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Development of a four-step Cu–Cl cycle for hydrogen production – Part I: Exergoeconomic and exergoenvironmental analyses

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ABSTRACT

Thermodynamic, economic and environmental impact assessments of a four-step Cu–Cl cycle developed for hydrogen production are performed using exergy, cost, exergoenvironmental and exergoeconomic analyses, and life cycle assessment. For the system considered under the baseline conditions, the total cost rate and environmental impact rate are determined to be 165 $/s and 37.6 Pt/s, respectively. The following Part II of this two companion papers leverages this paper's results to optimize the four-step Cu–Cl with respect to overall exergy efficiency, total cost rate and total environmental impact rate.

Introduction

Hydrogen is expected to become an important energy carrier that will help in solving several energy challenges. Hydrogen use does not negatively contribute to climate change -provided it is derived from clean energy sources, such as renewables-since its oxidation does not emit greenhouse gases (GHGs). Hydrogen production using thermochemical water splitting cycles has the exemplary potential to be cleaner, more efficient, more cost-effective and more environmentally-benign than conventional production methods (e.g. steam methane reforming). A variety of thermochemical water decomposition cycles have been identified [1], but few have progressed beyond theoretical calculations to working experimental demonstrations. Most of these cycles require process heat at temperatures exceeding 800 °C. Due to its lower temperature requirements (around 530 °C), the copper-chlorine cycle for thermochemical water decomposition is a promising hydrogen production method. Moreover, the Cu–Cl cycle has several other advantages over other existing hydrogen production methods, and it can utilize low-grade/waste heat to improve its efficiency [2].

The Clean Energy Research Laboratory of Faculty of Engineering and Applied Science at UOIT has been excelling about the development and experimental investigation of Cu–Cl

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based thermochemical cycle for sustainable hydrogen production. Although lab scale experiments of individual reactions within the Cu–Cl thermochemical cycle have been conducted, the overall integrated cycle has not yet been experimentally tested. Aspen Plus, a commercial process simulation package, can be used to evaluate characteristics of the complete cycle, including energy, exergy and cost effectiveness, before building a pilot plant. Studies that combine exergy analysis with economic/environmental assessments for the hydrogen production using thermochemical water splitting via the Cu–Cl cycle have been reported. Orhan et al. [3] investigated how exergy-related parameters can be used to reduce the cost of a copper-chlorine (Cu–Cl) thermochemical cycle for hydrogen production. The specific exergy cost (SPECO) method is used in the study to conduct exergoeconomic analysis. The results showed that the effect of exergy efficiency on the cost of hydrogen is high in the efficiency range of 5–30% and very low in the efficiency range of 30–60%. The hydrogen cost approaches the lowest and becomes roughly constant above an exergy efficiency of 60%.

An exergoeconomic assessment of the Cu–Cl thermochemical cycle using exergy-cost-energy-mass (EXCEM) analysis is previously described by Orhan et al. [4]. The exergetic cost allocations and various exergoeconomic performance parameters are determined for the overall cycle and its components. Exergy and cost are the only EXCEM quantities that are not subject to conservation laws. Exergy enters at the inlet at the rate of 0.151 GW and exit at the rate of 0.068 GW, since the remaining exergy is destroyed in the cycle and/or lost to the environment. The situation is reversed for cost. The cost flow rate at the inlet of the cycle is 0.893 $/kg while it is 2.24 $/kg at the outlet of the cycle, because 1.347 $/kg is generated within the cycle.

Exergoeconomic analysis is performed to four-step Cu–Cl cycle linked with geothermal energy using EXCEM method by Balta et al. [5]. The energy and exergy efficiencies are calculated to be 49% and 54%, respectively. The cost flow rates at the inlet and exit of the cycle are 0.51 $/kg and 2.046 $/kg, respectively. Because, 1.54 $/kg cost is generated within the cycle. The ratio of thermodynamic loss rate to capital cost varies between 0.004 and 0.012 (GJ/$) for the various hydrogen production capacities.

Ozbilen et al. [6] conduct a preliminary environmental impact assessment comprehensively using LCA for the five-step Cu–Cl cycle and compared with other hydrogen production methods: the sulphur–iodine (S–I) thermochemical cycle, high temperature water electrolysis, steam reforming of natural gas and electrolysis using renewable sources. The results, which are presented with respect to GWP, AP and Eco-indicator weighting factor, indicate that the thermochemical cycles have lower environmental impacts while steam reforming of natural gas has the highest.

The variations of environmental impacts with lifetime and production capacity are reported for nuclear based hydrogen production plants using the three-, four- and five-step (copper-chlorine) Cu–CI thermochemical water decomposition cycles by Ozbilen et al. [7]. The LCA is performed using GaBi 4 environmental impact assessment software. The parametric studies show that increasing plant hydrogen production capacity and lifetime does not significantly affect the values of the impact categories per kg hydrogen production, if the capacities and lifetimes are sufficiently great. The parametric studies also indicate that APs and GWPs for the four-step Cu–Cl can be reduced from 0.0031 to 0.0028 kg SO_2-eq and from 0.63 to 0.55 kg CO_2-eq, if the lifetime increases from 10 years to 100 years, respectively.

The environmental impacts of nuclear based hydrogen production via thermochemical water splitting using the Cu–Cl cycle are quantified and described, using the life cycle analysis and assessment, by Ozbilen et al. [8]. The LCAs for the three-, four- and five-step Cu–Cl cycles consider four scenarios, which relate to electrical power distribution. Multiple scenarios are considered to account for possible future Cu–Cl cycle designs using GaBi 4 LCA software. The results are presented in seven impact categories defined by CML, including global warming potential, and show that negative impacts can be associated with hydrogen production, depending on its source, even though hydrogen is a clean energy carrier. The four-step Cu–Cl cycle linked with a Generation IV SCWR, which supplies all electricity requirements for the production processes, is seen to have the lowest environmental impact due to its lower thermal energy requirement. If electrical energy output of the nuclear plant is used for all processes in nuclear-based hydrogen production, the GWP can be decreased from an initial value of 15.8 kg to 0.56 kg CO_2-eq. The four-step Cu–Cl thermochemical water splitting cycle exhibits lower environmental impacts compared to the three- and five-step cycles. The primary contributors to environmental impact categories are observed to be fuel processing, especially mining and conversion due to the fossil fuel use in these processes, and nuclear plant utilization.

