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Developments in the production of hydrogen by thermochemical water decomposition

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ABSTRACT

Recent developments in hydrogen production by thermochemical water decomposition are reported, with an emphasis on hydrogen production from non-fossil energy sources such as nuclear and solar. Numerous developments have been made on sulphur-iodine, copper-chlorine and other thermochemical cycles. Efforts are described to lower the temperatures required in thermochemical cycles, so as to broaden the range of potential heat supplies, including developments in the copper-chlorine thermochemical cycle, which has significant potential due to its requirement for process heat at lower temperatures than most other thermochemical processes. The thermodynamic evaluation of thermochemical water decomposition processes is explained and illustrated by applying informative methodologies like exergy analysis, which can assist in improving efficiencies and identifying limiting efficiencies. Thermochemical water decomposition has several advantages relative to other hydrogen production processes that could make it a competitive future option for hydrogen production, which is a key component of a hydrogen economy. Recent developments, particularly using such non-fossil energy sources as nuclear and solar, suggest that thermochemical hydrogen production could become commercial, and help meet the anticipated future demand for hydrogen as an energy currency in the context of a hydrogen economy. Consequently, research is likely to continue to improve thermochemical water decomposition processes.

Keywords

Energy, hydrogen, hydrogen production, thermochemical water decomposition, efficiency, exergy

1. Introduction

The general concept of a hydrogen economy has been investigated for several decades, and has received increasing attention in recent years [1]. Pathways to hydrogen as an energy carrier are investigated with special attention given to pathways involving the use of the renewable energy [2]. Drivers and obstacles for a hydrogen society are also examined in that article.

Some investigations have focused on specific countries. On the general idea of a hydrogen economy, for instance, the potential of a future hydrogen economy in Iceland was investigated [3]. The status of the transition to a hydrogen economy in the United States as of 2006 has been reported [4], as has the status and prospects for hydrogen in Canada [5].

Hydrogen is presently used extensively as a chemical feedstock, e.g., in fertilizer production and petrochemical processes, and this use is increasing. Hydrogen demand as an energy currency is expected to rise dramatically over the next few decades. This rapid growth coincides with the expected emergence of a hydrogen economy. In such an energy system, hydrogen will likely be used in power generation, transportation and oil sands processing. Development on technologies

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like fuel cells that facilitate such hydrogen use is expected to continue.

The potential of hydrogen energy in providing a future sustainable energy system has been studied [6]. Many have focused on the potential contributions of nuclear energy to a hydrogen economy [7,8].

The prospects for hydrogen energy, with particular attention on its potential to avoid climate changes and related problems, have been described [9]**.** The main steps involved in moving toward and implementing a hydrogen economy have been discussed [10,11], and hydrogen production has often been identified as a critical factor. In particular, hydrogen production from non-fossil fuel energy sources has received increasing interest, as it provides an avenue for avoiding many problems associated with society's extensive reliance on and use of fossil fuels.

In this article, recent developments in hydrogen production by thermochemical water decomposition are described. This method of hydrogen production is an alternative option that many consider to have significant potential for the future. This work extends an earlier review by the present author of advances in hydrogen production by thermochemical water decomposition [12], and is not intended to be comprehensive but rather to highlight the selected developments with a particular focus on efficiency improvement. Past work is reviewed, and the emphasis on hydrogen production from non-fossil energy sources, such as nuclear and solar, is highlighted. The copper-chlorine thermochemical cycle for hydrogen production is described and assessed.

The effect of temperature on thermochemical cycles is discussed and efforts to lower the required temperatures in thermochemical cycles are examined. The thermodynamic evaluation of such processes is explained by determining limiting efficiencies and applying exergy analysis. An efficiency and loss evaluation of a thermochemical water decomposition cycle is provided as an illustrative example.

2. Hydrogen production

Hydrogen production is a key component of a hydrogen economy. Consequently, numerous assessments of the potential of a hydrogen economy have focused on this topic. For instance, a long-term global vision of nuclear-produced hydrogen was recently presented [13].

Hydrogen can be produced using a range of processes and many energy sources. For instance, hydrogen can be produced via natural gas reforming (using steam methane reforming), gasification of coal and other heavy hydrocarbons, and water electrolysis (which uses electricity to split water into hydrogen and oxygen electrochemically). Such processes are commercially available. Holladay et al. [14] recently presented an overview of hydrogen production technologies.

Nonetheless, alternative technologies for hydrogen production have also been investigated [15], as have different energy sources. Such processes are of interest, as they have potential advantages in terms of economics, environmental impact and other factors. For instance, a detailed comparison has been provided of the three different primary energy-supply classes which may be used to implement the hydrogen economy: fossil fuels, nuclear energy and renewable energy sources.

The latter include energy from hydroelectric and wind energy systems, ocean thermal energy conversion systems, geothermal resources and solar energy-conversion systems (including biomass, photovoltaic energy conversion and solar thermal technologies) [10]. Turner et al. [16] recently examined options for renewable hydrogen production.

Thermochemical water decomposition is an alternative that many consider to have significant future potential for large-scale hydrogen production. In that process, as with water electrolysis, water is decomposed into hydrogen and oxygen using electricity. However, thermochemical water decomposition utilizes a series of intermediate reactions, which are mainly thermally driven.

Thermochemical water decomposition has several advantages relative to other hydrogen production processes. In particular, the process is often viewed as a competitor to water electrolysis. For instance, net electrolysis efficiencies are typically about 24%, whereas thermochemical hydrogen using nuclear heat can achieve heat-to-hydrogen efficiencies up to about 50%.

3. Thermochemical water decomposition

Much of the research into thermochemical production of hydrogen began in the 1970s [17-19], and efforts carried on at a moderate pace through the 1980s [20, 21] and 1990s [22].

3.1 Fundamentals

Thermochemical cycles for hydrogen production use a series of reactions to achieve the overall splitting of water into hydrogen and oxygen:

$$H_2O \rightarrow H_2 + \tfrac{1}{2} O_2 \qquad (1)$$

Thermochemical water decomposition generally involves at least three distinct steps: hydrogen production, oxygen production and materials regeneration. Thermochemical cycles are used to achieve water splitting because they allow appreciable amounts of hydrogen and oxygen to be attained at much lower temperatures (usually below 1000°C) than are needed for direct one-step thermal water decomposition.

