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Upgrading waste heat from a cement plant for thermochemical hydrogen production

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ABSTRACT

A calcium oxide/steam chemical heat pump (CHP) is presented in the study as a means to upgrade waste heat from industrial processes for thermochemical hydrogen production. The CHP is used to upgrade waste heat for the decomposition of copper oxychloride ($CuO.CuCl_2$) in a copper–chlorine (Cu–Cl) thermochemical cycle. A formulation is presented for high temperature steam electrolysis and thermochemical splitting of water using waste heat of a cement plant. Numerical models are presented for verifying the availability of energy for potential waste heat upgrading in cement plants. The optimal hydration and decomposition temperatures for the calcium oxide/steam reversible reaction of 485 K and 565 K respectively are obtained for the combined heat pump and thermochemical cycle. The coefficient of performance and overall efficiency of 4.6 and 47.8% respectively are presented and discussed for the CHP and hydrogen production from the cement plant.

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Introduction

Waste heat from energy intensive industrial processes such as cement and steel plants can be effectively utilized by other thermal processes to reduce energy losses and increase the system efficiency. Effective waste heat utilization depends on a combination of thermoeconomic analysis and needs of the industrial processes. This study specifically investigates the utilization of waste heat from cement plants. A waste heat case study of a cement plant in Bowmanville, Ontario, Canada is examined for this study of thermochemical production of hydrogen.

Several studies have investigated the commercial viability of the copper–chlorine (Cu–Cl) cycle [1–7]. An efficiency of about 45% has been reported when combined with Generation IV nuclear power plants [8]. 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. This paper studies the use of hydrogen as a fuel in the cement plant to reduce the overall greenhouse gas emissions from the plant and increase the overall efficiency of its operation.

Electrolysis is a commercial technology to produce hydrogen. When the overall efficiency of a system including the generation of electricity is considered, this efficiency

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Nomenclature

E_o	reversible cell potential, V
E	cell voltage, V
F	Faraday's Constant, 96,485 C/mol
$\bar{g}$	specific Gibbs energy, kJ/kmol
$G_{T,P}$	Gibbs energy at specific temperature and pressure, kJ
H	enthalpy, kJ
$\bar{h}$	specific enthalpy, kJ/kmol
K	rate of reaction, m^3/s
n	electron transfer
$\dot{N}$	molar flow rate, kmol/s
N	molar concentration, $kmol/m^3$
P	pressure, kpa
Q_{cell}	heat transfer from electrolytic cell, kJ
Q_{cond}	heat transfer from condenser, kJ
Q_f	energy available from flue gas, kJ/kmol
Q_{H_2O}	heat transfer to water entering electrolytic cell, kJ
$\bar{R}$	universal gas constant, kJ/kmol K
S	entropy, kJ/K
S_{gen}	entropy generation, kJ/K
T	temperature, K
V	volume, m^3
W_{gen}	steam cycle work output, kJ
W_{pump}	pump work, kJ
Greek	
η_E	efficiency of electrolytic hydrogen production
η_p	overall plant efficiency
μ_k	chemical potential
Subscripts	
d	decomposition
E	electrolytic cell
evap	evaporator
f	flue gas
o	environment
s	surface
Abbreviations	
CHP	chemical heat pump
COP	coefficient of performance
LHV	lower heating value, kJ/mol

typically becomes 18–24% [9]. 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) [10,11]. Although the reduced temperature is advantageous, materials to handle the highly corrosive HCl at high temperatures is a challenge. Naterer et al. [8] have demonstrated a large-scale Cu–Cl cycle at the University of Ontario Institute of Technology (UOIT). Brown et al. [11] have studied the S-I cycle. Past studies have shown the viability of using waste heat from high temperature industrial applications to supply the heat required by the Cu–Cl cycle [8].

This paper combines the thermochemical cycle presented by Naterer et al. [8] to a cement plant using a calcium oxide/steam (CaO/H_2O) chemical heat pump (CHP). The precalciner (340 °C) and the kiln (1067 °C) of a cement plant produce high temperature flue gas. This paper investigates a CaO/H_2O CHP 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. Zamfirescu et al. [12,13] proposed a system of vapour compression of $CuCl_2$ to upgrade waste heat for thermochemical hydrogen production.

CHPs are investigated for heat upgrading in this study due to their high storage capacity and heat of reaction. Several working pairs were investigated by Wongsuwan et al. [14], who outlined the preferred combination for the appropriate working conditions. Ogura and Mujumdar [15] proposed a CHP which produces hot dry air for an industrial drying process based on CaO hydration and decarbonization of $CaCO_3$. The system had a COP of about 1.52 with an output temperature of about 550 °C. Fujimoto [16] extended the work of Ogura et al. [17,18] experimentally and numerically for a smaller system with an output temperature of about 400 °C.

Naterer [19] also investigated the second law viability of upgrading waste heat for thermochemical hydrogen production using a magnesium oxide/vapour 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. Although a maximum COP of about 2.75 was reported for the CHP, this paper will show that higher COPs are achievable by replacing components in a CaO/H_2O cycle. Sharonov and Aristov [20] compared the thermodynamic performance of chemical heat pumps and adsorption heat pumps for non-regenerative cycles. The results indicated that the Carnot efficiency can be

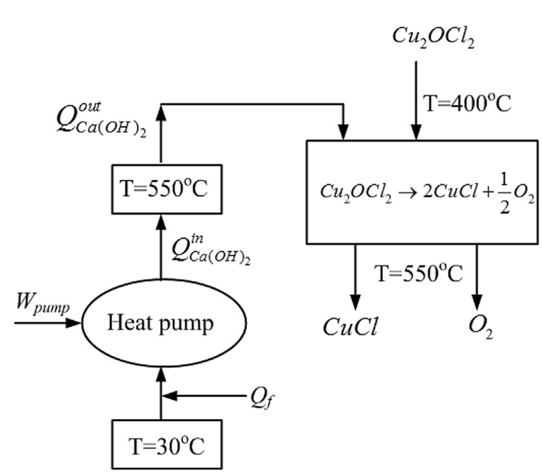

Fig. 1 – Schematic of combined CHP and Cu–Cl cycle.

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