ExLCA (Exergetci Life Cycle Assessment) is applied with life cycle assessment (LCA) to the five-step Cu–Cl hydrogen production process by Ozbilen et al. [9]. LCA, which is an analytical tool to identify, quantify and decrease the overall environmental impact of a system or a product, is extended to ExLCA. Exergy efficiencies and air pollution emissions are evaluated for all process steps, including the uranium processing, nuclear and hydrogen production plants. LCA results for 1 MJ exergy of produced hydrogen are presented in four categories: acidification potential, eutrophication potential, global warming potential and ozone depletion potential. A parametric study is performed for various plant lifetimes. Variation of environmental impacts (GWP and AP) with exergy efficiency of the five-step Cu–Cl cycle is also investigated. The ExLCA results indicate that the greatest irreversibility is caused by uranium processing. The primary contributor of the life cycle irreversibility of the nuclear-based hydrogen production process is fuel (uranium) processing, for which the exergy efficiency is 26.7% and the exergy destruction is 2916.3 MJ/kg hydrogen. The lowest global warming potential per megajoule exergy of hydrogen is 5.65 g CO_2-eq achieved a plant capacity of 125,000 kg H_2/day. The corresponding value for a plant capacity of 62,500 kg H_2/day is 5.75 g CO_2-eq. At present, the only study that relates thermodynamics to environmental impacts for the Cu–Cl cycle is reported by Ozbilen et al. [9] through an exergetic life cycle assessment (ExLCA). There is no study in the literature, to the best of the authors' knowledge that performs an exergoenvironmental analysis of the Cu–Cl cycle. The specific objective of the paper is to develop and perform exergoeconomic and exergoenvironmental analyses of the Cu–Cl cycle.

System description

Atomic Energy of Canada Limited (AECL) has identified the copper-chlorine (Cu–Cl) cycle as a promising method for thermochemical hydrogen production with the next generation CANDU super-critical water cooled reactor (SCWR) due to its lower operating temperatures and potentially lower cost materials. UOIT, AECL, Argonne National Laboratory (USA) and partner institutions are collaborating to scale this technology up to industrial capacities [2].

Several types of Cu–Cl cycles for thermochemical water decomposition are proposed in the literature, as mainly characterized by the number of major chemical steps they incorporate and their types of groupings. Although all cycles consist of a series of chemical reactions, the net reaction for each cycle is

$$H_2O\ (g) \rightarrow H_2\ (g) + ½\ O_2\ (g) \tag{1}$$

The Cu–Cl thermochemical cycle uses a series of intermediate copper and chlorine compounds. Its chemical reactions form a closed internal loop that recycles all chemicals on a continuous basis, without emitting any greenhouse gases or other substances [10]. Hence, water, thermal energy and electricity are the main inputs to the Cu–Cl thermochemical cycle considered here.

This research focuses on the four-step Cu–Cl thermochemical cycle, which is currently under experimental investigation in the Clean Energy Research Lab at UOIT. The four-step Cu–Cl cycle (Fig. 1) consists of the following four main sections:

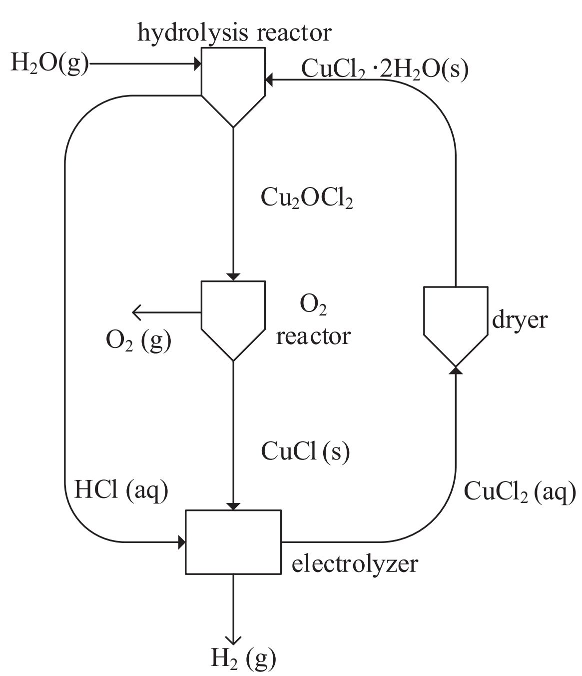

Fig. 1 – Conceptual schematic of the four-step Cu–Cl cycle.

- Step 1 (Hydrolysis at 370–400 °C):

$$2CuCl_2\ (s) + H_2O\ (g) \rightarrow Cu_2OCl_2\ (s) + 2HCl\ (g) \tag{2}$$

- Step 2 (Copper oxychloride decomposition at 500–550 °C):

$$Cu_2OCl_2\ (s) \rightarrow 2CuCl\ (s) + ½\ O_2\ (g) \tag{3}$$

- Step 3 (Hydrogen production, or electrolysis, at 25–100 °C):

$$2HCl\ (aq) + 2CuCl\ (aq) \rightarrow H_2\ (g) + 2CuCl_2\ (aq) \tag{4}$$

- Step 4 (Drying at 80–100 °C):

$$2CuCl_2\ (aq) \rightarrow H_2O\ (g) + 2CuCl_2\ (s) \tag{5}$$

The Aspen Plus simulations of the four-step Cu–Cl cycle are conducted by the authors; the simulated cycle is available in Fig. 2, which includes hydrolysis, copper oxychloride decomposition reactors, dryer, electrolyzer, heat exchangers and auxiliary equipment used in the hydrogen production system. The Aspen Plus is a process simulator that predicts the behaviours of chemical reactions and thermal processes using standard thermodynamic and electrochemical relationships, such as mass, energy and entropy balances, rate correlations, as well as phase and chemical equilibrium data. Also, another package, so-called: EES (Engineering Equation Solver), is employed for exergoeconomic and exergoenvironmental models and calculations. EES is known as a general equation solving program that can numerically solve couple linear/non-linear algebraic and differential equations with high accuracy thermodynamic property database. The calculations in Section Analysis and assessment base on the state numbers in Fig. 2 as the objective of this study is to optimize the simulated four-step Cu–Cl cycle. Further information (e.g. flow compositions, pressures of the each state) on the simulated four-step Cu–Cl cycle is presented elsewhere [11].

Analysis and assessment

Energy and exergy analyses of the four-step Cu–Cl cycle are presented in Ozbilen et al. [11]. This paper use the output mass and exergy flows of each state to apply exergoeconomic and exergoenvironmental approach.

