Life cycle assessment of hydrogen production via thermochemical water splitting using multi-step Cu–Cl cycles

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ABSTRACT

A comparative environmental impact study of the three-, four- and five-step copper–chlorine (Cu–Cl) thermochemical water splitting cycles is undertaken through life cycle assessment (LCA). This analytical tool is used to identify and quantify environmentally critical phases during the life cycle of a system or a product and/or to evaluate and decrease the overall environmental impact of the system or product. The LCA results for the hydrogen production processes indicate that the four-step Cu–Cl cycle has lower environmental impacts than the three- and five-step Cu–Cl cycles due to its lower thermal energy requirement. The global warming, acidification and eutrophication potentials of the system using the four-step Cu–Cl cycle are 0.56 kg CO_2-eq, 0.00284 kg SO_2-eq and 0.000232 kg Phosphate-eq, respectively.

1. Introduction

Global energy demand tends to increase with an increasing population. Today's energy systems, which are based mainly on fossil fuels, cannot be considered as sustainable. Concerns about energy supply security are increasing due to declines in the fossil fuel resources leading to increases in prices of energy carriers, local air pollution and global climate change. Petroleum is a central concern, with a share of more than one third of global primary energy consumption and more than 95% of the energy consumption in the transport sector. The negative environmental impacts of coal mining combined with the large contribution of coal usage to global carbon dioxide emissions, as well as the risks of the dwindling reserves of natural gas, are other factors of concern (Urbaniec et al., 2010). Hence, alternatives to fossil fuels have been sought. Increases in energy demand will likely lead to growth in nuclear and renewable energy utilization, partly to meet the objective of sustainability. The shift from fossil fuels to nuclear and renewable resources is expected due to increases in energy demand as well as concerns over environmental issues like global warming. Jaber (2009) states that in the future all energy systems are expected to be hybrid systems, which combine various energy resources and energy conversion methods to maximize efficiency while reducing environmental impacts and wastes. Hydrogen is a promising candidate as an energy carrier (not an energy source) that helps expand markets for renewable and nuclear energy resources and contributes to sustainability and environmental stewardship, and that can act as a link between these technologies when they are utilized in hybrid systems.

The energy carrier hydrogen is expected by many to become an important fuel that will help solve several energy challenges. Since its oxidation does not emit GHGs, its use does not contribute to climate change, provided it is derived from clean energy sources. Numerous researchers anticipate that hydrogen will replace petroleum products for fuelling of transportation vehicles, in turn decreasing dependence on petroleum. Industrial sectors are also interested in hydrogen energy. Hydrogen complements the energy carrier electricity, which can be generated from a variety of primary energy sources and is widely used in a broad range of applications. These two energy carriers are expected to have complementary roles in the future, in part since hydrogen adds the capability of storage (Urbaniec and Ahrer, 2010). Hydrogen exists in abundance in nature in the form of water. But pure hydrogen needs to be produced and there are several ways this can be accomplished including steam reforming of natural gas, coal gasification, water electrolysis and thermochemical water decomposition. Dufour et al. (2009) indicate that 96% of the world's hydrogen is produced using fossil fuels, and steam reforming is the most commonly used method.

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H_2 production using thermochemical water splitting cycles has the potential to be cleaner and more cost-effective than other production methods. Although H_2 production systems using thermochemical cycles have not yet been commercialized, studies have shown that such systems can be expected to compete with the conventional H_2 production methods including steam methane reforming (Orhan, 2008; Lewis et al., 2009; Pilavachi et al., 2009). Water can be directly split in one step, but the required process temperature is too high to be practical. However, a series of selected chemical reactions can be utilized to achieve same result at much lower temperatures (Funk, 2001). A variety of thermochemical water decomposition cycles have been identified (Funk, 2001), but a few have progressed beyond theoretical calculations to working experimental demonstrations. Considerations of several factors including availability and abundance of materials, simplicity, chemical viability, thermodynamic feasibility and safety, the following cycles have been identified as of possible commercial significance: sulphur–iodine (S–I), copper–chlorine (Cu–Cl), cerium–chlorine (Ce–Cl), iron–chlorine (Fe–Cl), magnesium–iodine (Mg–I), vanadium–chlorine (V–Cl), copper–sulphate (Cu–SO$_4$), Ni–Ferrite (NiFe$_2$O$_4$), cerium-oxide (CeO$_2$/Ce$_2$O$_3$), ZnO/Zn and Fe$_3$O$_4$/FeO redox reactions and hybrid chlorine (Naterer et al., 2008; Steinfeld, 2002; Ishihara et al., 2008; Abanades and Flamant, 2006). Most of these cycles require process heat at temperatures as high as 800 °C and above. Due to its lower temperature requirements (around 530 °C), the Cu–Cl thermochemical water decomposition cycle has some advantages over other cycles (Naterer et al., 2008), including reduced material and maintenance costs. Moreover, the Cu–Cl cycle has some advantages over other existing H_2 production methods, and it can utilize low-grade/waste heat to improve its efficiency (Naterer et al., 2009).

Fossil fuels, nuclear energy and renewables can be used as energy sources for H_2 production. Renewables are usually considered the most environmentally benign alternative. But, an important challenge is to obtain sustainable large-scale H_2 production, although daily production capacity of ∼38,000 kg H_2 can be obtained using solar power towers and electrolyzers (Kolb et al., 2007). Furthermore, fossil fuels negatively affect the environmental significantly. Using nuclear energy for H_2 production is consequently advantageous for two main reasons. First, nuclear plants do not emit GHGs during operation. Second, nuclear energy can contribute to large-scale H_2 production (Orhan, 2008). For these reasons, thermochemical water decomposition linked with nuclear plants is seen as a promising alternative for H_2 production. Despite rising concerns regarding uranium resources, the International Atomic Energy Agency (IAEA) and the Nuclear Energy Agency (OECD/NEA) project uranium reserves as 5.47 million tons and the reserve-production ratio as more than 100 years. Moreover, the reserve-production ratio becomes over 3000 years if a Fast-Breeder reactor becomes commercial (Saito, 2010). The Generation IV SCWR (super-critical water cooled reactor) is viewed as a particularly suitable option for pairing with the Cu–Cl thermochemical cycle.

Although hydrogen is a clean energy carrier since its oxidation mainly emits water, negative environmental impacts can arise during its production. Hence, the environmental impact of H_2 production methods should be investigated. H_2 production using thermochemical water splitting driven by clean energy sources has lower environmental impacts than conventional methods. A comprehensive study has not been performed of the environmental impacts of the Cu–Cl cycle, although related research is available for the other H_2 production methods.

Life cycle assessment (LCA) is essentially a cradle to grave analysis to investigate environmental impacts of a system or process or product. LCA provides an analytical tool for evaluating and decreasing environmental impact. Heikkila (2004) points out that LCA can also be used to identify environmentally critical phases in the life cycle of a system or a product. A life cycle assessment is required for the Cu–Cl thermochemical hydrogen production.

The objective of this study is to investigate the environmental impacts of nuclear-based hydrogen production via thermochemical water splitting using the Cu–Cl cycle by performing a life cycle assessment. Since a detailed assessment has not yet been performed of the environmental performance of the Cu–Cl cycle, this work fills an important need. Beyond the environmental performance of H_2 production, other factors (such as economical, safety, instrumental, chemical challenges) must be taken into consideration in decision making. However, this paper only deals with the issues related to emissions. The specific objectives are as follows:

- To conduct an LCA of nuclear-based hydrogen production using the three-, four-, and five- step Cu–Cl cycle for four different scenarios, which are defined as follows:
  1 All processes use power from the electrical grid.
  2 Electricity needed for electrolysis in the hydrogen production plant is provided by a nuclear power plant, while the remaining electricity needs are met using power from the electrical grid.
  3 Electricity needed for electrolysis and heavy water production is provided by a nuclear power plant, and electricity required for fuel processing is provided by the electrical grid.
  4 All electricity needs are met using power from a nuclear power plant.
- To determine based on the findings from the scenarios employed the corresponding measures for the processes of the following CML 2001 environmental impact categories: abiotic resource depletion potential (ADP), acidification potential (AP), eutrophication potential (EP), global warming potential (GWP), ozone depletion potential (ODP), photochemical ozone creation potential (POCP) and radiation (RAD).

2. Background: LCA of hydrogen production processes

Life cycle analyses of several H_2 production methods have been reported. Dufour et al. (2009) investigated from an environmental point of view four H_2 production systems: steam reforming of natural gas (the reference system), a coupling of the reference system with CO_2 capture, thermal cracking and autocatalytic decomposition of natural gas. The results show that autocatalytic decomposition with a total conversion is the most environmentally benign process. Steam reforming of natural gas with CO_2 capture and storage options leads to a lower GWP but a higher general environmental impact, as calculated with the Eco-indicator method, than conventional steam methane reforming without CO_2 capture.

Koroneos et al. (2008) compared two biomass-to-hydrogen systems: biomass gasification by reforming of the syngas, and gasification followed by electricity generation and electrolysis. Environmental impacts in terms of GWP, AP, and EP are determined, and a weighting using the Eco-indicator 95 method is also applied to compare the overall environmental impacts. While the gasification to electrolysis system has a greater eutrophication effect, biomass gasification by reforming of syngas has higher environmental impacts in terms of GWP and AP. In addition, weighting results demonstrate that the biomass–gasification–electricity–electrolysis route has better environmental performance than the process involving reforming of the syngas.

Djomo et al. (2008) proposed potato steam peels as a feedstock for producing H_2 through fermentation and conducted an LCA for this process. The authors utilized the IMPACT 2002 + method in the

LCIA phase. The results show that the two-stage bioreactor, which is used for H_2 production, emits 1000–1500 g of CO_2 per kg of H_2 produced. There are two main sources of CO_2 emissions. First, photoheterotrophic bacteria convert all organic acids to H_2 and CO_2. There is also an electricity requirement for both pre-treatment and fermentation processes in H_2 production, and this is another source of greenhouse gas emissions. The study also demonstrates that hydrogen production using potato steam peels offer advantages compared to direct use of peels to feed animals, including reductions in GHGs emissions, non-renewable resource utilization and human health impacts.

