Direct contact heat transfer from molten salt droplets in a thermochemical water splitting process of hydrogen production

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A B S T R A C T

It is important to recover heat within the copper–chlorine cycle of hydrogen production to improve its overall efficiency. A major portion of heat recovery may be achieved by cooling and solidifying the molten salt exiting the oxygen reactor step of the cycle. Heat can be recovered from the molten salt by breaking the molten stream into smaller dispersed droplets. In this paper, a predictive model is developed to analyze heat transfer from molten salt droplets. Characteristics of a spray column, in which recovered heat from molten copper(I) chloride (CuCl) is used to produce superheated steam, are presented. Decreasing the droplet size may increase the heat transfer rate from the droplet, and hence decrease the required height of the heat recovery system. For a 1 mm droplet size, the height of the heat-recovery system is predicted to be about 7 m.

1. Introduction

Hydrogen is anticipated to have an important role as an energy carrier of the future [16,17,22]. Hydrogen can be derived from non-fossil sources, burns cleanly to produce water with no pollutant emissions, is suitable for use in a fuel cell to generate electricity directly, and has an energy content per mass 2.5 times greater than that of any other conventional fuel [5,10,28]. However, hydrogen is not an energy source. It does not occur in nature in its elemental or molecular form, so hydrogen must be produced. Most of the world's hydrogen is currently derived from fossil fuels through some type of reforming process [4,13]. Developing sustainable, large-scale, low-cost methods of hydrogen production from energy sources other than fossil fuels is required to reduce greenhouse gas emissions and accelerate the transition to a low-carbon future. Thermochemical cycles provide alternative and potentially more efficient methods to produce hydrogen from water [14]. A thermochemical water splitting process includes decomposition of water into hydrogen and oxygen using heat or, in a hybrid thermochemical cycle, a combination of heat and electricity. The as follows:

$$H_2O(l) \rightarrow H_2(g) + 1/2O_2(g) \qquad (1)$$

Several thermochemical water splitting cycles have been proposed and examined. Abanades et al. [1] studied solar hydrogen production from a two-step thermochemical cycle based on a SnO$_2$/SnO redox reaction. A thermochemical cycle based on a Zn/ZnO redox reaction was presented by Steinfeld [25]. The sulfur–iodine thermochemical cycle, in which solar energy is used for the decomposition of sulfuric acid, was investigated by Huang and Raissi [11].

Alternative thermochemical cycles for hydrogen production have been evaluated by Lewis et al. [15]. Their results show that the copper–chlorine cycle is chemically viable, feasible with respect to engineering factors and energy-efficient. Recent advances in thermochemical cycles for hydrogen production, using non-fossil energy sources such as nuclear or solar, were reported by Rosen [24]. The copper–chlorine cycle was shown to have significant potential because of the lower temperature requirement for heat supplies compared to most other thermochemical processes.

The copper–chlorine (Cu–Cl) cycle decomposes water into hydrogen and oxygen, through intermediate copper chloride compounds, in a closed loop that recycles all chemicals continuously. There are three variations of the Cu–Cl cycle, based on the number of main chemical reactions: three step, four step, and five step. These variations of copper–chlorine cycles with different numbers of steps and methods of grouping were compared and major features of the cycles with different number of steps were discussed by Wang et al. [26]. It is noted that CuCl molten salt exists in all variations of copper chlorine cycle. A schematic of a four step cycle is shown in Fig. 1. The first step is CuCl/HCl electrolysis in which oxidation of copper(I) chloride (CuCl) occurs during an

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Nomenclature

A	area, m^2
Bi	Biot number
C_D	drag coefficient
c_p	specific heat at constant pressure, J/kg K
D_{vg}	vapor–gas mass diffusivity, m^2/s
Fo	Fourier number
g	gravitational acceleration, m/s^2
h	heat transfer coefficient, W/m^2 K
k	thermal conductivity, W/m K
k_g	thermal conductivity of ambient gas, W/m K
L	latent heat of phase change, kJ/kg
Le	Lewis number
m	mass, kg
Nu	Nusselt number
Pr	Prandtl number
q	heat transfer rate, W
R	droplet radius, m
r	radial coordinate, m
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
T	temperature, °C
t	time, s
v	velocity, m/s