3.2 Recent advances

Research into hydrogen production using thermochemical water decomposition has received increasing attention in recent years, with the rise in concerns about energy supplies and the environmental impact associated with their use. For instance, several thermochemical cycles have been proposed and investigated:

- Onuki et al. [23] have described for hydrogen production using thermochemical water splitting based on iodine and sulphur cycles. Kasahara et al. [24] performed a flowsheet study of the thermochemical water-splitting iodine–sulphur process, while O'Connell et al. [25] have performed a process model-free analysis for thermodynamic efficiencies of the processes in sulphur–iodine thermochemical water decomposition. Detailed aspects of the sulphur-iodine thermochemical cycle have been examined, such as a thermophysical model for hydrogen–iodide vapor–liquid equilibrium and decomposition [26]. Petkovic et al. [27] have proposed activated carbon catalysts for the sulphur–iodine thermochemical water splitting cycle. A pilot test of hydrogen production technology by iodine–sulphur thermochemical water splitting has been examined by Terada et al. [28], and research has been reported aimed at scaling and optimizing a potential reactive distillation column for the HI section of the cycle [29].
- A two-step water splitting thermochemical cycle based on an iron oxide redox pair for solar hydrogen production has been investigated by Charvin et al. [30] and others [31]. Kodama et al. [32] have examined a similar two-step process by ZrO_2-supported $Ni_xFe_{3-x}O_4$.
- Abanades et al. [33] have investigated solar hydrogen production using a two-step thermochemical water splitting cycle based on SnO_2/SnO.
- K.-S. Kang et al. [34] have examined the KIER 4 cycle, a two-step thermochemical cycle for hydrogen production from water using germanium oxide.
- The copper-chlorine (Cu-Cl) thermochemical cycle, which requires lower temperatures than most other thermochemical cycles, has also received increasing interest recently [35,36]. Furthermore, Gonzales et al. [37] have analyzed a hybrid copper oxide–copper sulfate cycle for the thermochemical splitting of water for hydrogen production.

Furthermore, the effect of adding Zr to CeO_2 in the hydrogen reduction and subsequent water splitting reactions is described for another cycle [38], and the potential of mixed conducting membranes to produce hydrogen by water dissociation has been studied [39].

Hybrid processes for hydrogen production based on thermochemical water decomposition and other processes have also bee proposed. For example, Jiang et al. [40] have examined the simultaneous production of hydrogen and synthesis gas by combining water splitting with the partial oxidation of methane in a hollow-fiber membrane reactor.

Research on technologies for thermochemical hydrogen production [41] is ongoing in Canada since such thermochemical processes are thought to couple synergistically with Canada's present and future nuclear reactors [42,43]. Also, several countries (Japan, U.S., France) are currently advancing nuclear technology and corresponding thermochemical cycles. Sandia National Laboratory in the U.S. and CEA in France are developing a hydrogen pilot plant with a sulphur-iodine (S-I) cycle. The KAERI Institute in Korea is collaborating with China to produce hydrogen with the HTR-10 reactor. The Japan Atomic Energy Agency plans to complete a large sulphur-iodine plant to produce 60,000 m^3/hr of hydrogen by 2020, an amount sufficient for about 1 million fuel cell vehicles.

Several countries are participating through multilateral collaborations in the Generation IV International Forum plan to develop the technologies for cogeneration of hydrogen by high-temperature thermochemical cycles and electrolysis.

Several studies of hydrogen production by thermochemical processes have been recently compiled, including reports of the statuses of several cycles [41]. Much of these cycles are driven by solar or nuclear heat, as noted in subsequent sections. Additionally, several reviews of thermochemical hydrogen production have been published [44], including a comprehensive listing of past and present activities [45]. Specific categories of thermochemical production of hydrogen have also been reviewed, including solar [46,47] and nuclear [48].

4. Solar-driven thermochemical water decomposition

The scientific principles and technological advances of thermochemical production of hydrogen using concentrated solar radiation as the source of high-temperature process heat have been reviewed recently [46], while of solar chemical processes for hydrogen production from water splitting thermochemical cycles have been analyzed [47].

A solar thermochemical plant for hydrogen production with the copper-chlorine cycle has been recently analyzed [49]. Also, a large research team has investigated thermochemical cycles for large-scale hydrogen production using solar energy as well as other energy sources [50].

The production of hydrogen from water using solar energy has been considered, based on Zn/ZnO redox reactions, via a two-step thermochemical cycle: 1) endothermic thermal dissociation of ZnO(s) into Zn(g) and O_2 at 2300 K using process heat derived from concentrated solar energy, and 2) the exothermic hydrolysis of Zn(l) at 700 K to form H_2 and ZnO(s) [31]. Vishnevetsky et al. [51] have examined features of solar thermochemical redox cycles for hydrogen production from water as a function of reactants' main characteristics.

5. Nuclear-driven thermochemical water decomposition

The use of high-temperature heat from nuclear plants to drive thermochemical processes for producing hydrogen has been studied extensively [52]. For instance, bench-scale tests have been carried out in Japan, demonstrating the ability of the sulphur-iodine process to produce hydrogen [53]. That report notes that heat at 900°C is generally required to achieve an overall efficiency of about 50%, and that an inorganic separation membrane can be used to separate reaction products and lower the temperature of the heat required for the sulphur-iodine process to about 700°C.

Nuclear reactors operating at various temperatures are considered, including conventional light water reactors, high-temperature gas cooled reactors, liquid metal-cooled fast reactors, the Very High Temperature Reactor (VHTR), a Generation IV concept expected to produce higher temperatures and higher efficiencies, and the Advanced High Temperature Reactor (AHTR). Hydrogen production from an advanced high-temperature nuclear reactor has been investigated in detail [54].

A research team has investigated long-term, large-scale hydrogen production by thermochemical cycles, particularly the S-I cycle and hybrid S cycle (the Westinghouse cycle), using solar and nuclear technologies [50]. Factors in selecting a water decomposition process using heat from high temperature nuclear sources have been investigated recently [41].

Others have also investigated thermochemical cycles using nuclear energy. After carrying out a detailed literature search of all published thermochemical cycles (more than 100 cycles from 800 references), the most promising thermochemical water-splitting cycles were identified for efficient, cost-effective, large-scale production of hydrogen utilizing high-temperature heat from an advanced nuclear power station [55].

The adiabatic UT-3 cycle and the sulphur-iodine cycle were considered by those authors to have the greatest potential, and the sulphur-iodine cycle was selected for further development and recommended for use as a demonstration plant.

The coupling of a copper-chloride hybrid thermochemical water splitting cycle with a desalination plant for hydrogen production from nuclear energy has also been examined [56].

To ascertain the overall environmental impacts of thermochemical cycles for nuclear hydrogen production, life cycle assessment (LCA) can be used [57]. For example, a life cycle assessment has been reported of the nuclear-driven Ispra Mark 9 thermochemical cycle [58]. LCA considers emissions of greenhouse gases (CO_2-equivalent) and acid gases (SO_2-equivalent).

