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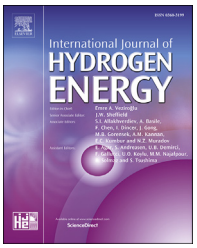

Experimental investigation of an improved version of the four-step magnesium-chlorine cycle

Hasan Ozcan [a,*], *Ibrahim Dincer* [b,c]

[a] *Karabuk University, Engineering Faculty, Mechanical Engineering Department, Baliklar Kayasi Mevkii Demir Celik Kampusu, Karabuk, 78050, Turkey*

[b] *University of Ontario Institute of Technology, Faculty of Engineering and Applied Science, Mechanical Engineering Department, 2000 Simcoe St N, Oshawa L1H 7K4, Ontario, Canada*

[c] *Faculty of Mechanical Engineering, Yildiz Technical University, Istanbul, Turkey*

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ABSTRACT

In this paper, an experimental study is undertaken to capture HCl in dry form in order to decrease the power consumption of the four-step Mg-Cl cycle using MgO as the capturing agent. A new experimental method is developed to capture HCl from its mixture with steam, and liberate HCl in a dry form. Several cases are studied to observe HCl capture performance, including testing of the resulting substances in detail using Thermogravimetric Analysis (TGA), and X-ray diffraction (XRD) tests. The results of these experiments show 30.8% HCl capture by solid MgO particles in a semi-batch packed bed reactor design with an uncertainty value of ±1.17%. The XRD results indicate that an optimum reactor temperature of ~275 °C is critical to prevent the process from side reactions and undesired products. The experimental results are adapted to the four-step Mg-Cl cycle to form a final design with HCl capture.

Introduction

Hydrogen is recognized as the most promising energy carrier which is expected to overcome the concerns caused by fossil fuels, and there are several possible ways to produce hydrogen in a sustainable way. Most of these methods are still in the development stage and energy production using these systems cannot currently compete with fossil fuel based applications. However, ongoing research on several methods looks promising and shows the possibility to compete with conventional methods. Thermochemical splitting of water appears to be an alternative to electrolytic splitting of water. This method requires more than one chemical reaction and sums the one step water thermolysis at decreased maximum temperatures. Water splitting at high temperature (thermolysis) is possible at very high temperatures (>2000 K) and results in production of oxygen and hydrogen as one input which requires a very challenging separation process [1].

Hybrid thermochemical cycles can be divided as thermo-electrochemical, thermo –photo -electrochemical, and thermo-radiochemical cycles. Thermo-electrochemical cycles utilize electricity at one of the steps throughout the cycle. Thermo-photo-electrochemical cycles require a photochemical reaction to complete the cycle, and a radiochemical reaction is required for thermo-radiochemical cycles. In this paper, we primarily focus on thermo-electrochemical cycles only.

The hybrid Mg-Cl cycle is proposed as a three-step thermo-electrochemical cycle utilizing heat and electrical work to produce hydrogen. Main steps of the cycle are; the hydrolysis

* *Corresponding author.*
E-mail address: hasanozcan@karabuk.edu.tr (H. Ozcan).

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of $MgCl_2$, the chlorination of MgO, and the electrolysis of HCl gas. It can be accomplished with two different options, namely $MgCl_2$-MgO and $MgCl_2$-MgOHCl cycles as reported in Ref. [2]. Feasible chemical reactions, mature electrolysis technology, and low maximum temperature of the cycle are promising features in terms of integrating this cycle with nuclear and solar energy sources. Schematic diagram of the $MgCl_2$-MgO cycle is illustrated in Fig. 1. ANL studied the hydrolysis step of the cycle with additives and reported promising results for reactant conversion at desired temperatures [3]. One of the main issues with the Mg-Cl cycle is possible steam/HCl mixture after the hydrolysis step. Aqueous HCl electrolysis is also a mature process where up to 1.8 V per mole of hydrogen is required with several solubility issues of oxygen and chlorine gas in water. Therefore, anhydrous HCl production is one of the crucial issues throughout the cycle in order to make it a feasible one. The electrolysis step can work below 80 °C at atmospheric pressure with both anhydrous and aqueous HCl [4].

The $MgCl_2$-MgOHCl cycle is also one of the alternatives to the ideal cycle where the hydrolysis reaction is exothermic and commences at 240 °C with a full reactant conversion at 300 °C. In order to produce the same amount of hydrogen as in $MgCl_2$-MgO cycle, the stoichiometry of this reaction should be doubled. The chlorination reaction produces a mixture of steam and oxygen, where possible problems may occur during the separation process due to solubility of oxygen in water. A fourth step for increased cycle performance as well as feasibility studies for the cycle with dry HCl capture has been recently studied in Refs. [5,6].