Marquevich et al. (2002) conducted a life cycle inventory analysis to assess the environmental load, specifically GWP, associated with H_2 production by steam reforming of feedstocks (methane and naphtha) and vegetable oils (rapeseed oil, soybean oil and palm oil). While the GWP of H_2 produced from rapeseed oil, palm oil and soybean oil are found to be 6.42, 4.32 and 3.30 kg CO_2-eq/kg H_2, respectively, the GWPs associated with the production of H_2 by steam reforming are 9.71 and 9.46 kg CO_2-eq/kg H_2. Thus, the GWP may be reduced by up to 60% if natural gas and naphtha are replaced by vegetable oils.

Utgikar and Thiesen (2006) have performed a life cycle assessment of high temperature electrolysis for H_2 production via nuclear energy. High temperature electrolysis is advantageous to low-temperature alkaline electrolysis because of its higher efficiency, which is due to reduced cell potential and consequent electrical energy requirements. The high temperature electrolysis system has a GWP of 2000 g CO_2-eq and AP of 0.15 g H_2 ion equivalent per kg of H_2 produced. A comparison of the environmental impact of the system with natural gas steam reforming and wind, solar photovoltaic, solar thermal, hydroelectric and biomass based electrolysis indicates that emissions of the high temperature water vapour electrolysis process are much lower than those for conventional natural gas steam reforming and comparable with the emissions for H_2 production using renewable based electrolysis.

Solli et al. (2006) presented a comparative hybrid life cycle assessment to evaluate and compare environmental impacts of two H_2 production methods: nuclear assisted thermochemical water splitting using the S–I cycle and natural gas steam reforming with CO_2 sequestration. An overall advantageous option could not be determined since a weighing method was not applied. The results show that thermochemical water splitting has lower environmental impacts in terms of GWP, AP and EP, and much higher impacts in terms of RAD and human toxicity potential (HTP). While the GWP of natural gas steam reforming is 1.3×10^4 kg CO_2 eq, the GWP of thermochemical water splitting via the S–I cycle is 2.9×10^3 kg CO_2 eq for the production of 1 TJ (on the basis of higher heating value (HHV)) of H_2.

In summary, the GWPs per kg H_2 produced for the H_2 production methods discussed above are as follows:

- 9.5–11.9 kg CO_2-eq for natural gas steam reforming,
- 1–1.5 kg CO_2-eq for biomass gasification using potato steam peels as a feedstock,
- 6.42, 4.32 and 3.30 kg CO_2-eq for steam reforming of vegetable oils (rapeseed oil, soybean oil and palm oil, respectively),
- 2 kg CO_2-eq for high temperature electrolysis,
- 0.41 kg CO_2-eq for thermochemical water decomposition using the S–I cycle.

3. Life cycle assessment (LCA): approach and methodology

LCA is a method used to help engineers, scientists, policy makers and others to assess and compare energy and material use, emissions and wastes, and environmental impacts for a product or process. The method can be used to evaluate the total environmental impact of a product or process. Overall environmental impact cannot be assessed by examining only operation, but must consider all the life stages from resource extraction to disposal during the lifetime of a product. LCA can also be conducted to compare impacts for competing products or processes. In addition, LCA can identify critical phases where process changes could significantly decrease impacts.

According to Curran (2006), LCA began in the 1960s as concerns grew about limitations of raw materials and energy sources, sparking an interest in finding ways to cumulatively account for energy use. Harold Smith presented a study on cumulative energy requirements for the production of chemical intermediates and products at the World Energy Conference in 1963 (Curran, 2006). LCA developed into a tool for analysing environmental issues when solid waste became a worldwide issue in 1988 (Curran, 2006). The LCA methodology has constantly been improving, expanding from inventory analysis to impact assessment and further. Curran (2006) also states that concerns over misuses of LCAs emerged in 1991. Pressure from environmental organizations to standardize the LCA methodology led to the development of LCA standards in the International Standards of Organization (ISO) 14000 series:

- ISO-14040, Life Cycle Assessment − Principles and Framework (ISO, 1997)
- ISO-14041, Life Cycle Assessment − Goal and Scope Definition and Inventory Analysis (ISO, 1998)
- ISO-14042, Life Cycle Assessment—Life Cycle Impact Assessment (ISO, 2000a)
- ISO-14043, Life Cycle Assessment—Life Cycle Interpretation (ISO, 2000b)
- ISO-14044, Life Cycle Assessment − Requirements and Guidelines (ISO, 2006)

Life cycle assessment consists of four main phases (see Fig. 1), which are explained further in the following sections. The arrows in
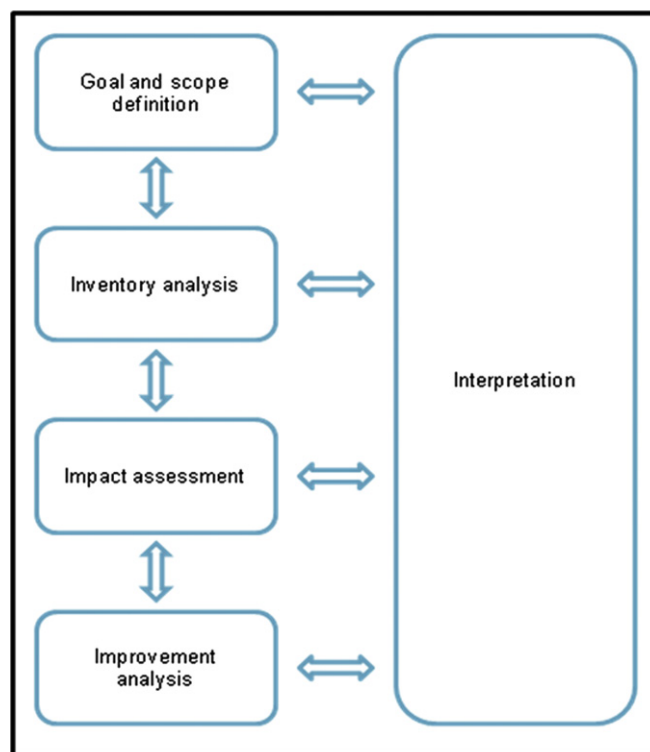

Fig. 1. Life cycle assessment framework.

Fig. 1 indicates that all phases of LCA are linked to each other. In this regard, a life cycle interpretation is also linked to all phases, since the phases of LCA should be reviewed and necessary modifications should be done according to results of the LCA study.

3.1. Goal and scope definition

The first phase of LCA is goal and scope definition. The LCA step is critical for clarifying the main objectives of an assessment and breadth of system considered. The goal and scope must be clearly defined and consistent with the intended application. The insights of interest from the LCA must be iterated clearly in this phase, and the intended audience and reasons for the study must be identified. In defining the scope of an LCA, a system boundary is normally drawn, which indicates the breadth and detail of the inventory analysis. Further information on this LCA step is available elsewhere, e.g. (ISO, 1997).

3.2. Life cycle inventory analysis

The second phase of LCA is the life cycle inventory analysis (LCI). All process steps within system boundary and the corresponding inputs/outputs of all flows are identified in as the first step of LCA. Consequently, LCI analysis includes data collection and calculation procedures to quantify relevant inputs and outputs of the system. Inputs associated with the system may be material or energy, while outputs may be releases to air, water and land (ISO, 1997). Several methods exist for data collection, often including the collection of process-specific data directly by measurements, obtaining data reported in the literature or by relevant organizations, or calculating data by process modelling. A combination of these techniques is generally required to obtain the required set of inputs and outputs for LCI. Solli (2004) indicates that LCA-databases that contain life cycle data are available for a number of generic processes (e.g., steel production and electricity generation, sometimes broken down by source, country or other factors).

3.3. Life cycle impact assessment

Life cycle impact assessment is the third phase of LCA. The purpose of LCIA is to evaluate environmental impacts of the material and energy flows identified in the inventory analysis. The goal and scope definition affects the level of details, impact categories and evaluation methodologies in LCIA. ISO-14042 (ISO, 2000a) divides LCIA into the following steps:

- Classification: In the first step of LCIA, impact categories are determined which are consistent with the goal and scope of the study. Then, inventory data (i.e., the flows in the analysis) are assigned to the impact categories, such as GWP and AP.
- Characterization: Characterization is defined as modelling of inventory data within impact categories. Once the inventory data are matched with impact categories, their contributions to these impact categories needs to be quantified. Hence, the impacts of different environmental flows are assessed using a common indicator unit in each impact category. This step is often done using previously developed characterization factors (Solli, 2004).
- Normalization and weighting: In this optional step, all environmental impacts are combined and reduced into a single score.

A number of impact assessment methods exist, such as CML 2001, Eco-indicator 95 & 99, EPS 2000, IMPACT 2002+, IPCC 200 and TRACI. The CML 2001 method is used in the present analysis.

The Center of Environmental Science of Leiden University (CML) published an operational guide to the ISO standards in 2001 (Guinée et al., 2002), which describes LCA procedures according to ISO standards. A set of impact categories and the characterization methods and factors for a list of substances (accounting for resources from and emissions to nature) are suggested for the impact assessment phase of LCA. Characterization factors for the elementary flows of resources and pollutants required to implement these methods are incorporated into the LCI database (Frischknecht and Jungbluth, 2007). Detailed explanations of the environmental impact categories used in this study are presented in the following seven subsections (Guinée et al., 2002).

3.3.1. Abiotic resource depletion potential

Abiotic resources are non-living natural resources, such as copper ore and crude oil, and can include energy resources, such as wind energy. Abiotic resource depletion potential (ADP) is a frequently utilized impact category and a wide variety of methods are available for characterising contributions to this category. In this study, extraction of non-renewable raw materials is taken into consideration. The unit of the indicator for this impact category is kg antimony equivalent (Sb-eq) which represents ADP for extraction of minerals and fossil fuels (in kg antimony equivalents/kg extraction).