6. Copper-chlorine thermochemical water decomposition cycle

The copper-chlorine cycle is an important cycle for thermochemical water decomposition, particularly because of its requirement for relatively low-temperature heat compared to other thermochemical water decomposition cycles.

Consequently it has attracted interest, and has been identified by Atomic Energy of Canada Ltd. (AECL) as a highly promising cycle for thermochemical hydrogen production. Other advantages of this proposed process are reduced construction materials, inexpensive chemical agents, minimal solids handling, and reactions going to completion with few side reactions. Past studies at Argonne technologies for the Cu-Cl thermochemical cycle, through an International Nuclear Energy Research Initiative[59].

The Cu-Cl cycle is well matched to Canada's nuclear reactors, since its requirement for heat is at temperatures producible by the Super-Critical Water Reactor (SCWR), which is being considered as Canada's Generation IV nuclear reactor.

6.1 Copper-chlorine thermochemical cycle processes

The steps in the copper-chlorine thermochemical cycle are shown in Tables 1a and 1b and a possible process diagram for the cycle is provided in Fig.1 [59].

This discussion focuses on the five-step copper-chlorine thermochemical cycle, although efforts are ongoing to develop cycles with less chemical steps. The primary components include five interconnected reaction vessels and several heat exchangers.

6.1.1 HCl production

High-temperature steam and solid $CuCl_2$ particles from the flash drying step mix to produce two exit flows: HCl(g) which is directed to the hydrogen production step and $CuO*CuCl_2$ solid particles for the oxygen production step.The HCl(g) is chemically produced at 430°C in a fluidized bed reactor:

$$2CuCl_2(s) + H_2O(g) \rightarrow CuO{*}CuCl_2(s) + 2HCl(g) \quad (2)$$

Table 1a. Five-Step Copper-Chlorine Thermochemical Water Decomposition Cycle: Main Chemical Reactions and Temperatures

Process	**Primary chemical reaction**	**Temperature range (°C)**
HCl production	$2CuCl_2(s) + H_2O(g) \rightarrow CuO{*}CuCl_2(s) + 2HCl(g)$	400
Oxygen production	$CuO{*}CuCl_2(s) \rightarrow 2CuCl(l) + 1/2O_2(g)$	500
Electrochemical process	$2CuCl(s) \rightarrow 2CuCl(aq) \rightarrow CuCl_2(aq) + Cu(s)$	Ambient
Flash drying	$CuCl_2(aq) \rightarrow CuCl_2(s)$	>100
Hydrogen production	$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(l) + H_2(g)$	430-475

Table 1b. Copper-Chlorine Thermochemical Water Decomposition Cycle: Main Material Inputs and Outputs to Main Processes

Process	**Material flows**	
	Inputs	**Outputs**
HCl production	Powder/granular $CuCl_2$ $H_2O(g)$	Powder/granular $CuO*CuCl_2$ $2HCl(g)$
Oxygen production	Powder/granular $CuO*CuCl_2(s)$	Molten CuCl salt Oxygen
Electrochemical process	Powder/granular CuCl HCl	Electrolytic Cu HCl and $CuCl_2$ slurry
Flash drying	HCl slurry $CuCl_2$	Powder/granular $CuCl_2$ H_2O/HCl vapours
Hydrogen production	Electrolytic Cu Dry HCl	H_2 CuCl(l) salt

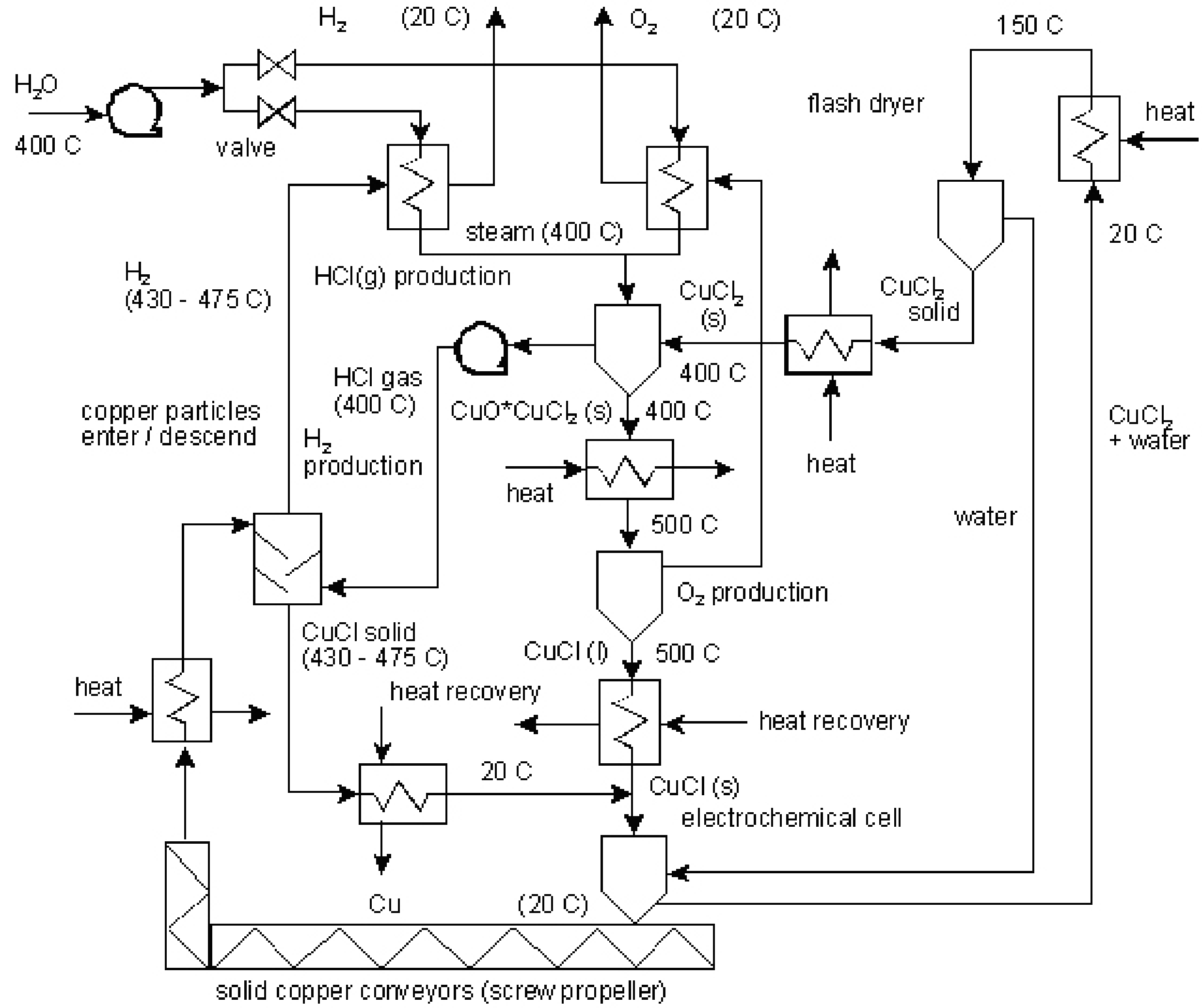

Fig.1: Possible process diagram of a thermochemical water decomposition process for hydrogen production based on the copper-chlorine cycle.