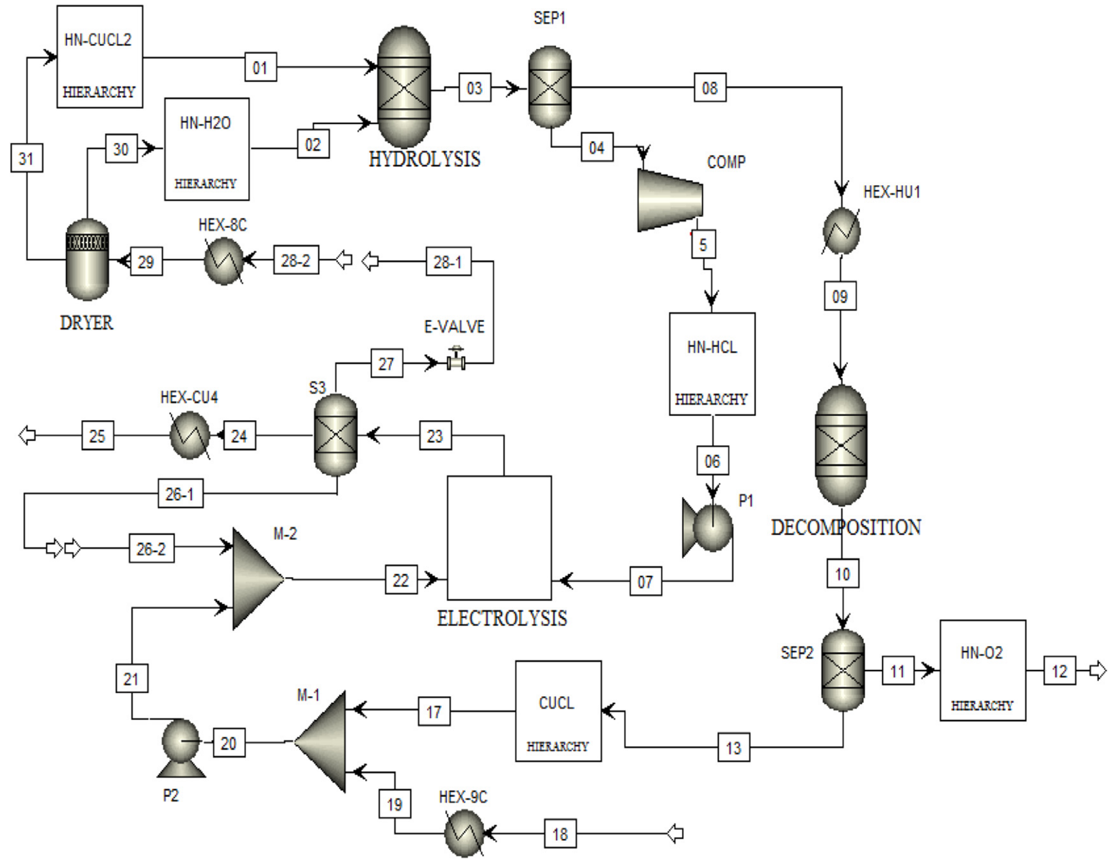

Fig. 2 – Aspen Plus flowsheet of the final design for the four-step Cu–Cl cycle (modified from Ref. [11]).

Exergoeconomic analysis for the Cu–Cl cycle

The cost balance equations and purchase equipment cost correlations are used for each component of the cycle. Unit costs of each stream are found via cost accounting, and exergoeconomic evaluation is performed. The main assumptions for the exergoeconomic analysis to calculate purchase equipment costs and cost parameters are as follows: (i) the maintenance factor is 1.06 [12], and (ii) the material factor is taken as 1.06, since a porcelain coating over carbon steel is used due to the acidic environment within the cycle [13]. Maintenance and material factors are to include the cost of the maintenance and ceramic coating of components used in the hydrogen production plant, respectively. In addition, the following additional assumptions are made:

- The interest rate is 5%.
- The equipment lifetime is selected to be 15 years.
- The plant capacity factor is taken as 0.85.
- The unit cost of electricity is taken as 0.09 \$/kWh.
- The unit cost of thermal energy is taken as 0.02 \$/kWh based on 2005 statistics [13]. The value is then normalized for 2012 using Chemical Engineering Plant Cost Index.
- The purchased equipment cost values are also normalized for the year 2012 using the Chemical Engineering Plant Cost Index.

Cost balance equations

The cost flow rate $\dot{C}$ (\$/s), is defined for each flow in a system, and a cost balance for each component is written in order to conduct an exergoeconomic analysis. Prior to analysis, however, the fuel and product exergies for each component are needed to be defined. The fuel exergy is defined as the resources consumed in generating the product, while the product exergy is the cost of owning and operating a component under consideration [12]. The fuel and product exergies for each component of the Cu–Cl cycle are shown in Table 1.

The cost balance equations with auxiliary equations for the main component of the Cu–Cl cycle are detailed below. The basic definitions of the F (Fuel) and P (Product) rules used for auxiliary equations are presented elsewhere [12]. The F rule refers to the removal of exergy from an exergy stream within the considered component when exergy differences between the inlet and outlet are considered in the fuel definition for this stream. Thus, this rule states that the specific cost (cost per exergy unit) associated with this fuel stream exergy removal must be equal to the average specific cost at which the removed exergy was supplied to the same stream in upstream components. The P rule refers to the supply of exergy to an exergy stream within the component and states that each exergy unit is applied to any stream associated with the product at the same average cost. Since this corresponds to an exiting stream, the number of

Table 1 – Fuel and product definitions with respect to the Cu–Cl cycle.

Component	Fuel	Product
Hydrolysis	$\dot{E}x_5 - \dot{E}x_{5-1}$	$(\dot{E}x_4 + \dot{E}x_8) - (\dot{E}x_1 + \dot{E}x_2)$
Copper oxychloride decomposition	$\dot{E}x_{Q,step\ 2}$	$(\dot{E}x_{11} + \dot{E}x_{13}) - \dot{E}x_9$
Electrolysis	$\dot{W}_{elec}$	$(\dot{E}x_{24} + \dot{E}x_{27}) - (\dot{E}x_{21} + \dot{E}x_7)$
Drying, HEX 6 and HEX 8	$\dot{E}x_{5-3} - \dot{E}x_{5-4}$	$(\dot{E}x_{30} + \dot{E}x_{31-1}) - \dot{E}x_{28}$
HEX 1	$\dot{E}x_{11-1} - \dot{E}x_{11-2}$	$\dot{E}x_{30-1} - \dot{E}x_{30}$
HEX 2	$\dot{E}x_{14} - \dot{E}x_{15}$	$\dot{E}x_{30-2} - \dot{E}x_{30-1}$
HEX 3	$\dot{E}x_{5-2} - \dot{E}x_{5-3}$	$\dot{E}x_{30-3} - \dot{E}x_{30-2}$
HEX 4	$\dot{E}x_{11} - \dot{E}x_{11-1}$	$\dot{E}x_{30-4} - \dot{E}x_{30-3}$
HEX 5	$\dot{E}x_{13} - \dot{E}x_{14}$	$\dot{E}x_2 - \dot{E}x_{30-4}$
HEX 7	$\dot{E}x_{5-1} - \dot{E}x_{5-2}$	$\dot{E}x_{31-2} - \dot{E}x_{31-1}$
HEX 9	$\dot{E}x_{15} - \dot{E}x_{16}$	$\dot{E}x_{19} - \dot{E}x_{18}$
HEX HU1	$\dot{E}x_{Q,\ HU1}$	$\dot{E}x_9 - \dot{E}x_8$
HEX HU2	$\dot{E}x_{Q,\ HU2}$	$\dot{E}x_1 - \dot{E}x_{31-2}$
HEX CU1	$\dot{E}x_{Q,\ CU1}$	$\dot{E}x_{5-4} - \dot{E}x_6$
HEX CU2	$\dot{E}x_{Q,\ CU2}$	$\dot{E}x_{16} - \dot{E}x_{17}$
HEX CU3	$\dot{E}x_{Q,\ CU3}$	$\dot{E}x_{11-2} - \dot{E}x_{12}$
HEX CU4	$\dot{E}x_{Q,\ CU4}$	$\dot{E}x_{24} - \dot{E}x_{25}$
Compressor	$\dot{W}_{comp}$	$\dot{E}x_5 - \dot{E}x_4$
Expansion valve	$\dot{E}x_{27}$	$\dot{E}x_{28}$
Pump – 1	$\dot{W}_{pump,1}$	$\dot{E}x_7 - \dot{E}x_6$
Pump – 2	$\dot{W}_{pump,2}$	$\dot{E}x_{21} - \dot{E}x_{20}$
Mixer -1	$\dot{E}x_{19} + \dot{E}x_{17}$	$\dot{E}x_{20}$