3.3.2. Acidification potential

Acidification potential (AP) is related to the deposition of acidifying pollutants on soil, groundwater, surface waters, biological organisms, ecosystems and materials. SO_2, NO_x and NH_x are the major acidifying pollutants. Protection areas are the natural environment, the anthropogenic environment, human health and natural resources. The unit of the indicator for this impact category is kg SO_2-eq.

3.3.3. Eutrophication potential

Nutrient enrichment may cause an undesirable shift in species composition and elevated biomass production in both aquatic and terrestrial ecosystems. Eutrophication covers all potential impacts of excessively high environmental levels of macronutrients, mainly nitrogen and phosphorus. All emissions that cause similar effects are also treated under the impact category "eutrophication". The unit of the indicator for eutrophication potential (EP) is kg PO_4-eq.

3.3.4. Global warming potential

GWP is defined as the impact of human emissions on the radiative forcing (i.e. thermal radiation absorption) of the atmosphere. Ecosystem health and human health may be affected by global warming, mainly through climate change. Most GHG emissions enhance radiative forcing, which cause a temperature rise at the earth's surface (the "greenhouse effect"). GWP is often examined and is considered in this study for a 100-year time horizon. The unit of the indicator for GWP 100-years is kg CO_2-eq.

3.3.5. Ozone depletion potential

The thinning of the stratospheric ozone layer as a result of ozone-depleting emissions is defined as stratospheric ozone depletion. The thinning allows a greater fraction to reach the earth's surface of solar UV-B radiation, which has potentially harmful impacts on human health, animal health, terrestrial and aquatic ecosystems, biochemical cycles and materials. Therefore, ODP impacts all four areas of protection: human health, the natural environment, the anthropogenic environment and natural resources. The unit of the indicator for ODP is kg R11-eq.

3.3.6. Photochemical ozone creation potential

Photo-oxidant formation is the formation of reactive chemical compounds such as ozone by the action of sunlight on certain primary air pollutants. These reactive compounds may cause serious human health problems. Photo-oxidants may be formed in the troposphere under the influence of ultraviolet light, through photochemical oxidation of volatile organic compounds (VOCs) and carbon monoxide in the presence of nitrogen oxides. The most important of these oxidising compounds is ozone, which can cause bronchial irritation, coughing, etc. The unit of the indicator for POCP is kg Ethylene-eq.

3.3.7. Radiation

The impact category RAD accounts for the impacts arising from releases of radioactive substances as well as direct exposure to radiation, such as can occur from exposure to building materials, and is harmful to both humans and animals. The specific radioactivity of a substance is expressed in becquerel (Bq) per kg and the indicator for this impact category is disability adjusted life years (DALY).

3.4. Life cycle interpretation (improvement analysis)

In life cycle interpretation (or improvement analysis), the final phase of LCA, the results of LCI and LCIA are combined and assessed, so as to allow conclusions to be drawn and recommendations to be made. These typically relate to the goal and scope of the study. Life cycle interpretation can help decision makers identify environmental beneficial options and inform the decision process, which is also affected by other factors, such as technical performance, economics and social concerns.

4. System description and analysis

The overall system and component subsystems are described for the nuclear-based hydrogen production via thermochemical water splitting using the Cu–Cl cycle. The data used in this study are obtained from literature and data normalization procedures are used. Nuclear-based hydrogen production system can be divided into three main subsystems:

- Fuel (uranium) processing
- Nuclear Plant
- Hydrogen Plant

Fig. 2 shows the simplified overview of the system considered for the LCA. The first stage is fuel processing, which consists of mining, milling, conversion, enrichment and fuel fabrication. After fuel processing, fabricated uranium (UO_2) is transferred to the nuclear plant. The output thermal energy from the nuclear plant is the input to the hydrogen plant. Electrical energy may also be transferred from the nuclear plant to the hydrogen plant but is not shown in the figure since different scenarios are considered regarding the utilization of electrical energy from the nuclear plant. The product output from the hydrogen plant is hydrogen. Both construction and utilization are considered for the nuclear and hydrogen plants.

Several types of Cu–Cl cycles for thermochemical water decomposition are proposed in the literature, 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 is
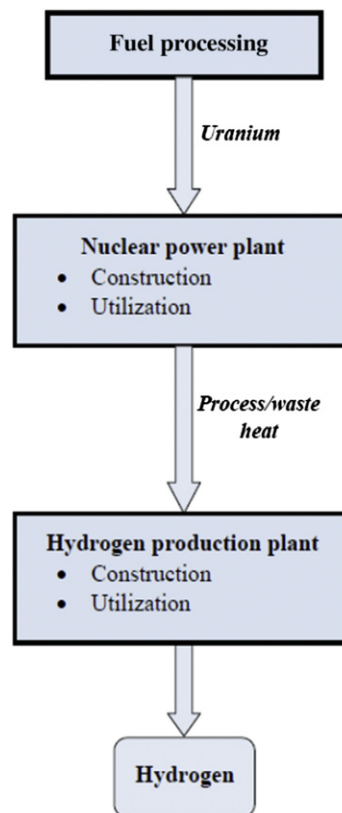
$$H_2O(g) \rightarrow H_2(g) + 1/2O_2(g) \tag{1}$$

Fig. 2. Simplified overview of the system used for the LCA.

The Cu–Cl thermochemical cycle uses a series of intermediate copper and chloride 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 (Naterer et al., 2008). In practice, the chemicals used in the Cu–Cl cycle has to be replaced from time to time. However, the Cu–Cl cycle is still in the research and development stage and few data exist on the level of corrosion caused by the processes in the cycle. Hence, it is difficult to estimate the degree of corrosion. Lubis et al. (2010) showed that the effects of chemicals on environmental impact categories are negligible compared to effects due to construction activities. Hence, water, thermal energy and electricity are the only inputs to the Cu–Cl thermochemical cycle considered here.

4.1. Hydrogen production plant

Three main types of Cu–Cl cycle for thermochemical water decomposition exist, i.e., three-, four- and five-step. These are described in the following sections.

4.1.1. Five-step Cu–Cl thermochemical cycle

A conceptual schematic diagram of the five-step Cu–Cl cycle is shown in Fig. 3 along with its principal chemical reactions. The five main chemical reaction steps in the cycle are (1) HCl (g) production using such equipment as a fluidized bed, (2) oxygen production, (3) copper (Cu) production, (4) drying and (5) hydrogen production. Some of the reactions are exothermic while others are endothermic, and the reaction temperatures differ for the steps. Heat exchangers are utilized to ensure appropriate temperatures are maintained and to allow for effective thermal management and waste heat recovery.

The heat requirements for each step, as evaluated by Wang et al. (2010), are presented in Table 1. This information is used to
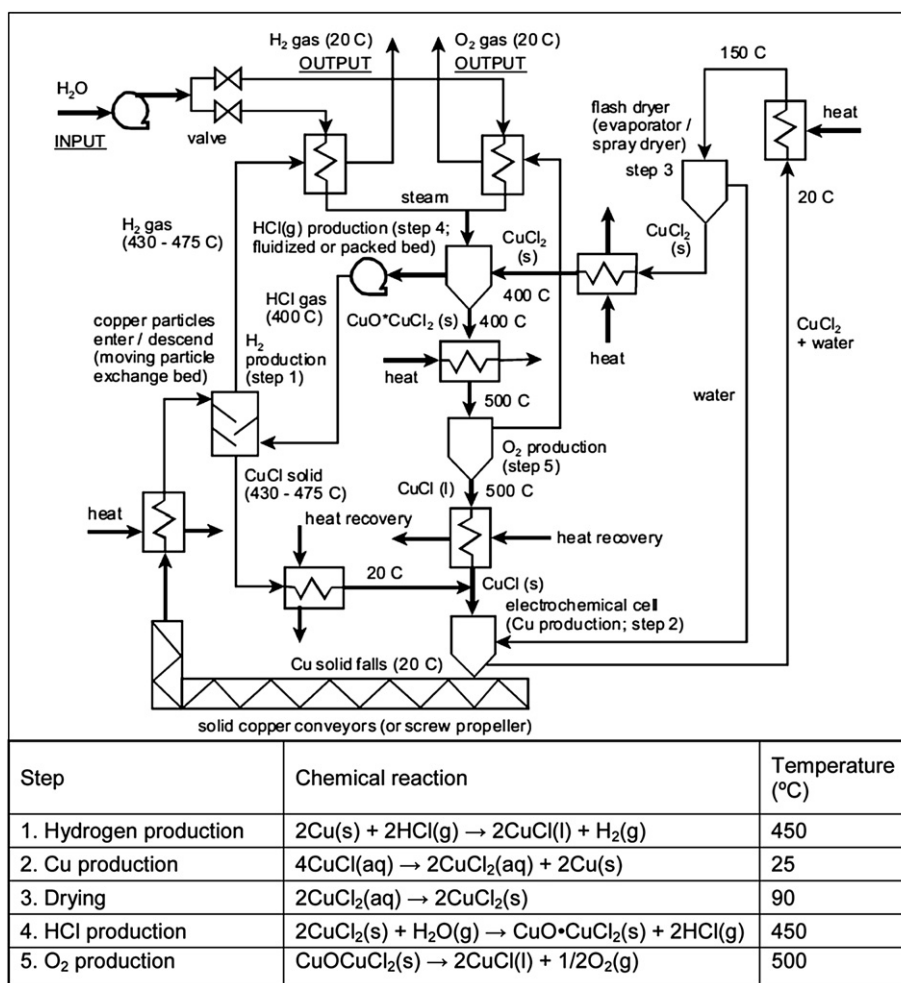
Fig. 3. Conceptual layout of the five-step Cu–Cl cycle for hydrogen production and primary chemical reactions (modified from Wang et al., 2008).

