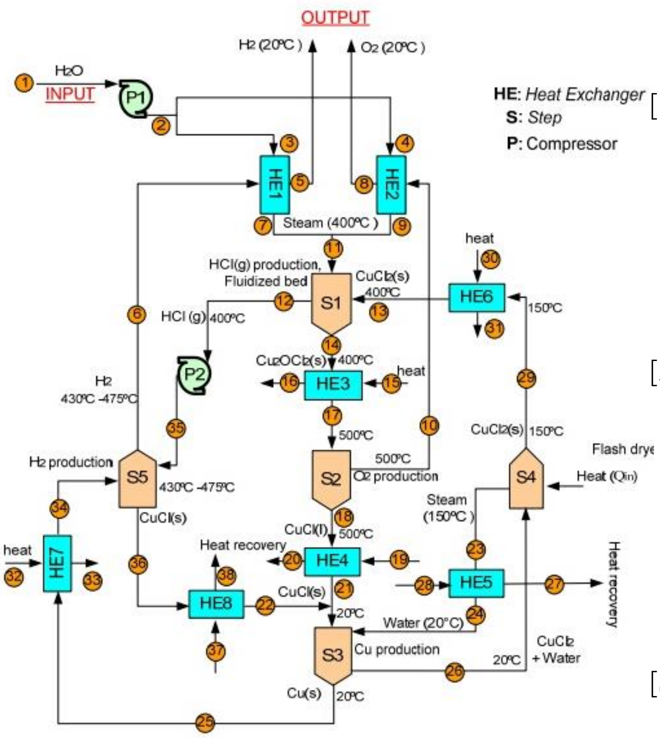
A. Figures and Tables



Energy and exergy efficiencies of the Cu-Cl thermochemical cycle.



Variation of the cost of hydrogen produced with the efficiencies of the Cu-Cl cycle.



Conceptual layout of a thermochemical Cu-Cl hydrogen production cycle.

IV. CONCLUSION

The numerical model is used to determine the performance of the heat upgrade via the CHP for thermochemical hydrogen production, using the flue gas available from the preclinker at 340 °C. The study further examines the output efficiency if the waste heat at 1,067 °C from the clinker is used directly in the CuO.CuCl2 decomposition chamber in the Cu-Cl cycle. The study also compares the heat used to produce electricity as a power source for high temperature electrolysis to split water to produce hydrogen. The parameters in the number modelling for the CHP are highlighted in Table 2. To sim the model constant pressure was assumed during each sub process. The reactor temperature was assumed to be equiva lent to the reaction temperature. The reference environment.

V. REFERENCES

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