auxiliary equations provided by this rule always equals $n_{e,p} - 1$, where $n_{e,p}$ is the number of exiting exergy streams that are included in the product definition. The specific cost at which the removed exergy was supplied to the same stream in upstream components [12].

Hydrolysis reactor (reactor 1):

$$\dot{C}_5 - \dot{C}_{5-1} + \dot{Z}_{R1} = \left(\dot{C}_4 + \dot{C}_8\right) - \left(\dot{C}_1 + \dot{C}_2\right) \tag{6}$$

$c_5 = c_{5-1}$ (F rule)

$c_4 = c_8$ (P rule)

Copper oxychloride decomposition reactor (reactor 2):

$$c_{thermal}\,\dot{E}x_{Q,step\ 2} + \dot{Z}_{R2} = \left(\dot{C}_{11} + \dot{C}_{13}\right) - \dot{C}_9 \tag{7}$$

$c_{11} = c_{13}$ (P rule)

Electrolysis:

$$c_{electricity}\dot{W}_{elec} + \dot{Z}_{elec} = \left(\dot{C}_{24} + \dot{C}_{27}\right) - \left(\dot{C}_{21} + \dot{C}_7\right) \tag{8}$$

$c_{24} = c_{27}$ (P rule)

Drying, Hex 6 and Hex 8:

$$\dot{C}_{5-3} - \dot{C}_{5-4} + \dot{Z}_{HEX6,8,dry} = \left(\dot{C}_{30} + \dot{C}_{31-1}\right) - \dot{C}_{28} \tag{9}$$

$c_{5-4} = c_{5-3}$ (F rule)

$c_{30} = c_{31}$ (P rule)

$$\frac{\left(\dot{C}_{31-1} - \dot{C}_{31}\right)}{\left(\dot{E}x_{31-1} - \dot{E}x_{31}\right)} = \frac{\left(\dot{C}_{29} - \dot{C}_{28}\right)}{\left(\dot{E}x_{29} - \dot{E}x_{28}\right)} \quad \text{(P rule)}$$

$$\frac{\left(\dot{C}_{29} - \dot{C}_{28}\right)}{\left(\dot{E}x_{29} - \dot{E}x_{28}\right)} = \frac{\left(\dot{C}_{30} + \dot{C}_{31-1} - \dot{C}_{29}\right)}{\left(\dot{E}x_{30} + \dot{E}x_{31-1} - \dot{E}x_{29}\right)} \quad \text{(P rule)}$$

Purchased equipment cost correlations

The capital investment rate can be calculated using the purchase cost of equipment and capital recovery, as well as the maintenance factor over the number of operation hours per year as given as follows:

$$\dot{Z}_k = \frac{Z_k \cdot CRF \cdot \varphi}{N} \cdot F_m \tag{10}$$

where N is the annual number of operation hours for the unit and φ is the maintenance factor, generally taken as 1.06 [12]. F_m is the material factor. The capital recovery factor, CRF, depends on the interest rate "i", and equipment life-time in years "n" as

$$CRF = \frac{i \cdot (1+i)^n}{(1+i)^n - 1} \tag{11}$$

where Z_k is the purchase equipment cost of the system components which should be written in terms of design parameters. The correlations for each component are given elsewhere [14].

Cost accounting

Cost balances for each component are needed to be solved in order to estimate the cost rate of exergy destruction in each component. Implementing a cost equation for each component together with the auxiliary equations form a system of linear equations as follows:

$$\left[\dot{E}x_k\right] \times [c_k] = \left[\dot{Z}_k\right] \tag{12}$$

where the equation entails matrices of exergy rate (from exergy analysis), exergetic cost vector (to be evaluated) and the vector of $[\dot{Z}_k]$ factors (from economic analysis) respectively. The size of the exergy rate matrix is 43 × 43, created using cost balance equations in Section Cost balance equations. By solving these equations simultaneously, the cost rate of each flow is calculated, which is used to determine the cost rate of exergy destruction in each system component.

Exergoeconomic evaluation

The performance of a component can be defined and the cost flow rates through components associated with the exergy loss are calculated using the cost history of the plant. This is provided by the exergoeconomic factor f and defined as

$$f = \frac{\dot{Z}}{\dot{Z} + c_f \dot{E}x_d} \tag{13}$$

The relative cost difference (RCD) is another useful variable for evaluating and optimizing a system component in thermoeconomic evaluations, which measures the relative increase in the average cost per exergy unit between fuel and product of the component. The relative cost difference for the cycle can be written as

$$RCD = \frac{c_p - c_f}{c_f} \tag{14}$$

where c_p is the unit exergetic cost of the product of the system and c_f is the unit exergetic cost of the required fuel used.

An exergoeconomic evaluation of the four-step Cu–Cl cycle is performed by means of exergoeconomic factor and relative cost difference. Also, the total cost rate provides the component with the highest priority from exergoeconomic viewpoint and is the combination of the cost rate of exergy destruction and the investment cost rates:

$$\dot{C}_{tot,k} = \dot{C}_{d,k} + \dot{Y}_k \tag{15}$$

Exergoenvironmental analysis

Exergoenvironmental analysis reveals the environmental impact associated with each system component and the real sources of the impact by combining exergy analysis with a comprehensive environmental assessment method.

In the environmental analysis, LCA is carried out in order to obtain the environmental impact of each relevant system components and input streams. It consists of goal definition, inventory analysis and interpretation of results, which incorporates the supply of the input streams (especially fuel) and full life cycle of components. The quantification of environmental impact with respect to depletion and emissions of a natural resource can be conducted using different methodologies. In this study, impact analysis using Eco-indicator 99 points along with previously determined impact analyses in the literature are used. For the LCA analysis, various damage categories are covered and the results are weighted and expressed in terms of Eco-indicator points (mPts) [15] by using SimaPro 7.1.