Step	Chemical reaction	Temperature (°C)
1. Hydrogen production	$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(l) + H_2(g)$	450
2. Cu production	$4CuCl(aq) \rightarrow 2CuCl_2(aq) + 2Cu(s)$	25
3. Drying	$2CuCl_2(aq) \rightarrow 2CuCl_2(s)$	90
4. HCl production	$2CuCl_2(s) + H_2O(g) \rightarrow CuO \cdot CuCl_2(s) + 2HCl(g)$	450
5. O_2 production	$CuOCuCl_2(s) \rightarrow 2CuCl(l) + 1/2O_2(g)$	500

calculate the thermal energy requirement of the system. As can be seen from Table 1, the required heat input to the system is 554.7 kJ/mol H_2 and the total heat output of the system is 232 kJ/mol H_2. Assuming only low grade heat, i.e., 163.3 kJ/mol H_2 (which is equivalent to 70% heat recovery), is recovered, the external thermal energy requirement of the system becomes 391.4 kJ/mol H_2. The electrical energy required for the copper production step is identified in Table 1 as 62.6 kJ/mol H_2. It has been estimated that 38 kJ/mol H_2 of work is required for auxiliary equipment (Rosen et al., 2010). Hence, the net energy requirement of the system can be estimated as 492 kJ/mol H_2.

To calculate the thermal and total energy requirements of the five-step cycle per kg H_2 produced, the calculated values in Table 1 are modified by using molar mass of H_2 (2 g/mol) as follows:

Total thermal energy requirement of five − step Cu − Cl cycle

$= [391.4\,kj/(1\,mol\,H_2)] \times [(1\,mol\,H_2)/(2\,g\,H_2)]$
$\times [(1000\,g)/(1\,kg)] = 195.7\,MJ/kg\,H_2$

(2)

and

Total electrical energy requirement of five − step Cu − Cl cycle

$= [(62.6 + 38)\,kj/(1\,mol\,H_2)] \times [(1\,mol\,H_2)/2\,g\,H_2]$
$\times [(1000\,g)/(1\,kg)] = 50.3\,MJ/kg\,H_2$

(3)

Using stoichiometry and molar masses, the input water (H_2O) and output oxygen (O_2) can be determined. To obtain 1 kg of H_2, i.e. 500 mol of H_2, 500 mol of H_2O (9 kg) must be input and 250 mol (8 kg) of O_2 output. The overall inputs and outputs for the hydrogen plant using the five-step Cu–Cl cycle are presented in Table 2, where it is seen that the inputs to the hydrogen plant are 195.7 MJ of thermal energy, 50.3 MJ of electrical energy and 9 kg of water, while the outputs are 8 kg of oxygen and 1 kg H_2.

4.1.2. Four-step thermochemical Cu–Cl cycle

The four-step copper–chlorine cycle combines step 2 and step 3 in the five-step cycle (Fig. 3), reducing complexity and equipment requirements. The principal chemical reaction steps for the four-step cycle are shown in Table 3.

Chukwu (2008) calculated the energy requirements for the four-step copper–chlorine cycle. Following the approach in section 4.1.1, the net energy requirement of the cycle is found to be 161.05 MJ/kg H_2 and the electrical energy requirement 67.15 MJ/kg H_2. The overall inputs and outputs for the hydrogen plant using the four-step Cu–Cl cycle are listed in Table 4.

4.1.3. Three-step thermochemical Cu–Cl cycle

In the three-step Cu–Cl cycle, the hydrogen production step (step 1 in Table 3) and the combined step in the four-step cycle (step 2 in Table 3) are combined. Hence, the main chemical reactions are as shown in Table 5.

Table 1
Thermal requirements of principal chemical reaction steps in the five-step Cu–Cl thermochemical cycle.

Step	Processes in the step	T (K)	Heat input (kJ/ mol H$_2$)		Heat output (kJ/mol H$_2$)
			Total	Low grade	
I	$2Cu_{(s)} + 2HCl_{(g)} = 2CuCl_{(l)} + H_{2(g)}$ Hydrogen production step				
	Vaporizing moisture from Cu$_{(s)}$	308→343	29.0	29.0	
	Heating Cu$_{(s)}$	298→723	23.4	0.1	
	Heating HCl$_{(g)}$	298→723	3.0	0.3	
	Heat of reaction	723			46.8
	Cooling & solidification of molten CuCl	723→298			80.8
	Cooling of H$_2$ product	723→298			12.2
II	$4CuCl_{(aq)} = 2CuCl_{2(aq)} + 2Cu_{(s)}$ Electrolysis step in HCl solution	308→343	62.6 (Electrical Energy)		
III	$2CuCl_{2(aq)} \rightarrow 2CuCl_{2(s)}$ Drying step				
	Vaporizing water from CuCl$_2$ precipitate $2.2H_2O_{(l)} \rightarrow 2.2H_2O_{(g)}$	308→343	122.0	122.0	
IV	$2CuCl_{2\ (s)} + H_2O_{(g)} = CuOCuCl_{2\ (s)} + 2HCl_{(g)}$ Hydrolysis step				
	Heating CuCl$_{2\ (s)}$	298→648	54.2	8.5	
	Heat of reaction	648	116.6		
	Steam production $H_2O_{(l)} = H_2O_{(g)}$	289→648	57.1	3.4	
V	$CuOCuCl_{2\ (s)} \rightarrow 2CuCl_{(l)} + 1/2O_{2\ (g)}$ Oxygen production step				
	Heating CuOCuCl$_{2\ (s)}$	648→803	20.2		
	Heat of reaction	803	129.2		
	Cooling & solidification of molten CuCl	803→298			84.8
	Cooling of O$_{2\ (g)}$ product	803→298			7.4
	Total		554.7	163.3	232

Source: Wang et al., 2010.

Chukwu (2008) also assessed the three-step Cu–Cl cycle. Following his approach, the net thermal energy required for the three-step cycle is found to be 365.48 kJ/mol H$_2$, while the electric energy requirements for electrolysis and auxiliary equipment are again 96.3 kJ/mol H$_2$ and 38 kJ/mol H$_2$, respectively. Chukwu (2008) found the electrical energy requirement of the three-step cycle to be the same as for the four-step cycle. The electricity requirement of the electrolysis step of the three-step Cu–Cl cycle can also be calculated using the study of Balashov et al. (2011). The corresponding voltage for an assumed current density of 0.3 A cm^2 is 0.45 V (at a flow rate 30 cm^3/min). This ideal voltage means an electrical energy requirement of 43 MJ per 1 kg H$_2$. The results are reasonably consistent with the study of Chukwu (2008), in which the electrical energy requirement is found to be 48.2 MJ. However, a slight change in the electrical energy requirement of three-step cycle does not affect the environmental impact factors, since it is supplied by the nuclear reactor. A change in the electrical energy requirement would be significant environmentally, however, if the electricity for the electrolysis step were supplied by an external fossil fuel-based source. Hence, the inputs to the hydrogen plant using the three-step Cu–Cl cycle are found to be 182.74 MJ of thermal energy, 67.15 MJ of electrical energy and 9 kg of water, and the outputs are 8 kg oxygen and 1 kg H$_2$ (see Table 6).

Table 2
Overall inputs and outputs for hydrogen plant using the five-step Cu–Cl cycle.

Input			Output	
Thermal energy (MJ)	Electrical energy (MJ)	Water (kg)	Oxygen (kg)	Hydrogen (kg)
195.7	50.3	9	8	1

Table 3
Principal chemical reaction steps in the four-step Cu–Cl cycle for thermochemical water decomposition.

Step	Chemical reaction	Temperature (°C)
1. Hydrogen production	$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(l) + H_2(g)$	450
2. Combined step	$4CuCl(aq) \rightarrow 2CuCl_2(s) + 2Cu(s)$	25–90
3. HCl production	$2CuCl_2(s) + H_2O(g) \rightarrow CuO\bullet CuCl_2(s) + 2HCl(g)$	450
4. O$_2$ production	$CuO\bullet CuCl_2(s) \rightarrow 2CuCl(l) + 1/2O_2(g)$	500

Source: Chukwu, 2008.

4.2. Nuclear plant

A Generation IV SCWR nuclear reactor is being considered by AECL (Atomic Energy of Canada Limited) to link with a hydrogen production plant using a Cu–Cl thermochemical cycle. This reactor will operate at sufficiently high temperatures to facilitate cogeneration of electricity and H$_2$ (Naterer et al., 2010).

The accident at the nuclear power facility in Fukushima, Japan is affecting some views about nuclear technology around the world. Pool (2011) explains the reasons behind the accident. Pool (2011) concludes that every country should update its nuclear safety protocols accounting for the lessons learned in Fukushima. Note that Fukushima Daiichi power plant was a Generation II reactor. Wheeler (2011) points out that Generation III+ reactors have a new common feature of passive cooling, which increases reliability and safety, and explains this passive safety feature in detail Generation IV reactors, which are still in design process, are anticipated to meet new and strict safety regulations.

The quantity of uranium needed to obtain the required thermal energy is evaluated as follows (Solli, 2004):

$$m_u = \frac{Q}{B_d} \qquad (4)$$

where m_u is the mass of uranium fuel required, Q is heat produced, and B_d is the discharge burn-up. Here Q must be the total heat produced by the nuclear plant, which is thermal energy (Q_{th}) plus electrical work (W_{el}). The discharge burn-up for UO$_2$ is 20,000 MWd/te U (megawatt day per tonne of uranium) (484.37 MWh/kg) (Pioro and Duffey, 2007), which is equal to 1743.75 GJ/kg U. Applying equation (4), the uranium needed by the nuclear plant when linked with the five-, four- and three-step Cu–Cl cycles can be calculated. In addition, results of Pioro and Duffey (2007) are used to determine the ratios of electrical energy produced to thermal energy (process heat and waste heat) output. The overall inputs and outputs of the nuclear plant integrated with the three-, four- and five-step Cu–Cl thermochemical cycles are shown in Table 7.