6.1.2 Oxygen production

The following reaction, requiring the highest cycle temperature (about 500°C), occurs in the oxygen production reactor:

$$CuO{*}CuCl_2(s) \rightarrow 2CuCl(l) + 1/2O_2(g) \qquad (3)$$

In this and the HCl production steps, a good understanding is required of the solubilities of $CuCl_2(s)$ and $CuO{*}CuCl_2(s)$ in a mixture of steam and HCl(g) since these components are sparingly soluble in dense supercritical steam and may poison catalyst surfaces.

6.1.3 Electrochemical process

CuCl(s) enters and solid copper particles are produced for the hydrogen production step via an electrically-driven electrochemical cell at ambient conditions:

$$2CuCl(s) \rightarrow CuCl_2(aq) + Cu(s) \qquad (4)$$

Solid particles exiting from the base are transported to the hydrogen production chamber. The chemical kinetics in the electrochemical cell, as a function of temperature, pressure and composition, is important. Innovative heat exchangers, with heat transfer correlations and pressure drop and friction coefficients, are needed to permit corrosive fluid processing at high-temperatures. To reduce the challenges of solid handling, Atomic Energy of Canada is investigating ways to replace the electrochemical and hydrogen production steps with the following reaction:

$$2CuCl(aq) + 2HCl(aq) \rightarrow H_2(g) + 2CuCl_2(aq) \qquad (5)$$

6.1.4 Flash drying

An aqueous $CuCl_2$ flow exiting the electrochemical cell is preheated to 150°C before entering the flash dryer to produce the $CuCl_2(s)$ required for the HCl production step. The device adds sufficient heat to remove water and recover solid $CuCl_2$.

6.1.5 Hydrogen production

Copper particles enter the mixing chamber in the reactor unit, descend along an inclined bed and melt to produce CuCl(l), while HCl(g) passes through the chamber to generate $H_2(g)$. The following reaction, which involves three distinct phases and turbulent gas mixing, occurs at 430-475°C:

$$2Cu(s) + 2HCl(g) \rightarrow H_2(g) + 2CuCl \qquad (6)$$

To increase hydrogen yield, efforts are underway to enhance mixing chamber performance and to better understand mixing with liquid and solid particle flows.

6.1.6 Heat exchange and recovery

The main cycle heat additions occur in HCl production, oxygen production, hydrogen production and flash drying, with the first three at temperatures of 400 to 550°C. Many heat exchangers are incorporated into the cycle, and options for heat recovery are being investigated to reduce thermal losses [60] and to determine the most appropriate flow rates and temperatures for each step. Also, as high performance metal alloys cannot withstand corrosive fluids over a long duration, alloys with coatings of silicon-based ceramics appear promising as alternatives.

6.2 Advances in the Copper-Chlorine thermochemical cycle

6.2.1 Improving understanding of chemical steps

Thermodynamic assessments of hydrogen production via copper-chlorine thermochemical water decomposition have been reported for the primary chemical operations, including the drying step [61], the fluidized bed [62], the oxygen production step [63], the copper production step [64] and the hydrogen production step [65].

6.2.2 Enhancing thermal management

The enhancement of this type of system via the use of a chemical heat pump has been subject to a thermodynamic analysis [66].

6.2.3 Integration of cycle with supercritical water-cooled nuclear reactor

A thermodynamic performance assessment of a system linking a supercritical water-cooled nuclear reactor and a thermochemical water splitting cycle for hydrogen production has been recently presented [67].

6.2.4 Simulation of the Cu-Cl cycle

Some process simulations of nuclear-based thermochemical hydrogen production with a copper-chlorine cycle have been reported [36,68]. Further work in this area is needed to improve the realism and accuracy of the simulations.

6.2.5 Economics of the Cu-Cl cycle

The economics of thermochemical hydrogen production with a copper-chlorine cycle have been examined on a preliminary basis. For instance, the present author has reported an exergoeconomic analysis of the cycle using the specific exergy cost (SPECO) method [69] and an exergy-cost-energy-mass analysis [70].

6.2.6 Life cycle analysis of the Cu-Cl cycle

A preliminary Life Cycle Assessment (LCA) of nuclear-based hydrogen production via thermochemical water decomposition with the Cu-Cl thermochemical cycle has been presented [71,57], which examines the environmental impacts of the nuclear and thermochemical hydrogen production plants. The thermochemical plant environmental impacts are found by examining data and applying several assumptions on inventories of raw materials and chemicals.

Some specific parameters included in the LCA are as follows:

- global warming potential (GWP), which is concerned with increasing concentrations amount of CO_2 and other greenhouse gases in the earth’s atmosphere.
- acidification potential (ACP), which is concerned with the impact of emissions of acidic substances on soil and water bodies.
- ozone depletion potential (ODP), which is concerned with destruction of the atmospheric ozone layer leads and subsequent increases in the amount of ultraviolet reaching the earth's surface.
- radiological potential (RP), which relates to the probability of radiogenic cancer mortality or morbidity due to internal or external radiation exposure.
- abiotic resource depletion potential (ADP), which is concerned with the extraction of non-renewable raw materials.
- ecotoxicity aquatic (ECA), which is concerned with exposure to toxic substances that lead to health problems.

The results indicate that the nuclear fuel cycle contributes significantly to the total environmental impacts, and the improvement analysis stage of LCA suggests the need for the development of more sustainable processes, particularly in the nuclear plant.

7. Effect on performance of temperature

7.1 Temperature dependence

The primary advantage of thermochemical water decomposition cycles is that they allow water to be split into hydrogen and oxygen using heat at lower temperatures than would be required to split water directly through heating. The advantages of a cycle increase as the required peak temperatures are reduced, in that a greater range of heat sources can then be considered for a given application. Consequently, research has been carried out to lower the peak temperatures required in thermochemical water decomposition cycles [72].

7.2 Lowering cycle temperature

Some research on lowering peak temperatures has focused on particular cycles. For example, research has been carried out on a lower-temperature iodine–Westinghouse–Ispra sulphur process for thermochemical production of hydrogen [73].