Environmental impact balance equations

The environmental impact flow rate $\dot{B}$ (Pt/s), is defined for each flow in a system, and an environmental impact balance for each component is written in order to conduct an exergoenvironmental analysis. Environmental impact balance equations with auxiliary equations (analogous to exergoeconomic equations) for the major steps of the Cu–Cl cycle are given below:

Hydrolysis reactor (reactor 1):

$$\dot{B}_5 - \dot{B}_{5-1} + \dot{Y}_{R1} = (\dot{B}_4 + \dot{B}_8) - (\dot{B}_1 + \dot{B}_2) \tag{16}$$

$$b_5 = b_{5-1} \ \text{(F rule)}$$

$$b_4 = b_8 \ \text{(P rule)}$$

Copper oxychloride decomposition reactor (reactor 2):

$$b_{thermal}\,\dot{E}x_{Q,step\ 2} + \dot{Y}_{R2} = (\dot{B}_{11} + \dot{B}_{13}) - \dot{B}_9 \tag{17}$$

$$b_{11} = b_{13} \ \text{(P rule)}$$

Electrolysis:

$$b_{electricity}\dot{W}_{elec} + \dot{Y}_{elec} = (\dot{B}_{24} + \dot{B}_{27}) - (\dot{B}_{21} + \dot{B}_7) \tag{18}$$

$$b_{24} = b_{27} \ \text{(P rule)}$$

Drying, Hex 6 and Hex 8:

$$\dot{B}_{5-3} - \dot{B}_{5-4} + \dot{Y}_{HEX6,8,dry} = (\dot{B}_{30} + \dot{B}_{31-1}) - \dot{B}_{28} \tag{19}$$

$$b_{5-4} = b_{5-3} \ \text{(F rule)}$$

$$b_{30} = b_{31} \ \text{(P rule)}$$

$$\frac{(\dot{B}_{31-1} - \dot{B}_{31})}{(\dot{E}x_{31-1} - \dot{E}x_{31})} = \frac{(\dot{B}_{29} - \dot{B}_{28})}{(\dot{E}x_{29} - \dot{E}x_{28})} \ \text{(P rule)}$$

$$\frac{(\dot{B}_{29} - \dot{B}_{28})}{(\dot{E}x_{29} - \dot{E}x_{28})} = \frac{(\dot{B}_{30} + \dot{B}_{31-1} - \dot{B}_{29})}{(\dot{E}x_{30} + \dot{E}x_{31-1} - \dot{E}x_{29})} \ \text{(P rule)}$$

Environmental impact correlations

In order to be able to solve the environmental balance equations, the environmental impacts associated with each component are determined with respect to Eco-indicator 99 points, which enable a fair comparison among different components. These impact points are approximated with respect to a combination of correlations developed from numerous studies conducted in literature, available data as well as the LCA developed for this study.

Environmental impacts of hydrolysis and copper oxychloride decomposition reactors are calculated based on material input during its production. Dimensions for those reactors are given elsewhere [14]. Wall thickness of the reactors is selected to be 4 cm [15]. A correction factor of 1.06 is used for the porcelain coating [13]. The Eco-indicator point associated with the spray dryer is given by Ciesielski and Zbicinski [16], which is normalized for the Cu–Cl cycle needs. The mass flow rate of the steam is the environmental impact attribute for the dryer. Data for the electrolyzer material is obtained from Gorensek et al. [17], and an LCA is conducted using SimaPro 7 software. The power input of the electrolyzer given by Gorensek et al. [17] is 7.5 MW. Therefore, the environmental impact results are normalized for the Cu–Cl electrolyzer.

The environmental impact correlations for the compressor and pumps are normalized from Eco-invent database and the study of Boyano et al. [18]. The expansion valve environmental impact is obtained from Hamut [19] and normalized. The criterion to assess the environmental impact of the pumps and compressor is work input, whereas mass flow rate is used as a criterion for the expansion valve.

The eco-indicator points are rough estimations, based on area for the heat exchangers, and are calculated by normalizing various case studies performed in the literature [18,20]. The component related heat exchanger environmental impacts associated with the non-heat exchanging areas are neglected due to their relatively small size and unavailability of the data.

The environmental impact rate of a component can be calculated with respect to the environmental impacts associated with its production and operational time. That is,

$$\dot{Y}_k = \frac{Y_k}{N \cdot n} \tag{20}$$

where N is the annual number of operation hours for the unit, and n is the equipment life-time. Impact points for the major components of the Cu–Cl cycle are listed in Table 2.

Environmental impact accounting

Environmental impact balances for each component are needed to be solved in order to estimate the environmental impact rate of exergy destruction in each component. Implementing environmental impact balance equations for each component, together with the auxiliary equations, form a system of linear equations as follows:

$$[\dot{E}x_k] \times [b_k] = [\dot{Y}_k] \tag{21}$$

where the equation entails matrices of exergy rate (from exergy analysis), environmental impact vector (to be evaluated) and the vector of $[\dot{Y}_k]$ factors (from environmental analysis) respectively. The size of the exergy rate matrix is 43 × 43, created using environmental impact balance equations in Section Environmental impact balance equations. By solving these equations simultaneously, the environmental impact rate of each flow is calculated, which is used to determine the cost rate of exergy destruction in each system component.

Exergoenvironmental evaluation

Exergoenvironmental evaluation is performed by means of the exergoenvironmental factor. The sources for the formation of environmental impact in a component are compared using the exergoenvironmental factor $f_{b,k}$, which expresses the relative contribution of the component-related environmental impact $\dot{Y}_k$ to the total environmental impact for the component.

Table 2 – Environmental impact correlations (Eco-indicator 99) developed.

Component	$\dot{Y}$ (mPts/h)	Criteria
Hydrolysis	0.387	$\dot{m}_{steam}$
Copper oxychloride decomposition	0.00675	$\dot{m}_{Cu_2OCl_2}$
Electrolysis	0.456	$\dot{W}_{elec}$
Spray dryer	0.0240	$\dot{m}_{CuCl_2(aq)}$
HEX 1	0.000537	A_{HEX1}
HEX 2	0.00693	A_{HEX2}
HEX 3	0.0645	A_{HEX3}
HEX 4	0.000895	A_{HEX4}
HEX 5	0.0138	A_{HEX5}
HEX 6	0.0803	A_{HEX6}
HEX 7	0.0127	A_{HEX7}
HEX 8	0.00136	A_{HEX8}
HEX 9	0.000552	A_{HEX9}
HEX HU1	0.000808	A_{HEXHU1}
HEX HU2	0.0159	A_{HEXHU2}
HEX CU1	0.00631	A_{HEXCU1}
HEX CU2	0.000803	A_{HEXCU2}
HEX CU3	0.000261	A_{HEXCU3}
HEX CU4	0.000674	A_{HEXCU4}
Compressor	0.0492	$\dot{W}_{comp}$
Expansion valve	8.69×10^{-7}	$\dot{m}_{CuCl_2(aq)}$
Pump – 1	0.000168	$\dot{W}_{Pump1}$
Pump – 2	0.000103	$\dot{W}_{Pump2}$

$$f_{b,k} = \frac{\dot{Y}_k}{\dot{Y}_k + b_{f,k}\dot{E}x_d} \tag{22}$$

Here, an exergoenvironmental evaluation is performed; results are presented in the results and discussion section.