4.3. Fuel (uranium) processing

Fuel processing (Fig. 4) for the nuclear reactor consists of five main steps: mining, milling, conversion, enrichment and fabrication. Uranium ore is extracted from the environment via mining, and then concentrated in the form of U$_3$O$_8$ in the milling stage. Conversion from U$_3$O$_8$ to the form UF$_6$ occurs in the conversion

Table 4
Overall inputs and outputs for hydrogen plant using the four-step Cu–Cl cycle.

Input			Output	
Thermal energy (MJ)	Electrical energy (MJ)	Water (kg)	Oxygen (kg)	Hydrogen (kg)
161.05	67.15	9	8	1

Table 5
Principal chemical reaction steps in the three-step Cu–Cl cycle for thermochemical water decomposition.

Step	Chemical reaction	Temperature (°C)
1. Combined Step	$2CuCl(aq) + 2HCl(aq) \rightarrow 2CuCl_2(s) + H_2(g)$	100
2. HCl production	$2CuCl_2(s) + H_2O(g) \rightarrow$ $CuO\bullet CuCl_2(s) + 2HCl(g)$	430
3. O$_2$ production	$CuO\bullet CuCl_2(s) \rightarrow 2CuCl(l) + 1/2O_2(g)$	550

Source: Chukwu, 2008.

Table 6
Overall inputs and outputs for hydrogen plant using the three-step Cu–Cl cycle.

Input			Output	
Thermal energy (MJ)	Electrical energy (MJ)	Water (kg)	Oxygen (kg)	Hydrogen (kg)
182.74	67.15	9	8	1

stage. Enrichment is then utilized to bring concentration of the fissile isotope U-235 to a desired level. The enrichment concentration for the SCWR is 4%. In the final stage, i.e. fuel production, the chemical composition is altered to UO$_2$.

The uranium requirements for each Cu–Cl thermochemical cycle are determined using equation (4). In the milling stage, mill tailings are considered since tailings continue to release radon gas after their disposal for thousands of year (Solli, 2004). Hence, Solli (2004) points out that the input uranium should be taken as double in mass of the output uranium, which is applied in the analysis.

In the enrichment stage, the amount of natural uranium required to achieve the desired the fuel enrichment can be found as follows:

$$\text{Natural uranium required} = \frac{x_p - x_t}{x_n - x_t} \quad (5)$$

Here, x_n is the natural enrichment level (0.71% U-235), x_p is the enrichment level to produce one kg enriched uranium and x_t is the tailings enrichment (assumed to be about 0.3% U-235). For one kg of 4% enriched uranium, 9.02 kg of natural uranium is input to the enrichment stage. The uranium inputs and outputs of each stage of fuel processing are given in Table 8 for three Cu–Cl thermochemical cycles.
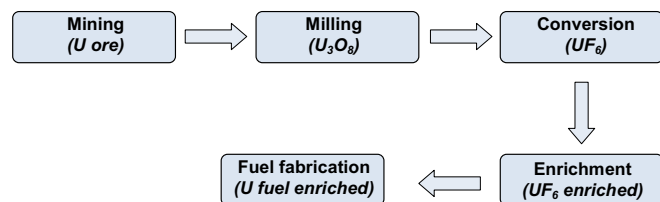
4.4. LCA of overall system

LCA is applied to the overall systems for nuclear-based hydrogen production using three-, four- and five-step Cu–Cl thermochemical cycles. The analyses are all based on one kg of hydrogen production and utilize data (inputs/outputs for the subsystems) from previous sections of this article as well as data from reports in the literature (Solli, 2004; Lubis et al., 2010) for some of the inputs and outputs associated with relevant processes. This section provides inventory data, i.e., overall inputs and outputs for all steps. The GaBi 4 LCA

Fig. 4. Stages of nuclear fuel processing.

software is used to conduct the LCIA. This involves modelled with GaBi 4 the overall system and all of its stages. The GaBi 4 LCA package allows the managing of large data sets and the modelling of product life cycles and it calculates different types of balances and helps in analysing, assessing, comparing and interpreting environmental impact results.

After subsystems (fuel processing, nuclear plant, hydrogen plant) and subprocesses (mining, milling, etc.), have been modelled, they are linked to determine the overall environmental impacts of the systems. Four scenarios regarding power distribution are considered:

1. All processes use power from the electrical grid.
2. Electricity needed for electrolysis in the hydrogen production plant is provided by a nuclear power plant, while the remaining electricity needs are met using power from the electrical grid.
3. Electricity needed for electrolysis and heavy water production is provided by a nuclear power plant, and electricity required for fuel processing is provided by the electrical grid.
4. All electricity needs are met using power from a nuclear power plant.

Fig. 5 shows the model of overall system for the first scenario. Uranium from fuel processing is utilized by the nuclear plant. Then, the nuclear plant produces electricity and heat, which is transferred to the hydrogen plant. In the first scenario, the generated electricity is not used by the system itself. A model of the second scenario is shown in Fig. 6. The second line from utilization of nuclear plant to hydrogen plant in the system denotes electrical energy transfer. Note in this scenario that not all of the generated electricity is used by hydrogen plant; excess electricity is transferred to the electrical grid. Figs. 7 and 8 show GaBi 4 models for the third and fourth scenarios. In all scenarios, the nuclear and hydrogen plants are constructed before their utilization and heavy water is produced. The envelopes at the right top corner of each box in the figures indicate that subprocesses exist.

Environmental impacts are then evaluated for the modelled three-, four- and five-step Cu–Cl thermochemical water decomposition cycles, for each of these four scenarios. Further information on these models are available elsewhere (Ozbilen, 2010)

Table 7
Overall inputs and outputs per kg H$_2$ production of SCWR nuclear plant linked with various Cu–Cl cycles.

Cu–Cl cycle	Input	Output		
	Uranium (g)	Electrical energy (MJ)	Reactor thermal energy (MJ)	Waste energy (MJ)
3-step	0.3773	292.38	182.74	182.74
4-step	0.3325	257.68	161.05	161.05
5-step	0.4040	313.12	195.70	195.70

Table 8
Uranium requirements for stages of fuel processing for three Cu–Cl thermochemical water decomposition cycles.

Fuel processing stage	3-step Cu–Cl cycle		4-step Cu–Cl cycle		5-step Cu–Cl cycle	
	Input (g)	Output (g)	Input (g)	Output (g)	Input (g)	Output (g)
Mining	6.81	6.81	6.00	6.00	7.29	7.29
Milling	6.81	3.40	6.00	3.00	7.29	3.64
Conversion	3.40	3.40	3.00	3.00	3.64	3.64
Enrichment	3.40	0.377	3.00	0.333	3.64	0.404
Fuel production	0.377	0.377	0.333	0.333	0.333	0.404

Nuclear Based Hydrogen Production
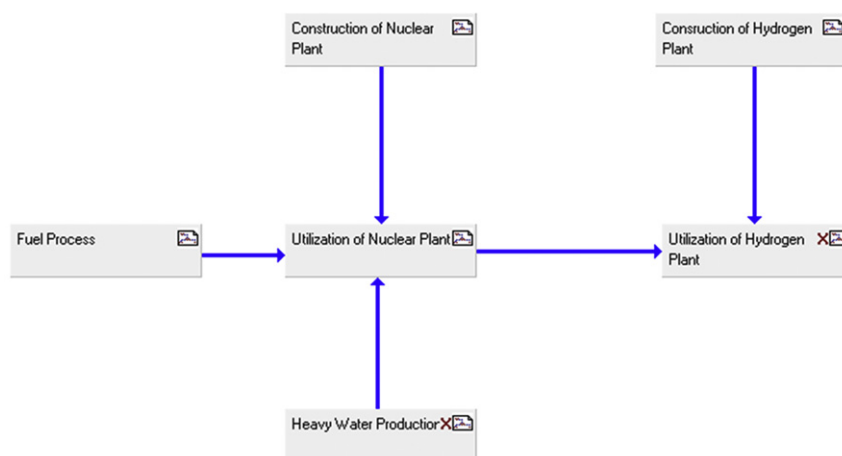GaBi 4 process plan:Reference quantities

Fig. 5. GaBi 4 model of nuclear-based hydrogen production system for the first scenario (Valid for three-, four- and five-step Cu–Cl cycle).

5. Results and discussion

Environmental impacts for the three thermochemical hydrogen production processes, based on one kg of H_2 production, for the four scenarios related to electrical power use, are presented in this section. For each scenario description, a reference case is considered (a plant lifetime of 60 years and a plant production capacity of 125,000 kg H_2/day). A plant lifetime of 60 years is used to be consistent with the literature (Solli, 2004). The effect of plant lifetime on environmental impacts is presented elsewhere (Ozbilen et al., 2011). The following CML 2001 impact categories are examined: ADP, AP, EP, GWP, ODP, POCP and RAD. Tables 9 and 10 show the results of these scenarios. Each of these impact categories is discussed in the following subsections, for the different scenarios.

It can be observed in Table 9 that the environmental impacts for nuclear-based hydrogen production using all Cu–Cl thermochemical cycles are higher when all electricity need is supplied by the electrical grid. For instance, the GWP for the three-, four- and five-step Cu–Cl cycles are 15.9, 15.8 and 12.3 kg CO_2-eq/kg H_2, respectively. But the GWP for the three-, four- and five-step Cu–Cl cycles

are 1.27, 1.18 and 1.33 kg CO_2-eq/kg H_2 respectively, when the electricity needed for electrolysis in the hydrogen production plant is provided by a nuclear power plant. The grid electrical power used in this analysis are assumed to be derived from nuclear energy, lignite, hard coal, natural gas, heavy fuel oil, hydro and wind. Data related to the electrical grid, such as fuels, fractions of the fuels and conversion technologies, for U.S. electrical grid are used, by selecting this option in GaBi 4 software. The five-step Cu–Cl cycle exhibits the lowest emissions for the first scenario, mainly because the primary source of environmental impacts is electricity used in the copper production step of the Cu–Cl cycle.