This work was motivated by noting that many thermochemical processes to produce hydrogen required heat at high temperatures (often exceeding 850°C), and that such heat can be provided by nuclear reactors if peak temperatures can be reduced by 100°C or more. Other researchers have focused on finding alternative thermochemical cycles that inherently require heat at lower temperatures. For instance, research in the US on processes for hydrogen production at temperatures below 550°C, including thermochemical cycles, has been reported recently [74].

Again the motivation for much of this work has been to allow present and near-term nuclear technology to be used in hydrogen generation. The authors note that it will be many years before very high temperature reactors become commercially available.

Other cycles for hydrogen generation that require lower peak temperatures, like the copper-chlorine (Cu-Cl) thermochemical cycle which requires temperatures lower than approximately 550°C, have been investigated [35,36].

8. Efficiencies and losses for thermochemical water decomposition cycles

8.1 Upper limit efficiencies

Limiting thermodynamic efficiencies of thermochemical cycles for hydrogen production have been investigated [75].

Similar activities have been carried out for specific cycles. For instance, research has been carried out on the upper efficiency bound for the sulphur-iodine thermochemical cycle [76].

8.2 Assessing efficiencies and losses using exergy methods

Exergy analysis, an advantageous alternative to the more conventional energy analysis, can be used to identify meaningful efficiencies and thermodynamic losses in an overall process and its steps. Exergy losses occur through both waste exergy emissions and internal exergy destructions. Exergy destruction is a valuable parameter for identifying locations and magnitudes of efficiency losses. Exergy analysis often reveals insights not identified with energy analysis [77].

Exergy methods have been applied to hydrogen technologies [78] and other processes [77,79]. Several hydrogen production processes have been investigated by the present author using exergy, including steam-methane reforming [80,81], coal gasification [81,82] and water electrolysis [81,83].

8.3 Exergy analyses of thermochemical water decomposition cycles

Several exergy analyses of thermochemical water decomposition processes for hydrogen production have been reported.

Some of these have been directly focused on the benefits and insights provided by applying exergy methods [84-86]. For instance, an exergy analysis of thermochemical hydrogen production using a vanadium/chlorine cycle has been reported [87].

Exergy analysis has been used to evaluate a hybrid thermochemical solar process for producing hydrogen based on sulphuric acid decomposition and the synthesis processes [88]. The energy and exergy efficiencies of a daily cycle were determined to be 58% and 36%, respectively.

Also, an exergy-based investigation was reported by the present author of the thermodynamic performance of the Ispra Mark-10 thermochemical water decomposition process for hydrogen production [89,90], which forms the basis of the illustrative example presented in the next section. Other studies of hydrogen production by thermochemical water decomposition have not focused on the application of exergy methods, but rather have included the results of exergy analyses to complement the energy and other information presented. For example, in an assessment of solar hydrogen production via a two-step water-splitting thermochemical cycle based on Zn/ZnO redox reactions, a maximum exergy conversion efficiency of 29% is reported for the closed cycle when using a solar cavity-receiver operating at 2300 K and subjected to a solar flux concentration ratio of 5000 [31]. More generally, exergy efficiencies are considered in solar thermochemical production of hydrogen [46].

Exergy considerations are also taken into account in an investigation of the oxygen generation step for producing hydrogen with a sulphur-iodine thermochemical cycle [91]. Energy and exergy analyses of the four-step adiabatic UT-3 thermochemical process for hydrogen production were undertaken, and determined the efficiencies of the process to be 49% based on energy and 53% based on exergy [92].

A recent assessment of the principles and bases for thermodynamic evaluations of water-splitting thermochemical cycles also takes into account exergy factors [93]. Also, exergy analyses of the copper-chlorine thermochemical cycle have been reported by the present author and others, to enhance understanding and reduce losses and thereby to improve efficiencies [94].

9. Efficiency and loss evaluation of a thermochemical water decomposition cycle: an example

An analysis of the Ispra Mark-10 thermochemical water decomposition cycle by the present author [89,90] is the basis of this example.

9.1 Process steps

The Ispra Mark-10 cycle (Fig.2) was proposed to produce hydrogen from water on a large scale for fuel and major industrial chemical uses [95,96]. The assumed energy source for the required high-temperature process heat is a helium-cooled, high-temperature gas-cooled reactor (HTGR), although other sources could suffice. Process data [95, 96] are listed in Tables 2a through 2c. The process consists of four main steps.

9.1.1 Thermal energy generation

It is assumed that thermal energy is produced in a HTGR, and that helium transports the thermal energy from the HTGR, leaving at 1255 K and returning at 773 K. The heat is used for both electricity generation and process heat over a range of temperatures for thermal requirements and endothermic chemical reactions.

9.1.2 Electrical energy generation

Some thermal energy from the HTGR is used for electricity generation, mainly for use in the primary reactors. The electricity is assumed to be generated at 80% of the thermodynamic ideal efficiency. This is an optimistically high value, but is premised on possible future advances in electricity generation technology.

Table 2a. Process data for the Ispra Mark-l0 cycle: material flows

Flow number (Figure 2)	**Temperature (°C)**	**Pressure (MPa)**	**Mass flow rate (kg/s)**	**Mass fraction**		
				H_2O	**H_2**	**O_2**
1	17	0.101	43.24	1.000	0.000	0.000
2	27	0.210	4.7	0.000	1.000	0.000
3	27	5.00	37.6	0.000	0.000	1.000
4	52	0.101	0.032	0.063	0.031	0.906

Table 2b. Process data for the Ispra Mark-l0 cycle: thermal flows

Flow number (Figure 2)	**Energy rate (MW)**
5	1709
6	714
7	2009
8	102
9	192
10	99
11	2184