Greek letters

ε	emissivity
ζ_n	positive roots of transcendental equation
μ_∞	viscosity of fluid at the free-stream temperature, Pa s
ρ	density, kg/m^3
ρ_g	density of gas, kg/m^3
σ [5.67×10^{-8} W/m^2 K^4]	Stefan–Boltzmann constant

Subscripts

c	convection
d	droplet
g	gas
i	initial
m	mass transfer
r	radiation
s	surface
v	vapor

Superscripts

*	non-dimensional

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electrochemical reaction, in the presence of hydrochloric acid (HCl) to produce hydrogen (H_2) and copper(II) chloride ($CuCl_2$). Step 2 of the cycle is the drying step in which aqueous $CuCl_2$ exiting the electrolysis cell is dried to produce $CuCl_2$ particles, which are then moved to the hydrolysis unit (step 3) and reacted with superheated steam to produce copper oxychloride solid (Cu_2OCl_2) and hydrochloric gas. In step 4 (oxygen production), copper oxychloride particles decompose into molten CuCl and O_2 gas.

Canadian advances in nuclear-based production of hydrogen by the Cu–Cl cycle were presented by Naterer et al. [18–21]. A solar plant coupled with a Cu–Cl plant to produce hydrogen at three locations in Canada was analyzed by Ghandehariun et al. [6]. The results showed the feasibility of a solar thermochemical Cu–Cl cycle as a promising and efficient pathway for large-scale hydrogen production.

Heat recovery within the copper–chlorine cycle is important for its efficient performance and overall viability. Pinch analysis was used to determine the maximum recoverable heat within the Cu–Cl cycle, and where in the cycle the recovered heat can be used efficiently [7]. It was shown that about 88% of the heat recovery can be achieved by cooling and solidifying molten copper(I) chloride (CuCl) exiting the oxygen reactor step. It was also shown that it would be more appropriate to use the recovered heat in the hydrolysis step.

Several configurations for heat recovery from molten CuCl, based on existing industrial processes for molten materials, were presented and investigated by Ghandehariun et al. [9]. A direct contact process using air or steam as a coolant was shown to be one of the most promising methods for heat recovery from molten CuCl in the Cu–Cl cycle.

The hazards involving CuCl were also investigated, as were corresponding hazard reduction options [8]. If a direct contact method is used for heat recovery from molten CuCl, the heat recovery fluid should be circulated in the cycle so as to confine the CuCl vapor within the cycle, and a secondary heat exchanger may be used to release heat to an endothermic process.

In this paper, a predictive model is developed to investigate a direct contact heat recovery process from molten CuCl. The objective is to provide information that can assist efforts to design an efficient and practical heat recovery system for the Cu–Cl cycle.

2. Modeling a direct contact heat recovery process

This section describes a mathematical model which predicts thermal behavior of a falling droplet in a gas during cooling and solidification, which represents one option for direct contact heat recovery.
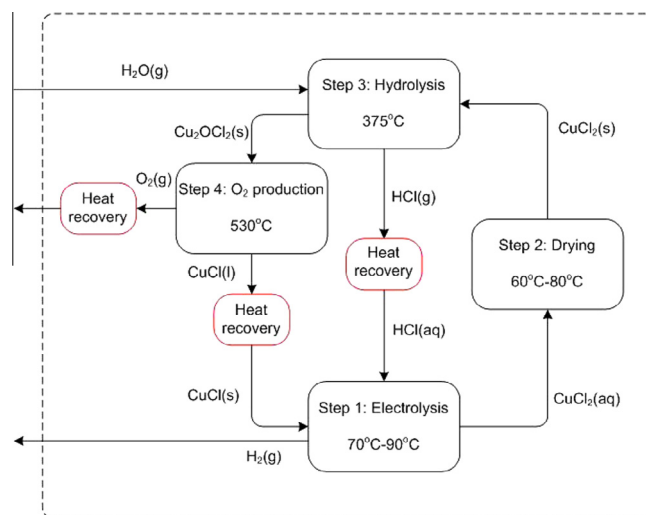

Fig. 1. Schematic of a four step copper–chlorine cycle for thermochemical water splitting.