Despite the results noted for the first scenario, the four-step Cu–Cl cycle exhibits the lowest environmental impact among the thermochemical processes considered, primarily because the environmental impacts associated with electricity use in the copper production stage are eliminated by using nuclear electrical power. The environmental impacts are also lower than for the first scenario. The second scenario does not appear to be an environmentally benign option since its impacts are greater than those for the third and fourth scenarios. Note that the environmental

Nuclear Based Hydrogen Production
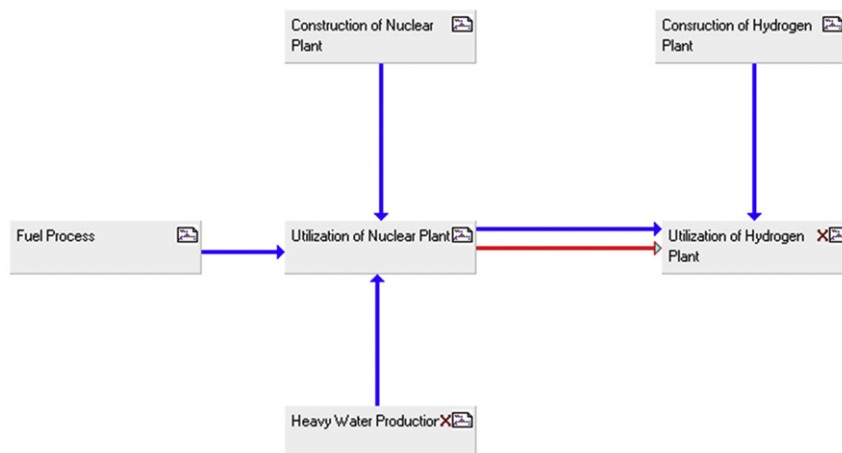GaBi 4 process plan:Reference quantities

Fig. 6. GaBi 4 model of nuclear-based hydrogen production system for the second scenario (Valid for three-, four- and five-step Cu–Cl cycle).
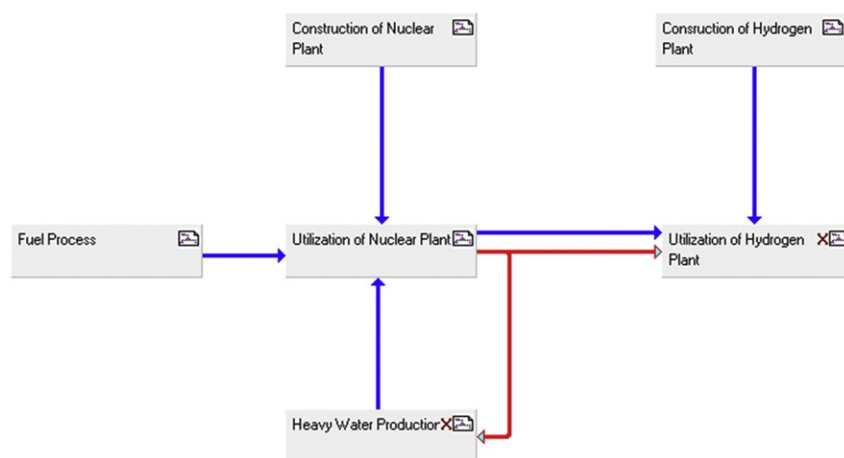
Fig. 7. GaBi 4 model of nuclear-based hydrogen production system for the third scenario (Valid for three-, four- and five-step Cu–Cl cycle).

impacts for the second scenario are almost 10 times lower than the impacts for the first scenario. This result again shows the environmental challenges associated with power use when it is provided by the grid, which includes fossil fuel-based electricity. Hence, the power requirement of the hydrogen production plant should be provided by nuclear power plant in order to have environmentally benign hydrogen production.

In the third scenario, electricity requirements relate not only to the utilization of the hydrogen plant but also to heavy water production for the nuclear plant. As can be observed in Table 10, the impacts are lower for the third scenario compared to the first two scenarios. The ADP (per kg H_2 production) for the five-step Cu–Cl cycle are 9.91×10^{-2} and 4.05×10^{-2} kg Sb-eq. for the first and the second scenarios, respectively, but only 3.78×10^{-2} kg Sb-eq. for the third scenario. The ADP (per kg H_2 production) for the fourth scenario (3.70×10^{-2} kg Sb-eq), in which all electricity needs are met using power from a nuclear power plant, is even lower. The influence of energy use on environmental impacts can be seen once more by examining the GWP values for the first, second, third and fourth scenarios. For instance, the GWP values (per kg H_2

production) for the five-step Cu–Cl cycle are 12.3, 1.33, 0.826 and 0.676 kg CO_2-eq for the first, second, third and fourth scenarios, respectively.

The entire electricity demand for the overall system, which is used for fuel processing, heavy water production and the hydrogen plant, is supplied by the nuclear plant in the fourth scenario. Hence, the negative environmental impacts, which arise from fossil fuel use to produce electricity, are eliminated in that scenario. Thus, the environmental impacts in terms of the impact categories listed in Table 10 are the lowest for scenario 4. Moreover, emissions for the four-step Cu–Cl cycle are lowest for this scenario. Further discussions on the environmental impacts for different scenarios in Tables 9 and 10 are presented in subsequent sections using charts for each impact category.

The percentage contributions of the main stages of nuclear-based hydrogen production to the total environmental impact for several impact categories are presented in Fig. 9. Since all three Cu–Cl thermochemical cycles exhibit similar results in terms of percentage contributions to environmental impacts, only results for the four-step Cu–Cl cycle are displayed in these figures.
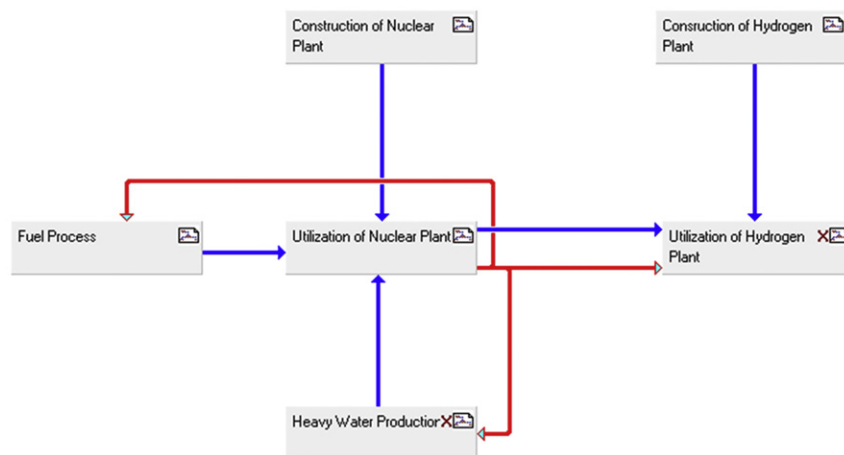

Fig. 8. GaBi 4 model of nuclear-based hydrogen production system for the fourth scenario (Valid for three-, four- and five-step Cu–Cl cycle).

Table 9
Environmental impacts for hydrogen production by thermochemical water decomposition, for analysis scenarios 1 and 2.

Impact category	5-step Cu–Cl cycle		4-step Cu–Cl cycle		3-step Cu–Cl cycle	
	Scenario 1	Scenario 2	Scenario 1	Scenario 2	Scenario 1	Scenario 2
ADP (kg Sb-eq)	9.91×10^{-2}	4.05×10^{-2}	1.12×10^{-1}	3.38×10^{-2}	1.16×10^{-1}	3.80×10^{-2}
AP (kg SO2-eq)	7.66×10^{-2}	7.55×10^{-3}	9.90×10^{-2}	6.79×10^{-3}	9.95×10^{-2}	7.27×10^{-3}
EP (kg phosphate-eq)	3.18×10^{-3}	4.44×10^{-4}	4.04×10^{-3}	3.88×10^{-4}	4.08×10^{-3}	4.23×10^{-4}
GWP (kg CO2-eq)	12.3	1.33	15.8	1.18	15.9	1.27
ODP (kg R11-eq)	1.19×10^{-6}	8.09×10^{-8}	1.56×10^{-6}	7.57×10^{-8}	1.56×10^{-6}	7.89×10^{-8}
POCP (kg ethene-eq)	4.45×10^{-3}	6.16×10^{-4}	5.66×10^{-3}	5.39×10^{-4}	5.71×10^{-3}	5.87×10^{-4}
RAD (DALY)	3.11×10^{-8}	2.10×10^{-9}	4.06×10^{-8}	1.96×10^{-9}	4.07×10^{-8}	2.05×10^{-9}

Fig. 9a shows that the dominant stage affecting all environmental impact is utilization of the hydrogen plant, and this result is due to grid electricity usage for the electrolysis step in the Cu–Cl cycle. Fuel processing, heavy water production and nuclear plant utilization are the other important factors affecting the environment.

Fig. 9b presents percentage contributions to environmental impacts for the second scenario, in which electrical energy need for electrolysis is supplied using the nuclear plant output. Hence, the environmental impact associated with utilization of the hydrogen plant is reduced and the effect of heavy water production and fuel processing is increased. The greatest contributor to ADP is seen to be fuel processing, which accounts for 90%. Fuel processing is also the dominant factor for several impact categories (AP, EP, GWP and POCP). The primary process contributing to ODP and RAD is heavy water production.

Fig. 9c shows the percentage contributions to environmental impacts for the third scenario where electrical energy required for electrolysis during the utilization of hydrogen plant and heavy water production is supplied by nuclear plant. The environmental impacts are mainly associated with heavy water production while the contribution of hydrogen plant utilization diminishes in the third scenario compared to the previous two scenarios. Hence, fuel processing and nuclear plant utilization are the main contributors to environmental impacts (see Fig. 9c and d). While fuel processing is the greatest contributor for all impact categories for the third scenario, Fig. 9d suggests that the effect of fuel processing is slightly decreased, and that the nuclear plant utilization is the main contributor in terms of ODP and RAD for the fourth scenario.