Results and discussion

Exergoeconomic analysis results

The exergy analysis is provided in Ozbilen et al. [11] to gain a further understanding regarding irreversibilities within components of the Cu–Cl cycle. This analysis, however, does not provide any information about economic constraints, cost of irreversibilities and component related costs. An exergoeconomic analysis, therefore, is carried out so that the cost formation can be determined for the Cu–Cl cycle. Table 3

Table 3 – Exergy rate, cost rate and specific cost of flows.

State no.	$\dot{E}x$ (MW)	$\dot{C}$ ($/s)	c ($/kJ)
1	45.22	85.53	0.001891
2	123.6	294.4	0.002382
3	156.2	466.5	0.002986
4	148.9	444.5	0.002986
5	221.9	446.5	0.002012
5-1	178.9	360	0.002012
5-2	169.4	340.9	0.002012
5-3	139.7	281	0.002012
5-4	13.48	27.11	0.002012
6	2.685	27.1	0.0101
7	3.269	27.14	0.0083
8	7.368	22	0.002986
9	13.348	22.05	0.001653
10	31.20	22.5	0.0007212
11	2.406	1.736	0.0007212
11-1	0.996	0.7186	0.0007212
11-2	0.1878	0.1355	0.0007212
12	0.001714	0.1322	0.07713
13	28.80	20.76	0.0007212
14	8.783	6.333	0.0007212
15	1.088	0.7848	0.0007212
16	0.5988	0.4318	0.0007212
17	0.2168	0.431	0.001988
18	0	0	0
19	0.1506	0.3537	0.002348
20	0.3674	0.7847	0.002136
21	0.4134	0.7925	0.001917
22	0.4675	0.9002	0.001925
23	5.134	30.27	0.005895
24	0.8220	4.879	0.005937
25	0.7562	4.878	0.006452
26	0.05420	0.1078	0.001988
27	4.259	25.28	0.005937
28	3.730	25.28	0.006777
29	5.377	28.64	0.005327
30	100.51	212.9	0.002119
30-1	100.9	213.5	0.002116
30-2	105.7	219.1	0.002072
30-3	130.2	279	0.002144
30-4	131.3	280	0.002132
31	2.623	5.556	0.002119
31-1	32.40	66.31	0.002047
31-2	39.76	85.43	0.002148

shows the specific cost, cost flow rate and exergy flow rate of each stream in the four-step Cu–Cl cycle. Specific costs of streams are calculated by solving cost balance equations presented in Section Environmental impact balance equations.

The cost rate of hydrogen (state 25) is calculated to be 4.878 $/s for 1.45 kg/s hydrogen mass flow rate. Hence, the unit cost of hydrogen is calculated to be 3.36 $/kg hydrogen produced. The cost estimate of the Argonne National Lab (ANL) is 3.30 $/kg hydrogen [21,22]. The updated cost of ANL using CEPCI is found to be 3.6 $/kg hydrogen. Moreover, Orhan [23] calculated the unit cost of the hydrogen production as 2.8 $/kg hydrogen. The updated value of the hydrogen cost is 2.73 $/kg. The 2012 value is lower than the 2011 hydrogen production value due to a decreasing cost index in 2012 [24].

The cost distribution among investment and exergy destruction rates for components with the greatest cost rates are presented in Fig. 3, showing that costs associated with exergy destructions are dominant relative to component related costs.

A sensitivity analysis is also conducted in order to determine the effects of the interest rate used in the analysis. Thus, variations of total cost flow rate with lifetime of the plant are investigated for various interest rates as illustrated in Fig. 4. This figure then shows the total cost rate increases with interest rate and decrease with total lifetime of the plant. Fig. 5 shows the variations of total cost rate per kg hydrogen produced with plant daily capacity for three plant lifetimes (10, 15 and 20 years). It primarily shows that the cost flow rate per kg hydrogen produced decreases with increasing plant lifetime. The cost flow rate per kg hydrogen produced is the lowest for a daily capacity of 100 tons, respectively.

The exergoeconomic factors and relative cost differences of some major components of the four-step Cu–Cl cycle are presented in Table 4. The exergoeconomic factor is close to zero when cost rate of exergy destruction is significantly higher than capital cost rate according to Eq. (13), whereas it is close to 100% for the components with higher capital cost rate. Exergoeconomic factors indicate that the cost associated with exergy destruction is dominant over the component related cost for all major components, excluding the compressor and pumps. For components with a very low exergoeconomic factor, it would be worthwile to consider improving the component efficiency by increasing the capital investment.

The variations of the exergoeconomic factor for the four-step Cu–Cl cycle with lifetime of the cycle for various interest rates is given in Fig. 6. The exergoeconomic factor

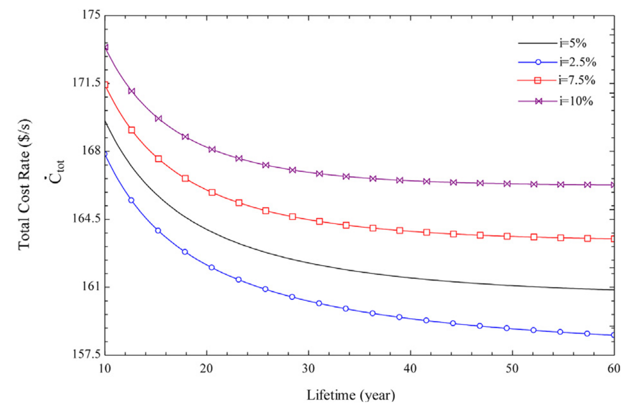

Fig. 4 – Variations of total cost flow with lifetime of the Cu–Cl cycle for several interest rates.

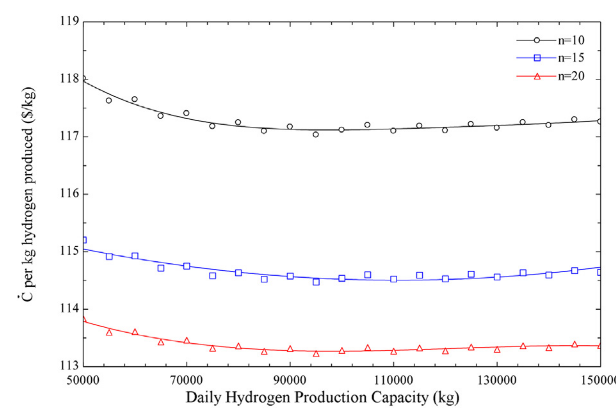

Fig. 5 – Variations of cost flow per kg hydrogen produced with daily production capacity of the Cu–Cl cycle.

