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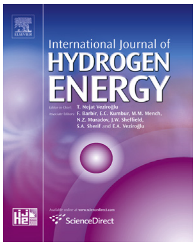

Calcium oxide/steam chemical heat pump for upgrading waste heat in thermochemical hydrogen production

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ABSTRACT

This paper presents a numerical study of a chemical heat pump (CHP) for upgrading waste heat from a cement plant for thermochemical hydrogen production. A calcium oxide/steam CHP is investigated as a potential system to upgrade waste heat from industrial processes for thermochemical hydrogen production. The heat produced by the CHP drives the decomposition of copper oxychloride ($CuO \cdot CuCl_2$) in a copper–chlorine (Cu–Cl) thermochemical cycle. A transient analysis of the temperature distribution in each sub process in the combined CHP/Cu–Cl cycle is presented in this study. The numerical results of hydration temperature distribution are compared with experimental results to validate the predictive model. A maximum hydrogen production of 12.28 mol/kg $Ca(OH)_2$ can be achieved from the combined system analyzed in this study. The effect of heating load and oxygen decomposition supply temperature is reported for the hydration, dehydration, condenser and evaporator heat transfer processes.

Introduction

Chemical heat pumps (CHP) represent a viable method for upgrading waste heat from industrial processes. Using a CHP to upgrade the waste heat from energy intensive industrial processes such as cement and steel plants can be effectively utilized for thermochemical hydrogen production. Combining the hydrogen production system with industrial processes could potentially reduce the carbon footprint of the industrial process. This study specifically investigates the upgrading waste heat from a cement plant using a Calcium oxide/steam (CaO/H_2O) CHP for thermochemical production of hydrogen.

Several studies have investigated the commercial viability of the copper–chlorine (Cu–Cl) cycle [1]. An efficiency of about 45% has been reported when combined with Generation IV nuclear power plants [1]. Steam methane reforming is the most common commercial method of producing hydrogen, while high temperature steam electrolysis is another alternative. Hydrogen is required as a feedstock in many applications such as the oil sands industry, pharmaceutical, biochemical and food industries. The use of hydrogen as a fuel can significantly reduce the greenhouse gas emissions of industrial processes. The viability of using hydrogen as a fuel in a cement plant to reduce the overall greenhouse gas

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Nomenclature

A	cross-sectional, area m^2
C	molar concentration, mol/m^3
$\dot{C}$	molar flow rate, mol/s
C_p	specific heat capacity, J/mol K and J/kg K
$C_{p,r}$	specific heat capacity reactor, J/mol K
H	enthalpy, kJ
I	current (Amps)
k	rate of reaction, mol/s
m_r	mass of reactor, kg
$\dot{N}_{H_2}$	molar flow rate hydrogen, kJ/mol
Q_{cell}	heat transfer from electrolytic cell, kJ
Q_{cond}	heat transfer from condenser, kJ
Q_f	energy available from flue gas, kJ
Q_{H_2O}	heat transfer to steam, kJ
R_u	universal gas constant, kJ/mol K
R	electrical resistance, Ω
T	temperature, K
t	time, s
U	overall heat transfer coefficient, W/m^2K

Subscripts

a	reactor 1
b	reactor 2
c	condenser
d	decomposition
e	evaporator
f	flue gas
fgH_2O	latent heat of vaporisation water (kJ/mol)
h	hydration
p	particle
r	reactor

Superscript

in	inlet flow stream
out	outlet flow stream

emissions from the plant and increase the overall efficiency of its operation in the focus of this study.

Electrolysis is a commercial technology to produce hydrogen. When the overall efficiency of a system including the generation of electricity is considered, this efficiency typically becomes 18–24% [2]. Thermochemical splitting of water is an emerging technology and promising alternative to electrolysis of water. Two of the thermochemical cycles are the sulphur-iodine (S–I) and copper–chlorine (Cu–Cl) cycles. The Cu–Cl cycle (up to 550 °C) requires lower temperature heat input to produce hydrogen than the S–I cycle (up to 825–900 °C) [3,4]. Naterer et al. [1] have demonstrated a large-scale Cu–Cl cycle at the University of Ontario Institute of Technology (UOIT). Brown et al. [4] reported that the S–I cycle developed by Japan Atomic Energy Research Institute (JAERI) has an adiabatic efficiency of 38% if coupled with a fusion reactor.

The thermochemical cycle presented by Naterer et al. is combined with a CaO/H_2O CHP by using the flue gas of the cement plant as heat input to the CHP. The precalciner (340 °C) and the kiln (1067 °C) of a cement plant produce high temperature flue gas. A CaO/H_2O CHP is used to upgrade the flue gas from the cement plant to provide the heat required by a Cu–Cl plant for the decomposition of copper oxychloride ($CuO.CuCl_2$) when the flue gas temperature is 340 °C. This flue gas is typically not recycled in the plant and it is sent directly through the stack. The heat pump is used to upgrade the flue gas from the cement plant to a temperature required in the oxygen decomposition reactor. The higher temperature (1067 °C) available from the kiln is normally recirculated within the cement plant to improve the efficiency of the cement plant. Fig. 1 shows a schematic of the proposed system when combined with the oxygen reactor in the Cu–Cl cycle.

Several working pairs for CHPs were investigated by Wongsuwan et al. [5], who outlined the preferred combination for the appropriate working conditions. Oguru and Mujumdar [6] proposed a CHP which produces hot dry air for an industrial drying process based on CaO hydration and dehydration of $CaCO_3$. The system had a coefficient of performance (COP) of about 1.52 with an output temperature of about 550 °C. Fujimoto [7] extended the work of Oguru et al. [8,9] experimentally and numerically for a smaller system with an output temperature of about 400 °C.

Naterer [10] also investigated the second law viability of upgrading waste heat for thermochemical hydrogen production using a magnesium oxide/vapor CHP. The results showed that the COP increased with a higher evaporator temperature. The Carnot cycle for both cooling and heating were also reported and compared analytically. Sharonov and Aristov [11] compared the thermodynamic performance of CHPs and adsorption heat pumps for non-regenerative cycles. The results indicated that nearly the Carnot efficiency can be obtained for mono-variant equilibrium gas–solid reactions but cannot be applied to di-variant equilibrium systems. Kato et al. [12–14] also investigated a high temperature heat pump using a combination of CaO/CO_2 and PbO/CO_2. A temperature of about 860 °C was achieved experimentally and optimal kinetics of the reactions was presented. The possibility of lead poisoning makes the system less attractive for commercialization.

The CaO/H_2O CHP is well suited for thermochemical production of hydrogen since $Ca(OH)_2$ can be produced from limestone used to produce cement. This will reduce the possibility of contamination within the cement plant and also enhance possible integration. The combined system is investigated numerically using a transient energy balance of the heat flow streams and chemical mass transfer reactions. A pinch analysis is used to determine the molar flow rate of hydrogen produced from the combined system. The effect of heating load from the cement plant and temperature required by the oxygen decomposition reactor are analyzed for the hydration, dehydration, condensation, and evaporation processes.

System description

Various cycle configurations have been proposed for thermochemical hydrogen production using the Cu– Cl cycle. These ranges from three to five major chemical reactions [15].