



Heat transfer from molten salt droplets in various gases



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ABSTRACT

Heat recovery within the copper–chlorine cycle of hydrogen production is necessary to improve its overall thermal efficiency, and hence it is an essential part of the thermochemical cycle. A major portion of heat recovery can be achieved by cooling and solidifying the molten salt exiting the oxygen reactor of the cycle. Heat can be recovered from the molten salt by breaking the exiting molten stream into smaller dispersed droplets. This paper presents a predictive model to investigate a direct contact heat recovery process from molten copper(I) chloride (CuCl) using various gases including nitrogen, helium, and argon. The results are compared with those of air. As CuCl may react with water vapor in the presence of oxygen, inert gases are considered as the coolants for the direct contact heat recovery process. The results indicate that better heat transfer performance is observed in helium compared to other gases studied.

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1. Introduction

Hydrogen is considered a clean energy carrier [1–5]. Most of the hydrogen currently produced in the world is derived from fossil fuels through various types of reforming or gasification processes [6–8]. Among the various methods of hydrogen production, thermochemical water decomposition cycles provide alternative and potentially more efficient methods to produce hydrogen from water [9,10]. A thermochemical cycle decomposes water into hydrogen and oxygen using heat or, in a hybrid thermochemical cycle, a combination of heat and electricity. All the chemicals are used in a closed cycle; therefore, the net material outputs are oxygen and hydrogen.

Several thermochemical water splitting cycles have been proposed and examined. Abanades et al. [11] reported solar hydrogen production from a two-step thermochemical cycle based on a SnO₂/SnO redox reaction. A thermochemical cycle based on a Zn/ZnO redox reaction was presented by Steinfeld [12]. The sulfur–iodine thermochemical cycle, in which solar energy is used for the decomposition of sulfuric acid, was investigated by Huang and Raissi [13]. Xinxin and Kaoru [14] studied the sulfur–iodine (S–I) cycle for hydrogen production using nuclear energy. Energy and economic assessments of an industrial plant for hydrogen production by a sulfur–iodine thermochemical cycle were presented by Liberatore et al. [15]. The energy efficiency of the thermochemical cycle itself was about 34%, based on the higher heat value.

Combining this value with the efficiency of electricity production, including the efficiency of the solar plants, the total heat-to-hydrogen efficiency obtained was 21%.

Lewis et al. [16] investigated various thermochemical cycles for hydrogen production. Their results showed that the copper–chlorine cycle is chemically viable, feasible with respect to engineering factors and relatively energy efficient compared with other methods. Recent advances in thermochemical cycles for hydrogen production, using non-fossil energy sources such as nuclear or solar, were reported by Rosen [17]. The copper–chlorine cycle was shown to have significant potential because of the lower temperature requirement for heat supply 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. [18]. It is noted that CuCl molten salt exits a thermolysis reactor in all variations of the 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 electrochemical reaction, in the presence of hydrochloric acid (HCl) to produce hydrogen (H₂) and copper (II) chloride (CuCl₂). The second step is drying or crystallization, in which water from aqueous CuCl₂ exiting the electrolysis cell is

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Nomenclature

A	area, m^2
Bi	Biot number
C_D	drag coefficient
c_p	specific heat at constant pressure, $J/kg.K$
$ Fo$	Fourier number
g	gravitational acceleration, m/s^2
k	thermal conductivity, $W/m.K$
h	heat transfer coefficient, $W/m^2.K$
L	latent heat of phase change, kJ/kg
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, $^{\circ}C$
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, $Pa.s$
ν_g	kinematic viscosity of gas, m^2/s
ρ	density, kg/m^3
ρ_g	density of gas, kg/m^3
σ	Stefan–Boltzmann constant ($5.67 \times 10^{-8} W/m^2.K^4$)

Subscripts

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

Superscripts

*	non-dimensional
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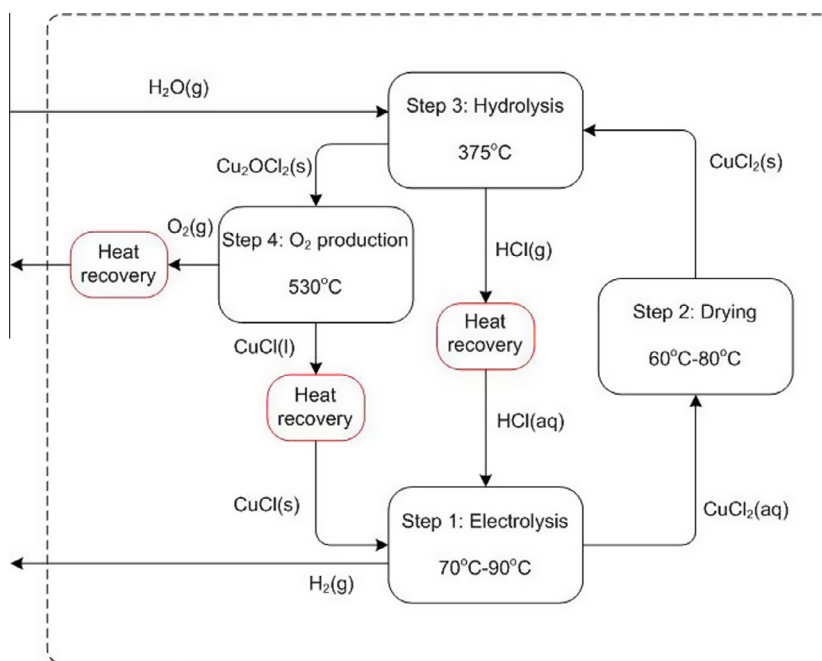


Fig. 1. Schematic of a four step copper–chlorine cycle for thermochemical water splitting.

separated from the solution to produce solid $CuCl_2$ particles. $CuCl_2$ particles are moved to the third step which is hydrolysis, and reacted with superheated steam to produce copper oxychloride solid (Cu_2OCl_2) and hydrochloric gas (HCl). In the last step, 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. [19–22]. A solar plant coupled with a Cu–Cl plant to produce hydrogen at three locations in Canada was analyzed by Ghandehariun et al. [23]. 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 efficient performance and viability. A pinch analysis was used to determine the maximum recoverable heat within the Cu–Cl cycle, and the location in the cycle where recovered heat can be used efficiently [24]. 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. It was also shown that it would be more appropriate to use the recovered heat in the hydrolysis step.

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