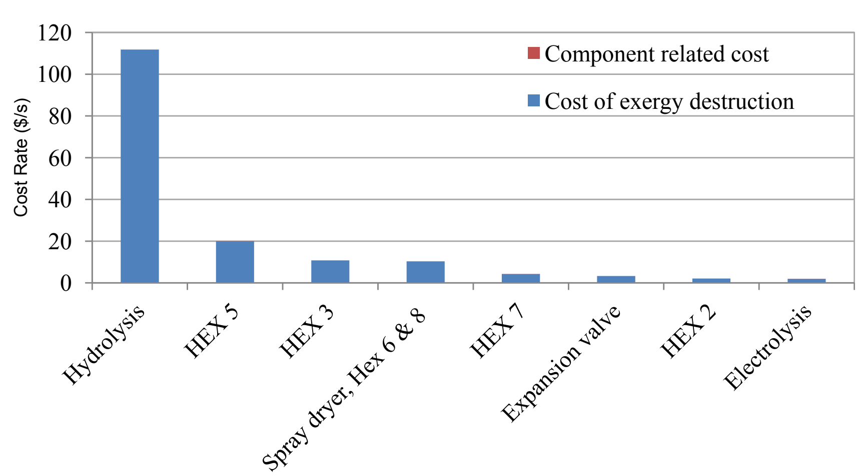

Fig. 3 – Cost distributions among investment and exergy destruction rates.

Table 4 – Exergoeconomic factors and relative cost differences of some major components of the four-step Cu–Cl cycle.

Component	f (%)	RCD
Hydrolysis	0.06	0.4839
Copper oxychloride decomposition	0.37	105.5
Electrolysis	1.59	236.5
Spray dryer, Hex 6 & 8	0.45	0.0139
Compressor	52.87	0.0878
HEX 1	0.22	0.9851
HEX 2	0.17	0.5935
HEX 3	0.31	0.2195
HEX 4	0.48	0.2107
HEX 5	0.03	−3.6
HEX 7	0.14	0.289
HEX 9	0.27	2.255
Pump – 1	77.06	1.622
Pump – 2	57.05	1.529

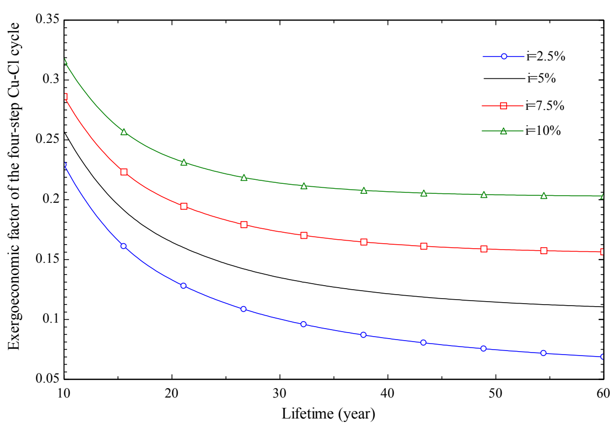

Fig. 6 – Variations of exergoeconomic factor of the four-step Cu–Cl cycle with lifetime for various interest rates.

decreases with increasing lifetime of the cycle, as the unit cost for purchased equipment decreases.

The effect of unit electricity price on total cost flow rate and the exergoeconomic factor for the four-step Cu–Cl cycle is also investigated. Fig. 7 shows that total cost flow dramatically

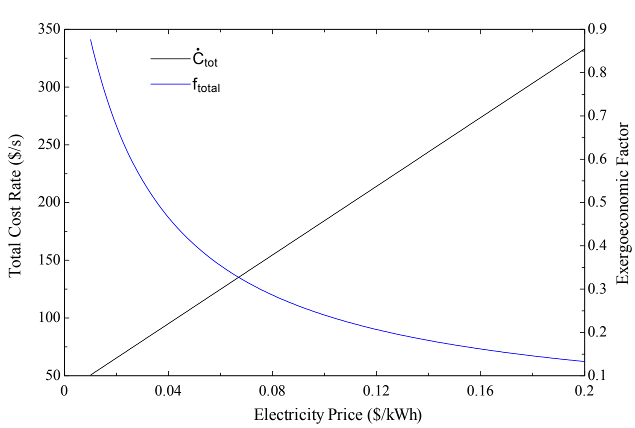

Fig. 7 – Variations of exergoeconomic factor and cost flow rate of the four-step Cu–Cl cycle with electricity price.

increases with increasing electricity price, since cost related with the exergy destruction is dominant for the Cu–Cl cycle. The exergoeconomic factor, however, decreases with increasing electricity price. Figs. 4 and 7 show that for the baseline conditions (i.e., 5% interest rate, 15 years equipment lifetime and 0.09 $/kWh unit cost of electricity) total cost rate is 165 $/s. The result is for 125,000 kg/day hydrogen production plant, hence the cost of total cost rate is 114 $/kg hydrogen.

Exergoenvironmental analysis results

The exergy analysis is provided in the previous section to gain a further understanding of the irreversibilities within components of the Cu–Cl cycle. This analysis, however, does not provide any information about environmental impact constraints, environmental impact of irreversibilities and component related environmental impacts. Exergoenvironmental analysis, therefore, is carried out for the four step Cu–Cl cycle to determine the locations of the associated environmental impact formations. Specific environmental impacts of streams are calculated by solving environmental impact balance equations presented in Section Environmental impact balance equations simultaneously. Table 5 shows the specific environmental impact, environmental impact flow rate and exergy flow rate of each stream in the four-step Cu–Cl cycle.

The assumptions for the exergoeconomic are also valid for the exergoenvironmental analysis. Additional assumptions regarding the environmental impacts of energy sources are given as follows:

- The unit environmental impact of electricity is taken as 22 mPt/kWh (Eco-indicator 99 manual).
- The unit environmental impact of thermal energy is taken as 6 mPt/kWh (SimaPro 7).

Table 5 shows exergy flow rates, environmental impact flow rates and the unit environmental impact of flows. The environmental impact distribution among investment and exergy destruction rates for components with the greatest rates are presented in Fig. 8, where it is seen that environmental impacts associated with exergy destructions are dominant compared to component related costs. The impact rates shown in the figure are outputs of the life cycle impact study. Fig. 8 also shows that hydrolysis reactor is the component with the highest environmental impact rate. Heat exchangers used in the process are also the main contributors to the hydrogen plants environmental impact.

Some parametric studies are also conducted to evaluate the effect of lifetime, power and thermal sources. Fig. 9 shows lifetime effect on total environmental impact rate and the exergoenvironmental factor. The higher the lifetime of the cycle, the lower the environmental impact rate. The exergoenvironmental factor also decreases with lifetime, indicating that the ratio of environmental impact of exergy destruction, to component related environmental impact, increases. Fig. 9 also shows that environmental impact rate is 37.4 Pt/s for the baseline plant lifetime, i.e. 15 years.

Fig. 10 shows the total environmental impact rate for the four-step Cu–Cl cycle using electricity generation mixed for

Table 5 – Exergy flow rates, environmental impact flow rates and the unit environmental impact of flows.