Table 2c. Process data for the Ispra Mark-l0 cycle: electrical flows

Flow number (Figure 2)	**Energy rate (MW)**
12	475

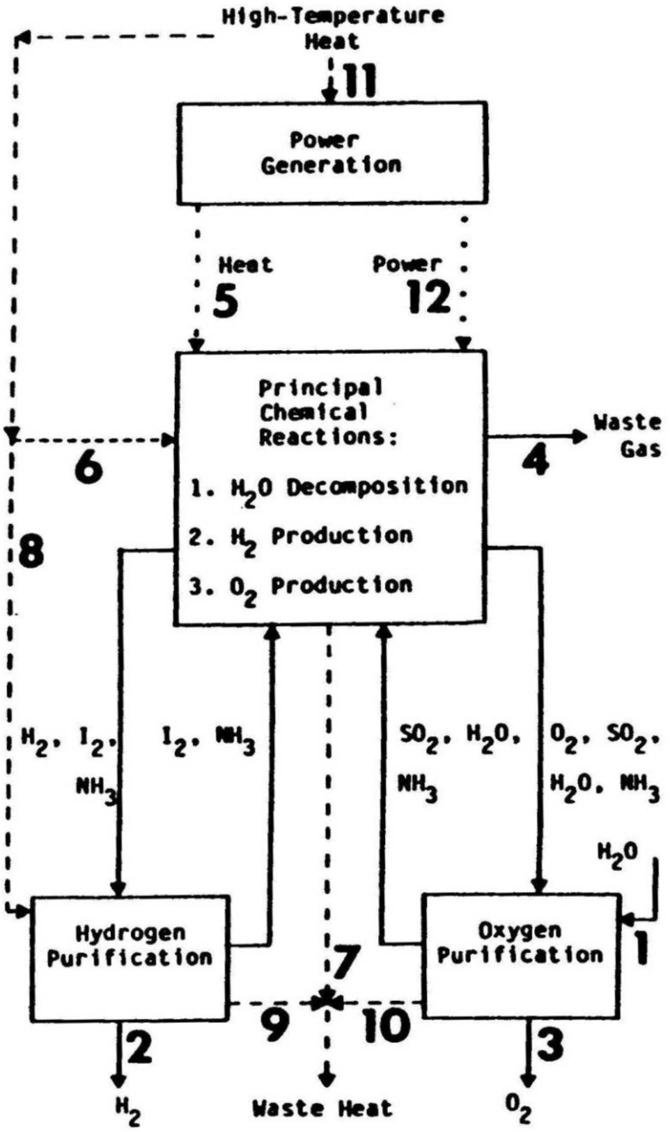

Fig.2: Detailed process diagram for the Ispra Mark-10 cycle, considering high-temperature heat as the driving input. Material flows are represented by solid lines, electrical flows by dotted lines and heat flows by dashed lines.

9.1.3 Primary chemical reactions

This step can be separated into three subprocesses:

- water splitting
- hydrogen production
- oxygen production

Five principal reactions occur in this thermochemical water decomposition process:

$$2H_2O + SO_2 + I_2 + 4NH_3 \rightarrow 2NH_4I + (NH_4)2SO_4 \quad (7)$$

$$2NH_4I \rightarrow 2NH_3 + H_2 + I_2 \quad (8)$$

$$(NH_4)_2SO_4 + Na_2SO_4 \rightarrow Na_2S_2O_7 + H_2O + 2NH_3 \quad (9)$$

$$Na_2S_2O_7 \rightarrow SO_3 + Na_2SO_4 \quad (10)$$

$$SO_3 \rightarrow SO_2 + 0.5(O_2) \quad (11)$$

These five reactions in Equations 7 to 11 occur at 325 K, 900 K, 675 K, 825 K and 1140 K, respectively. Seventeen per cent of the water in the cycle decomposes, and waste gas exits at 325 K and 0.101 MPa.

9.1.4 Oxygen purification

Oxygen is separated and cooled, exiting at 300 K and 5.00 MPa. Also, feedwater is input at 290 K and 0.101 MPa.

9.1.5 Hydrogen purification

Helium delivers thermal energy for purification, entering at 815 K and exiting at 798 K. The product gas, purified to 99.9 wt% H_2, is cooled and exits at 300 K and 0.210 MPa.

9.2 Balances and flow characteristics

The principal results are presented as overall energy and exergy balances in Figures 3a and 3b. The overall energy and exergy balances in Fig.3a consider a source of high-temperature heat as the driving process input, while those in Fig.3b consider high-temperature heat itself as the driving process input.

Figures 3a and 3b lead to interesting observations about inputs and outputs for the cycle:

- The input exergy is entirely associated with high-temperature heat. The same observation applies for the input energy.
- The output exergy is mainly associated with the product hydrogen. The output energy is mostly associated with hydrogen and waste cooling water.

Several related observations for the cycle also follow from Figures 3a and 3b:

- The product (hydrogen) has high energy and exergy contents.
- The by-product (oxygen) has low energy and high exergy contents.
- The wastes (spent cooling water and waste gas) have high energy and low exergy contents.

The energy results indicate that the wastes are more valuable than the by-product, while the exergy analysis results indicate that the by-product is more valuable. Also, to reduce losses (and consequently to increase efficiency), energy analysis results indicate that quantities of waste effluents must be reduced, while exergy analysis results indicate that internal consumptions must be reduced.

9.3 Efficiencies

Energy and exergy efficiencies are determined as follows:

$$\text{Energy efficiency} = (\text{Energy in products})/(\text{Total energy input}) \qquad (12)$$

$$\text{Exergy efficiency} = (\text{Exergy in products})/(\text{Total exergy input}) \qquad (13)$$

9.3.1 Overall efficiencies

The overall efficiencies depend on whether or not oxygen by-product credits are permitted. Without an oxygen by-product credit, energy and exergy efficiencies for the cycle are 21% and 25%, respectively.

The oxygen by-product credit affects the efficiencies by less than 1%. The oxygen stream possesses exergy due to its purity. The overall energy and exergy efficiencies are similar even though, in general, energy and exergy efficiencies differ.

9.3.2 Component efficiencies

Energy and exergy efficiencies differ for some devices in the system. The energy efficiency of the primary reactions subsection is reasonably high (almost 60%), while the corresponding exergy efficiency is almost half of that value.

The efficiencies of the hydrogen purification subsection are both relatively high, with the exergy efficiency (about 92%) exceeding the energy efficiency (71%).

Efficiencies for the oxygen purification subsection depend on whether or not oxygen by-product credits are considered.