Note that an up-to-date literature review for the hydrolysis of $MgCl_2$ at both low and high temperatures superimposes that HCl would be in mixture with steam which would result in aqueous HCl electrolysis requiring high cell potentials during the electrolysis step of the Mg-Cl cycle. Dry HCl capture can be accomplished using a suitable solid metal oxide sorbent which possesses low solubility in water [7].

$MgCl_2$ is highly desiccant in water where a mole of this substance can absorb up to 12 mol of water. The high adsorbance capacity can be utilized to capture water from the steam/HCl mixture. However, there has not been a study showing its characteristics for capturing HCl gas. An ion interaction model to predict solubility of this ternary system has been studied in Ref. [8]. The study has been conducted at 20 °C and has been validated with the experimental studies. A considerable amount of HCl has made a physical bond with the solid particles at this temperature. The ternary system HCl-$MgCl_2$-H_2O has been evaluated using Pitzer's ion interaction model at varying temperatures [9]. The solubility of HCl has been lower at a higher rate of $MgCl_2$ in the ternary system. The ternary system has led to production of $HCl \cdot MgCl_2 \cdot 7H_2O$. The resulting data have presented that it might be possible for $MgCl_2$ to absorb more H_2O than HCl with a possible concentrated mixture. Prediction of the solubility phase diagram for the HCl-$MgCl_2$-H_2O system at 273 K has been conducted in Ref. [10]. Higher HCl concentration leads to $HCl \cdot MgCl_2 \cdot 7H_2O$ formation. It has been suggested that the HCl concentration should be controlled to prevent double salt formation. Existing studies have not validated any results for the higher temperature capturing of HCl gas, or occurrence of double salts.

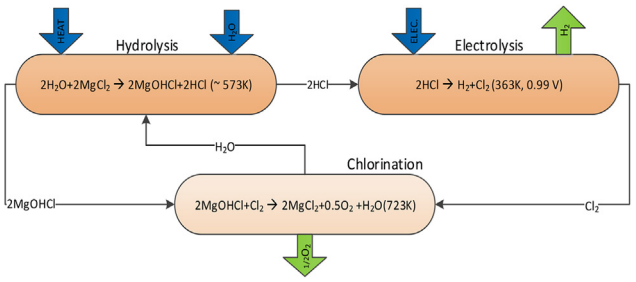

Fig. 1 – Schematic diagram of the three step $MgCl_2$-MgOHCl cycle.

MgO solubility in an aquaeous HCl solution has been studied in Ref. [11]. Higher concentrations have been achieved for highly concentrated HCl solutions at room temperature. An experimental study has been conducted to determine the reaction characteristic of an intermediate step of MgO chlorination in a molten salt reactor [12]. The alkalimetric titration results have shown that MgOHCl is formed before the chlorination of MgO particles with chlorine, and it has reached to a maximum before $MgCl_2$ production. It has been imposed that this intermediate step can play a significant role to absorb HCl from the mixture gas. Rappold and Luft have proposed a novel process to capture HCl gas from exhaust emissions using MgO particles as sorbents [13]. This reaction has been conducted at the exhaust gas temperature (120 °C) to validate MgO hydrochlorination. Products have been heated up to 450 °C to form back MgO particles in a steam environment. Partanen et al. have studied the absorption of HCl gas in limestone by considering the reaction atmosphere and absorbent characteristics. Several limestone types containing several metal oxides have been determined [14]. The main issues with this process have been the corrosive nature of $CaCl_2$ at high temperatures and fouling of the boiler. Another study have shown that the Cl/Ca ratio is the most influencing factor to determine the amount of sorbent for practical applications [15].

In this study, MgO is utilized as the HCl capturing agent from an aquaeous HCl in a horizontal semi batch reactor in order to validate the feasibility of forming MgOHCl and liberating HCl at relatively low temperature that does not exceed the maximum temperature of the four-step Mg-Cl cycle.

Experimental apparatus and procedure

Experimental setup

Since the electrolysis of HCl in an anhydrous form requires less electrical work, a process for separation of HCl from H_2O is one of the most crucial steps of the Mg-Cl cycle for better system performance and less electricity consumption. The aqueous HCl electrolysis may also lead to possible problems such as wet hydrogen and chlorine production requiring an additional downstream separation, oxygen evolution at anode, and high current densities etc. The interaction between $MgCl_2$ and H_2O with their thermochemical data and reaction conditions are given in Fig. 2, and the corresponding chemical reactions are written as follows:

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