5.1. Abiotic resource depletion potential

ADP addresses the effect on non-living natural resources. Fig. 10 shows ADP values per kg H2 produced for the four defined scenarios, for the three-, four- and five-step Cu–Cl cycles. ADP is the highest for the first scenario as expected due to all the electrical energy demand by the system being supplied by the electrical grid. For example, while ADP for the five-step Cu–Cl cycle is around

0.04 kg Sb-eq for the second, third and fourth scenarios, it is 0.1 kg Sb-eq for the first scenario.

The primary contributor to ADP is fuel processing. More specifically, diesel fuel use in milling and hard coal use in conversion are the most important factors.

5.2. Acidification potential

AP is related to acid deposition of acidifying pollutants on soil, groundwater, surface waters, biological organisms, ecosystems and materials. Fig. 11 shows the AP/kg H2. The lowest AP (2.84×10^{-3} kg SO2/kg H2) is observed for the four-step Cu–Cl cycle and the fourth scenario, mainly because of the lower thermal energy requirement of the four-step Cu–Cl cycle which directly affects the amount of uranium consumed to produce this thermal energy. Hence, the fuel cycle is the greatest contributor to this impact category. The highest AP (approximately 0.1 kg SO2-eq/kg H2) is observed for the three-step Cu–Cl cycle and for the first scenario.

5.3. Eutrophication potential

Eutrophication potential accounts for impacts of excessive environmental levels of macronutrients. EP values per kg H2 production using the Cu–Cl cycle are illustrated in Fig. 12. It is seen that the heavy water production, and milling and mining in fuel processing are the primary contributors to this impact category for the second scenario. The lowest value for EP (2.32×10^{-4} kg Phosphate-eq) is observed for the four-step Cu–Cl cycle and the fourth scenario, and the highest (4.04×10^{-3} kg Phosphate-eq) for the three-step Cu–Cl cycle and the first scenario. Also, the four-step cycle exhibits lower impacts for each scenario.

5.4. Global warming potential

GWP accounts for the impact of anthropogenic emissions on the radiative forcing of the atmosphere which increases the temperature at the earth's surface. The most significant contributions to

Table 10
Environmental impacts for hydrogen production by thermochemical water decomposition, for analysis scenarios 3 and 4.

| Impact category	5-step Cu–Cl cycle		4-step Cu–Cl cycle		3-step Cu–Cl cycle	
	Scenario 3	Scenario 4	Scenario 3	Scenario 4	Scenario 3	Scenario 4
ADP (kg Sb-eq)	3.78×10^{-2}	3.70×10^{-2}	3.12×10^{-2}	3.05×10^{-2}	3.53×10^{-2}	3.46×10^{-2}
AP (kg SO2-eq)	4.38×10^{-3}	3.44×10^{-3}	3.62×10^{-3}	2.84×10^{-3}	4.10×10^{-3}	3.21×10^{-3}
EP (kg phosphate-eq)	3.18×10^{-4}	2.81×10^{-4}	2.63×10^{-4}	2.32×10^{-4}	2.97×10^{-4}	2.63×10^{-4}
GWP (kg CO2-eq)	8.26×10^{-1}	6.76×10^{-1}	6.82×10^{-1}	5.59×10^{-1}	7.72×10^{-1}	6.33×10^{-1}
ODP (kg R11-eq)	2.98×10^{-8}	1.44×10^{-8}	2.46×10^{-8}	1.19×10^{-8}	2.79×10^{-8}	1.35×10^{-8}
POCP (kg ethene-eq)	4.40×10^{-4}	3.87×10^{-4}	3.63×10^{-4}	3.20×10^{-4}	4.11×10^{-4}	3.62×10^{-4}
RAD (DALY)	7.67×10^{-10}	3.65×10^{-10}	6.32×10^{-10}	3.01×10^{-10}	7.16×10^{-10}	3.41×10^{-10}
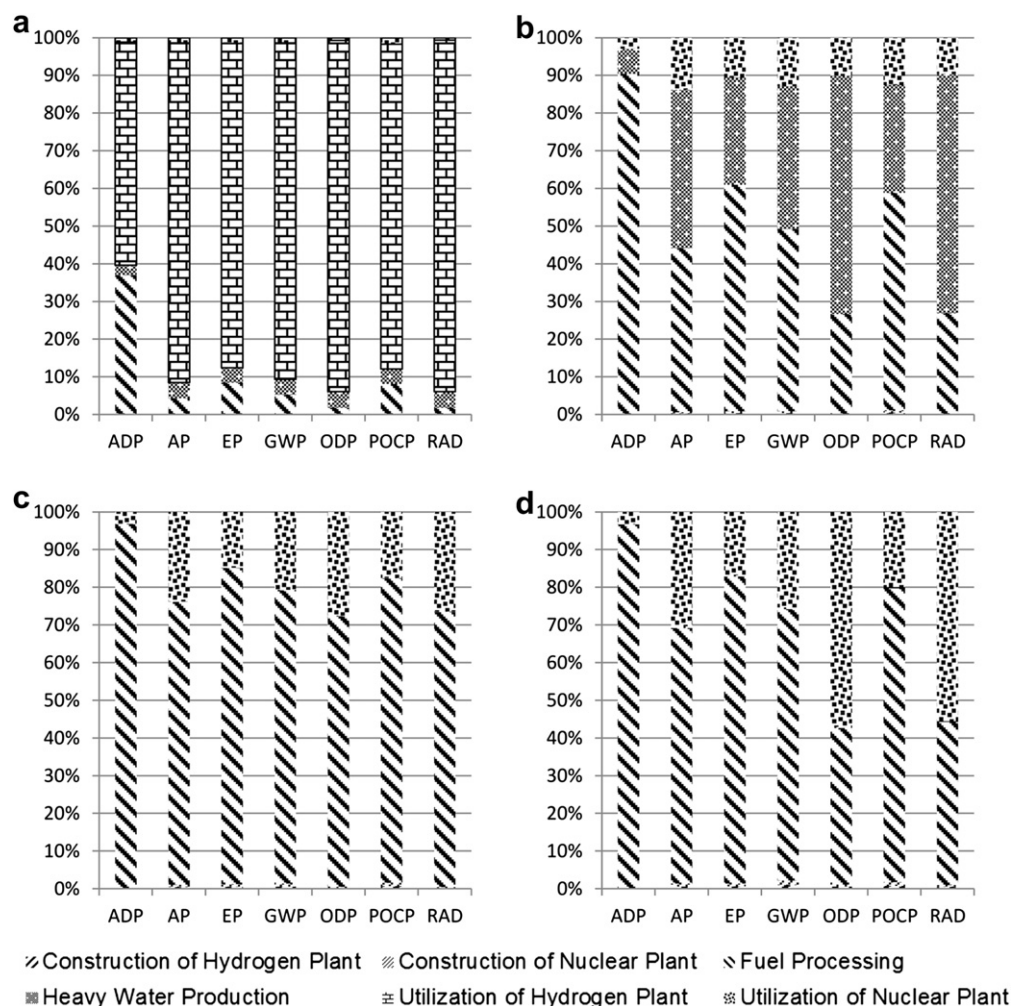
Fig. 9. Percentage contributions from processes (utilization of nuclear and hydrogen plants, heavy water production, fuel processing, construction of nuclear and hydrogen plants) to total environmental impact for (a) The first, (b) The second, (c) The third and (d) The fourth scenario.

GWP are from nuclear plant utilization and the milling and mining steps in fuel processing. The lowest GWP (0.559 kg CO$_2$-eq/kg H$_2$) is obtained for the fourth scenario and the four-step Cu−Cl cycle (see Fig. 13).