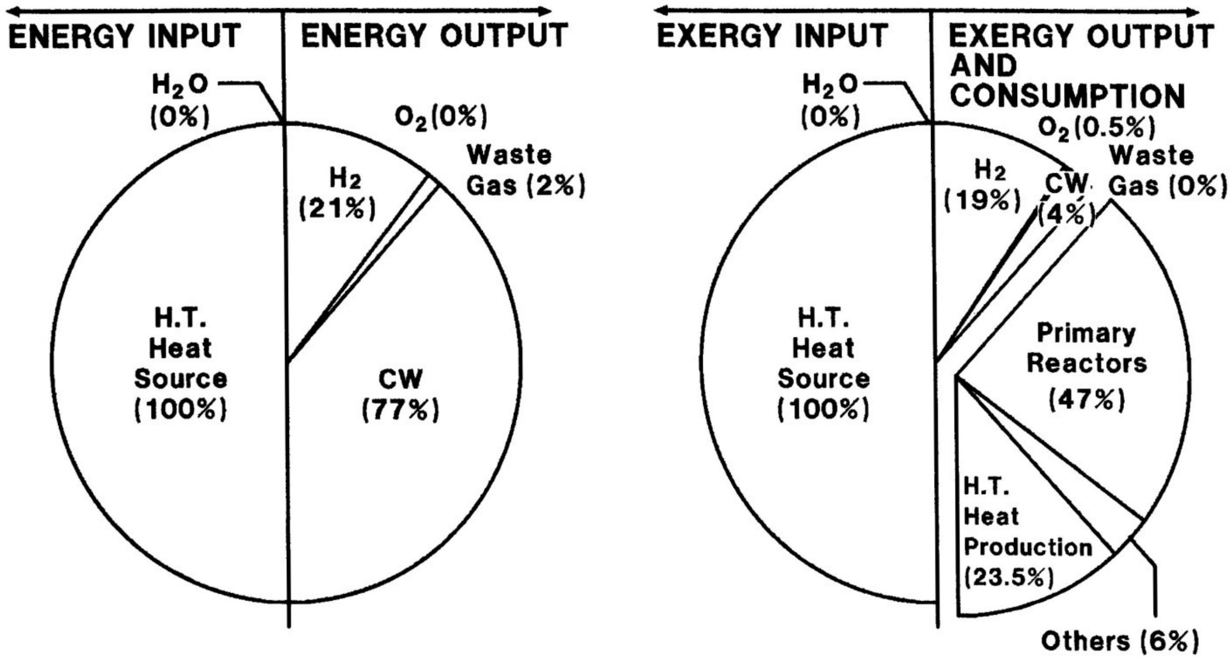

Fig.3a: Overall energy and exergy balances for the Ispra Mark-l0 cycle, considering a source of high-temperature heat as the driving process input. The left and right halves of the energy balances represent respectively energy inputs and energy outputs. The left and right halves of the exergy balances represent respectively exergy inputs and exergy outputs and consumptions (exploded section of balance). CW denotes cooling water and H.T. high-temperature.

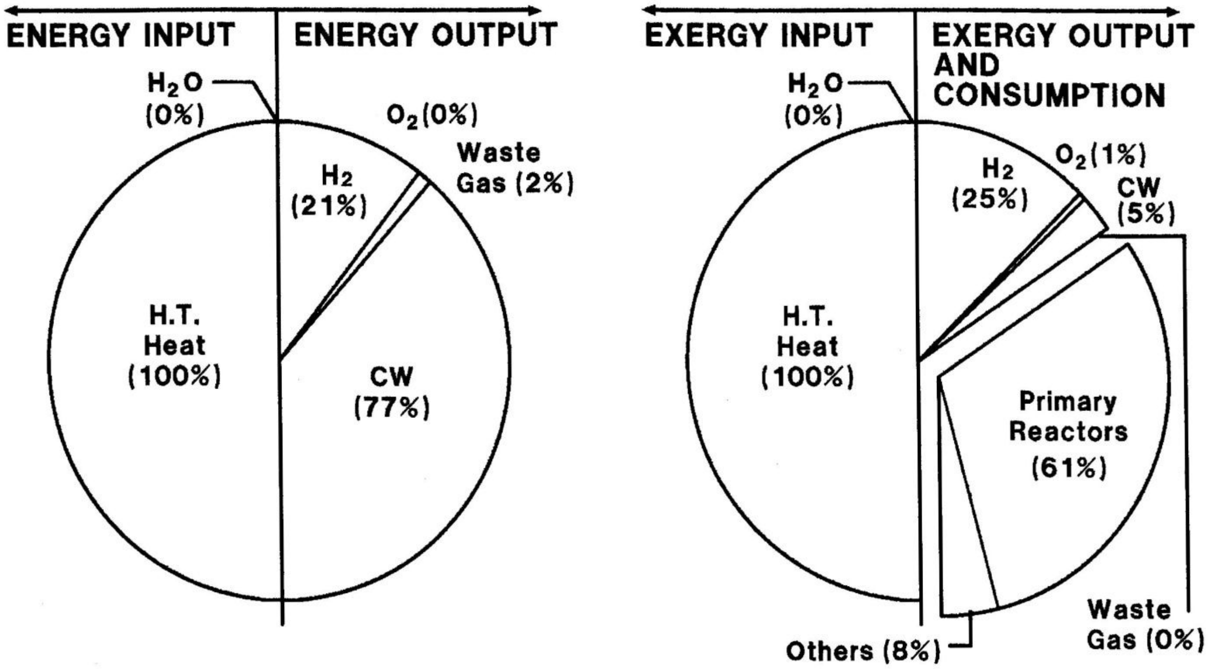

Fig.3b: Overall energy and exergy balances for the Ispra Mark-l0 cycle, considering high-temperature heat as the driving process input. Other details are as in Fig.3a.

9.4 Losses

Energy and exergy loss rates are shown in Table 3. The exergy losses are divided into those associated with waste emissions and those due to internal exergy consumptions due to irreversibilities. Energy losses are only associated with waste emissions; "energy consumptions" cannot occur according to the principle of energy conservation. Most exergy losses are due to chemical reaction and heat transfer across large temperature differences. The stark difference in the breakdown of energy and exergy losses is illustrated in Fig.4.

The results suggest that substantial potential exists in theory for improved efficiency in thermochemical water decomposition using the Ispra Mark-10 cycle.

Also, directions for research in thermochemical water decomposition should be guided, at least in part, by the results of exergy analyses, which indicate, in general, that research should concentrate on those subprocesses having large exergy losses.

Of course, it is not certain that significant potential improvements are possible for a process with large thermodynamic losses, even if the margin for improvement is theoretically found to be significant via exergy analysis, as actual improvements are dependent on the circumstances and engineering ingenuity and creativity.

Table 3. Breakdown of energy and exergy losses for the Ispra Mark-10 cycle, considering by-product oxygen

Type of loss	Energy loss rate		Exergy loss rate	
	MW	% of total	MW	% of total
External emissions*	1740	100	90	7
Internal consumptions**	—	—	1150	93

* Includes emissions of waste gas, spent cooling water and miscellaneous heat losses.

** Includes consumptions for heat and electricity generation section, primary chemical reactions section and purification of hydrogen and oxygen sections.