State no.	$\dot{E}x$ (MW)	$\dot{B}$ (Pt/s)	b (mPt/kJ)
1	45.22	18.88	0.4175
2	123.6	65.02	0.5260
3	156.2	103.0	0.6592
4	148.9	98.14	0.6592
5	221.9	98.61	0.4444
5-1	178.9	79.51	0.4444
5-2	169.4	75.29	0.4444
5-3	139.7	62.06	0.4444
5-4	13.48	5.986	0.4444
6	2.685	5.943	2.214
7	3.269	5.948	1.819
8	7.368	4.857	0.6592
9	13.348	4.870	0.3649
10	31.2	4.980	0.1596
11	2.406	0.3842	0.1596
11-1	0.996	0.1591	0.1596
11-2	0.1878	0.02999	0.1596
12	0.001714	0.02857	16.67
13	28.8	4.595	0.1596
14	8.783	1.402	0.1596
15	1.088	0.1737	0.1596
16	0.5988	0.09558	0.1596
17	0.2168	0.09256	0.4270
18	0	0	0
19	0.1506	0.07813	0.5187
20	0.3674	0.1707	0.4646
21	0.4134	0.1717	0.4153
22	0.4675	0.1948	0.4166
23	5.134	6.680	1.301
24	0.822	1.077	1.310
25	0.7562	1.076	1.423
26	0.0542	0.02314	0.4270
27	4.259	5.580	1.310
28	3.73	5.580	1.496
29	5.377	6.321	1.176
30	100.51	47.01	0.4679
30-1	100.9	47.15	0.4673
30-2	105.7	48.37	0.4575
30-3	130.2	61.60	0.4733
30-4	131.3	61.82	0.4708
31	2.623	1.227	0.4679
31-1	32.4	14.64	0.4519
31-2	39.76	18.86	0.4743

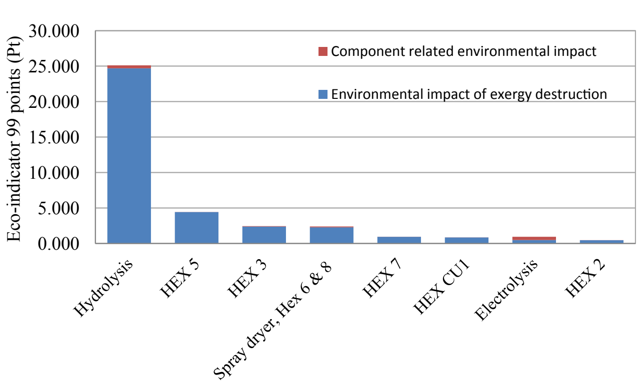

Fig. 8 – Environmental impact distributions among component related and exergy destruction rates for the four-step Cu–Cl cycle components.

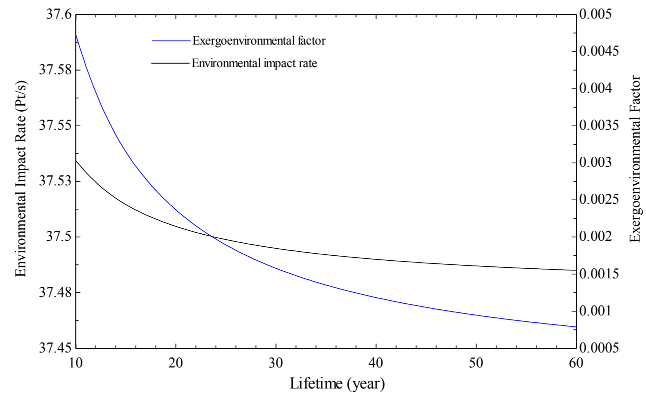

Fig. 9 – Variations of environmental impact rate and exergoenvironmental factor with lifetime of the Cu–Cl plant.

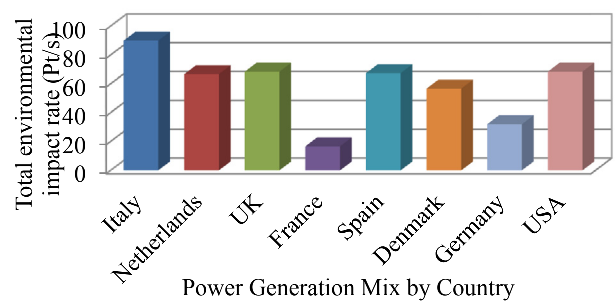

Fig. 10 – Total environmental impact rates for the four-step Cu–Cl cycle using electricity generation mixed for various countries.

various countries. Eco-indicator points per kWh are obtained using SimaPro 7. France has the most environmentally benign power and hydrogen production among others, whereas impact rate for the power mix in Italy is the highest.

Conclusions

A novel configuration of the four-step Cu–Cl cycle, with reduced excess steam requirements, is optimized with respect to exergy efficiency, economic and environmental impacts in Part II of two companion papers. In this regard, both exergoeconomic and exergoenvironmental analyses are comprehensively conducted for the four-step Cu–Cl cycle. The following conclusions are also drawn:

- The hydrolysis reactor is the component with the highest total cost and environmental impact rate.
- Exergoeconomic and exergoenvironmental analysis results show that the rate of exergy destruction dominates the component related rates.
- Under the baseline conditions, total cost rate and environmental impact rate are determined to be 165 \$/s and 37.4 Pt/s.

- The optimized unit cost of hydrogen production is found to be more compelling as 3.36 $/kg which appears to be less than the prices presented by the ORF project researchers between 2.73 $/kg and 3.60 $/g.

Acknowledgement

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Nomenclature

b	environmental impact per unit of exergy, Pt/kJ
$\dot{B}$	environmental impact rate, Pt/s
c	cost per unit of exergy, $/kJ
$\dot{C}$	cost rate, $/s
$\dot{Ex}$	exergy rate, kW
ex	specific exergy, kJ/kg
F_m	material factor
f	exergoeconomic factor
f_b	exergoenvironmental factor
I	interest rate
$\dot{m}$	mass flow rate, kg/s
N	annual number of operation hours
n	equipment lifetime, years
RCD	relative cost difference, $/$
Y	environmental impact of a component, Pt
$\dot{Y}$	component related environmental impact, Pt/s
Z	purchased equipment cost, $
$\dot{Z}$	cost rate of owning and operating the cycle, $/s

Greek symbols

η	efficiency
φ	maintenance factor

Subscripts

d	destruction
ex	exergy
f	fuel
p	product
R	reactor
elec	electrolysis

Acronyms

AP	acidification potential
AECL	Atomic Energy of Canada Limited
ANL	Argonne National Lab
CEPCI	chemical engineering plant cost index
CRF	capital recovery factor
EXCEM	exergy-cost-energy-mass
ExLCA	exergetic life cycle assessment
GHG	greenhouse gas
GWP	global warming potential
LCA	life cycle assessment
ORF	Ontario Research Fund
RCD	Relative Cost Difference
SCWR	super-critical water cooled reactor
SPECO	specific exergy cost
UOIT	University of Ontario Institute of Technology

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