It is also seen in Fig. 13 that the four-step Cu−Cl cycle exhibits low GWP values for the second, third and the fourth scenarios. This observation is attributable to the lower thermal energy requirements in these instances. However, for the first scenario the five-
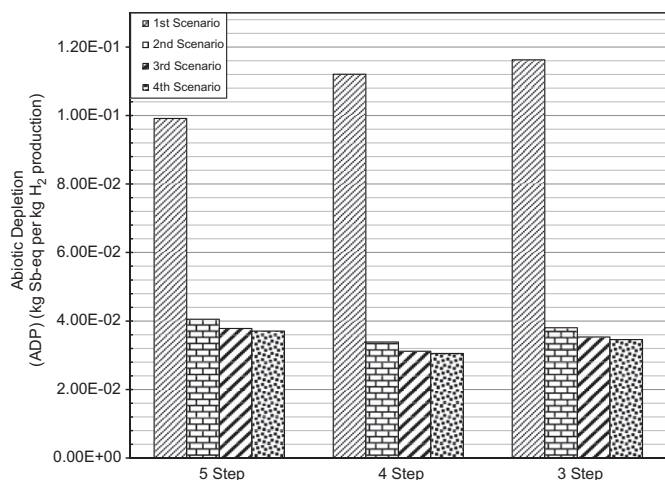
Fig. 10. ADP per kg H$_2$ production for three-, four- and five-step Cu−Cl cycles considering four scenarios.
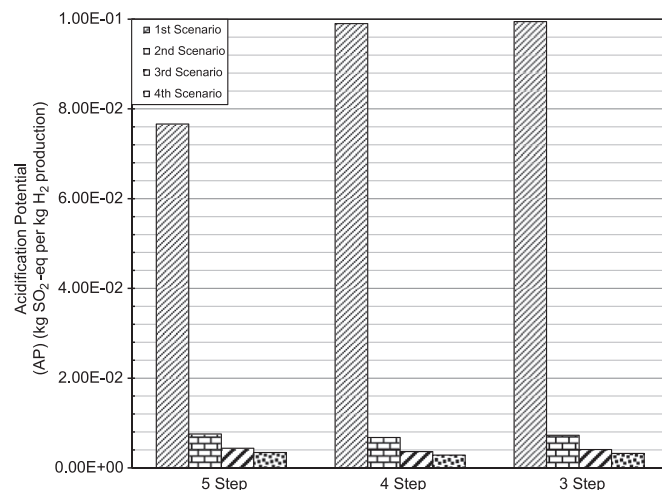
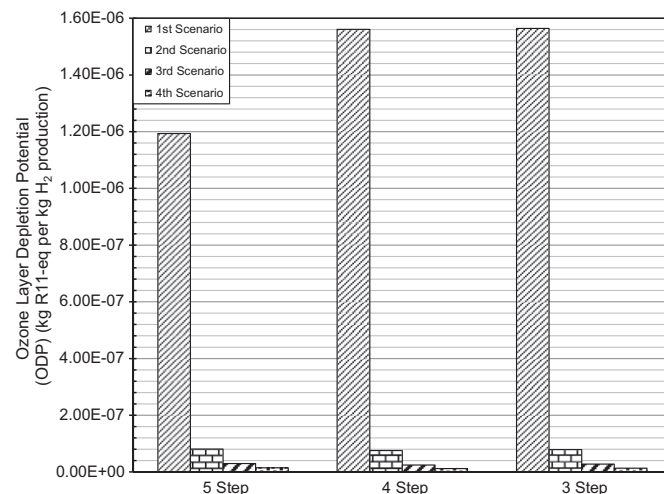**Fig. 11.** AP per kg H$_2$ production for three-, four- and five-step Cu−Cl cycles considering four scenarios.
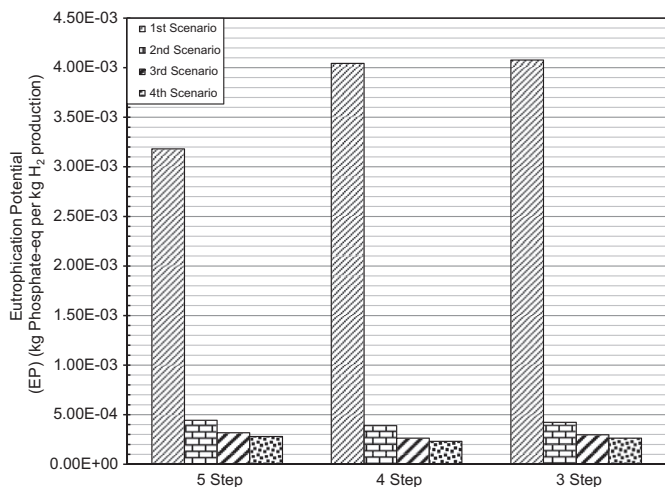
Fig. 12. EP per kg H_2 production for three-, four- and five-step Cu—Cl cycles considering four scenarios.

Fig. 14. ODP per kg H_2 production for three-, four- and five-step Cu—Cl cycles considering four scenarios.

step Cu—Cl cycle has the lowest value. Although the four-step Cu—Cl cycle also exhibits the lowest thermal energy requirement for the first scenario, the electrical energy required for electrolysis significantly affects the GWP; the five-step Cu—Cl cycle has the lowest electrical energy requirement.

5.5. Ozone depletion potential

ODP accounts for the thinning of the stratospheric ozone layer as a result of emissions and the ensuing increase in solar UV-B radiation reaching the earth's surface. Utilization of the nuclear plant is the primary contributor to ODP, accounting for 57% of total impact for the fourth scenario. Fig. 14 shows ODP values for the 12 cases, and highlights the significant difference between the first scenario and the other three scenarios. This difference is attributable to the relatively greater effect of electricity use on ODP.

The lowest value for ODP (1.19×10^{-8} kg R11-eq) is observed for the four-step Cu—Cl cycle and the fourth scenario, and the greatest value (2.98×10^{-8} kg R11-eq) for the three-step Cu—Cl cycle and the first scenario. The four-step cycle is also observed to have lower impacts for each case.

### 5.6. Photochemical ozone creation potential

Photo-oxidants can form in the troposphere under the influence of ultraviolet light through photochemical oxidation of VOCs and carbon monoxide in the presence of nitrogen oxides. Fossil fuel use during milling in fuel processing is observed to be the most important contributor to POCP, accounting for 51% of the value. Fig. 15 also displays POCP values for the various scenarios. The minimum POCP (3.2×10^{-4} kg ethene-eq) is observed for the four-step Cu—Cl cycle for the fourth scenario.

5.7. Radiation

Radiation accounts for the impacts, particularly on humans and animals, of releases of radioactive substances and direct exposure to radiation. Fig. 16 presents RAD values. The main contributor to RAD is operation of nuclear plant for the fourth scenario; the lowest RAD value (3.01×10^{-10} DALY) is obtained for that scenario. The significant decrease in radiation for the fourth scenario relative to the first is observed.
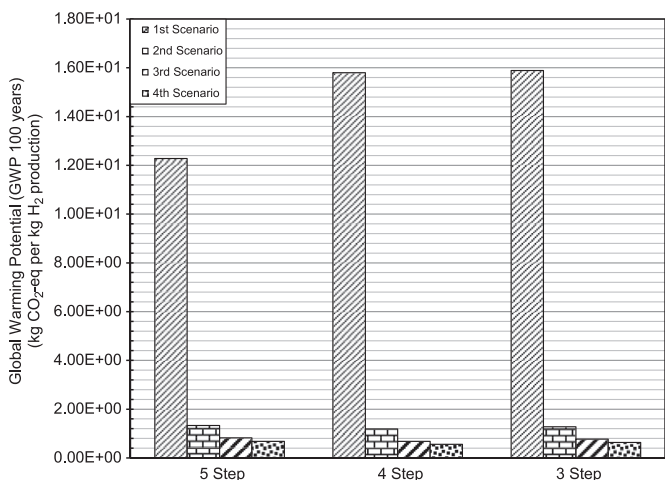
Fig. 13. GWP 100-years per kg H_2 production for three-, four- and five-step Cu—Cl cycles considering four scenarios.
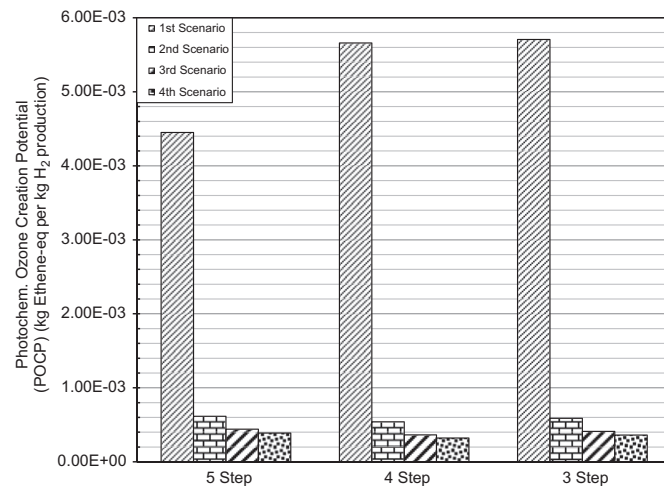
Fig. 15. POCP per kg H_2 production for three-, four- and five-step Cu—Cl cycles considering four scenarios.
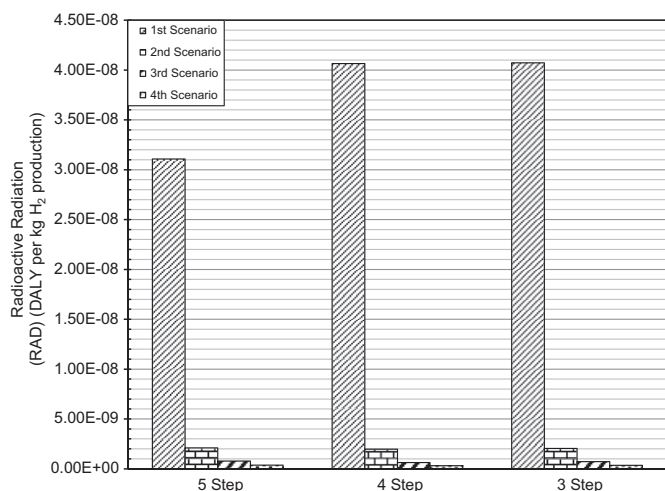
Fig. 16. RAD per kg H_2 production for three-, four- and five-step Cu–Cl cycles considering four scenarios.

6. Conclusions

The environmental impacts of nuclear-based hydrogen production via thermochemical water splitting using the Cu–Cl cycle have been quantified and described using life cycle analysis. 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. 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. The following conclusions are also drawn from the study:

- 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 15.8 kg–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.

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Nomenclature

B_d	Discharge burn-up, GJ/kg U
m_u	Mass of uranium fuel, kg
Q	Heat, MJ
Q_{th}	Thermal energy requirement of hydrogen plant
x_n	Natural uranium U-235 concentration
x_p	Enriched uranium U-235 concentration
x_t	Uranium tailings U-235 concentration
W_{el}	Electrical work requirement of hydrogen plant

Acronyms

ADP	Abiotic Resource Depletion Potential
AP	Acidification Potential
AECL	Atomic Energy of Canada Limited
CML	The Center of Environmental Science of Leiden University
DALY	Disability Adjusted Life Years
EP	Eutrophication Potential
GHG	Greenhouse Gas
GWP	Global Warming Potential
HHV	Higher Heating Value
HTP	Human Toxicity Potential
IAEA	International Atomic Energy Agency
ISO	International Organization for Standardization
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
ODP	Ozone Depletion Potential
OECD/NEA	Nuclear Energy Agency
POCP	Photochemical Ozone Creation Potential
RAD	Radiation
SCWR	Super-Critical Water cooled Reactor
VOC	Volatile Organic Compound

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