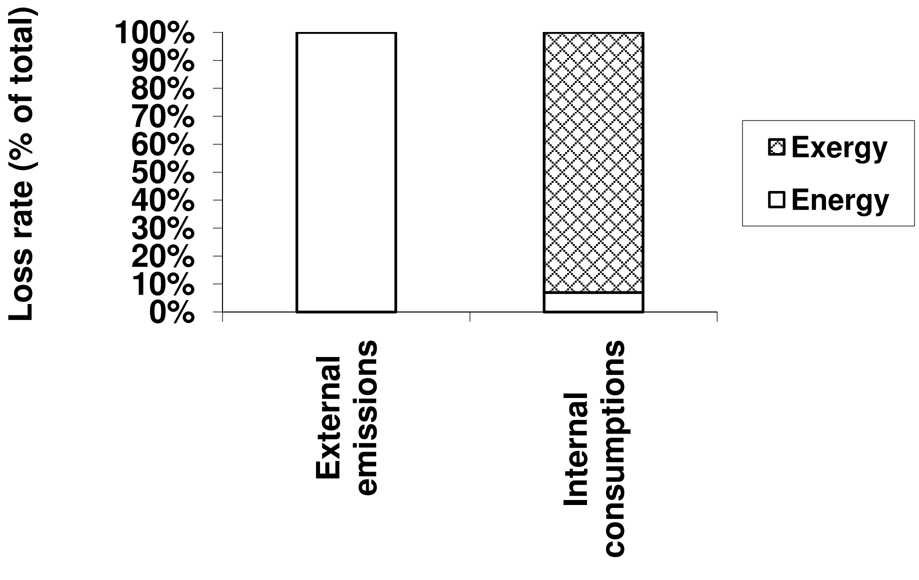

Fig.4: Comparison of energy and exergy losses for the Ispra Mark-10 cycle, with oxygen treated as a by-product.

10. Comparative evaluation

Much research has been done on thermochemical water decomposition cycles that operate on thermal energy and electro-thermochemical processes that require electricity in addition to thermal energy.

Two-step cycles require thermal energy input above 1100°C so, to avoid the need for excessively high temperatures, most cycles that have received attention have three or more steps. Cycles with more steps usually have lower peak temperature requirements than thermochemical water decomposition cycles consisting of two or three steps.

The benefits of successful development of thermochemical water decomposition cycles are significant, as they have the potential of overall energy efficiencies exceeding of 40%.

Also these technologies can facilitate the broader use of solar and nuclear energy, since the two main high-temperature heat sources envisioned for use with thermochemical cycles are solar thermal energy systems (e.g., concentrating collectors and central receiver systems) and high temperature nuclear reactors.

More than three hundred thermochemical cycles for hydrogen production have been reported. Many combinations of chemical reactions have been studied to determine viability and potential competitiveness relative to other hydrogen production methods. Some of the more advantageous thermochemical water decomposition cycles, based on varying criteria, have been identified to be the following:

- The sulphur-iodine cycle consists of three main chemical reactions. One is the Bunsen reaction, in which exothermic sulphur dioxide gas absorption occurs in the liquid phase at 20°C-100°C. Gaseous sulphur dioxide reacts with iodine and water to generate an aqueous solution of hydriodic acid and sulfuric acid, which are separated by liquid-liquid phase separation in the presence of excess iodine. The hydriodic acid breakdown reaction generates hydrogen with a low endothermic heat of reaction at 300°C-500°C in the gas or liquid phase. The sulfuric acid decomposition is an endothermic reaction that produces oxygen.
- The Ispra Mark 9 thermochemical cycle consists of three steps involving iron chlorides: decomposition of Fe (III) chloride at 430°C, hydrolysis at 650°C and chlorination at 150°C.
- In the hybrid sulphur cycle developed by Westinghouse, sulfuric acid is decomposed to sulphur dioxide at 850°C to produce oxygen. Then, the sulphur dioxide is reconverted to sulfuric acid in an electrolyzer at 80°C to produce hydrogen.
- In the calcium-bromine cycle, CaO and $CaBr_2$ are recycled in fixed bed reactors at about 730°C and oxygen is produced. Also, HBr is converted to bromine in an electrolyzer at 80°C to produce hydrogen.
- The copper-chlorine thermochemical cycle operates at relatively low temperatures, allowing it to accommodate heat sources around 550°C.

Many thermochemical cycles (e.g., sulphur-iodine cycles) have challenges associated with their requirements for process heat at high temperatures, often exceeding 850°C. Such temperatures can cause challenging engineering and materials problems.

A challenge with the sulphur-iodine cycles is the pH effects. Such processes cannot operate on today's nuclear power plants, which are typically water-cooled plants operating at 250°C to 500°C. Some thermochemical cycles (e.g., copper-chlorine cycles) operate at lower temperatures that provide several advantages, e.g., ability to use thermal energy from some nuclear reactors and fewer materials problems.

Furthermore, some cycles have challenges associated with reaction rates for some of the chemical steps. Since it is necessary that all of the reactions proceed at the same rate for continuous operation of a cycle, a slow rate of reaction for one step adversely affects the whole process efficiency.

The probability that thermochemical water decomposition cycles will be introduced in the next decade is small, as many advances are required in the technologies before they can become viable and competitive with other hydrogen production processes. In addition, advanced nuclear reactor technologies need to be developed for nuclear-based thermochemical cycles to be introduced, and the costs of solar thermal technologies need to be significantly reduced for solar-based thermochemical cycles to become economically attractive. But the likelihood that thermochemical water decomposition cycles will be introduced over the next two decades is significantly greater, as the challenges associated with the cycles and their energy sources are more likely to be resolved by then.

11. Conclusions

In line with the expected emergence of a hydrogen economy, efforts to develop improved processes for hydrogen production are likely to continue. Although several processes are commercially available for hydrogen production, some alternatives are under development that may be advantageous.

One of these is thermochemical water decomposition. Recent advances in hydrogen production by thermochemical water decomposition, particularly using non-fossil energy sources such as nuclear and solar, suggest that commercial thermochemical hydrogen production could become a reality in the next decade.

Improvements in efficiencies and performance are likely to be obtained with informative assessment methodologies like exergy analysis, which also allows losses to be better understood and reduced. Numerous advances have been made on sulphur-iodine cycles, and the copper-chlorine thermochemical cycle for hydrogen production is observed to have significant potential due to the lower temperatures it requires for heat supplies compared to most other thermochemical processes.

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Biography

Marc A. Rosen is a Professor of Mechanical Engineering at the University of Ontario Institute of Technology, where he served as founding Dean of the Faculty of Engineering and Applied Science from 2002 to 2008. Dr. Rosen has also served as President of the Engineering Institute of Canada and as President of the Canadian Society for Mechanical Engineering. Dr. Rosen is an active teacher and researcher in thermodynamics, energy technology, sustainable energy and the environmental impact of energy and industrial systems. Dr. Rosen has worked for such organizations as Imatra Power Company in Finland, Argonne National Laboratory near Chicago, and the Institute for Hydrogen Systems near Toronto. Dr. Rosen has received numerous awards and honours, including an Award of Excellence in Research and Technology Development from the Ontario Ministry of Environment and Energy.