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# Coupling of copper–chloride hybrid thermochemical water splitting cycle with a desalination plant for hydrogen production from nuclear energy

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## ABSTRACT

Energy and environmental concerns have motivated research on clean energy resources. Nuclear energy has the potential to provide a significant share of energy supply without contributing to environmental emissions and climate change. Nuclear energy has been used mainly for electric power generation, but hydrogen production via thermochemical water decomposition provides another pathway for the utilization of nuclear thermal energy. One option for nuclear-based hydrogen production via thermochemical water decomposition uses a copper–chloride ( $\text{Cu}-\text{Cl}$ ) cycle. Another societal concern relates to supplies of fresh water. Thus, to avoid causing one problem while solving another, hydrogen could be produced from seawater rather than limited fresh water sources. In this study we analyze a coupling of the  $\text{Cu}-\text{Cl}$  cycle with a desalination plant for hydrogen production from nuclear energy and seawater. Desalination technologies are reviewed comprehensively to determine the most appropriate option for the  $\text{Cu}-\text{Cl}$  cycle and a thermodynamic analysis and several parametric studies of this coupled system are presented for various configurations.

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## 1. Introduction

Problems due to the use of fossil fuels can be resolved in part by utilizing renewable resources, such as biomass, solar, wind and geothermal energy. Such resources can be beneficial in urban centers as well as remote and isolated areas. Many developing countries that have large land areas but limited access to electric grids have found renewable energies to be advantageous.

Energy resources that are clean, economic, safe and abundant and related technologies provide the potential to mitigate global warming and to become large-scale energy supply options. Many suggest that nuclear energy may

contribute a significant share of energy supply well into the future. Nuclear energy has been almost exclusively utilized in the past for electricity generation, but the direct utilization of nuclear thermal energy provides the potential to increase efficiency and thereby facilitate energy savings. Hydrogen production has been cited as a potentially beneficial use for nuclear thermal energy for over 30 years and interest is now growing [1].

Hydrogen is considered by many to be a useful and necessary future chemical energy carrier, and interest in hydrogen energy is correspondingly growing. Most of the hydrogen produced worldwide today is from fossil fuels, primarily through steam reforming of natural gas. The nuclear

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energy-driven thermochemical cycle is one of several water splitting processes for producing hydrogen that has good potential for the future. Another is water electrolysis, which is commercial but also potentially subject to lower overall efficiencies, partly due to inefficiencies in converting heat to electricity. These inefficiencies can be avoided through thermochemical cycles that consist of a sequence of chemical reactions yielding a net reaction of decomposition of water. Estimates from Japan are that the cost of nuclear-based thermochemical H<sub>2</sub> production could be as low as 60% of that for nuclear H<sub>2</sub> production by the electrolysis of water [2]. Moreover, greenhouse gas emissions can be mitigated if the hydrogen is produced from non-fossil sources, thereby helping to avoid global warming.

Thermochemical water splitting with a copper-chloride (Cu-Cl) cycle can be linked with nuclear reactors to thermally decompose water into oxygen and hydrogen, through intermediate copper and chlorine compounds. This cycle consists of several chemical reactions that form a closed internal loop and continually recycle the copper-chloride compounds without emitting any greenhouse gases.

A parallel societal concern is that nearly one fourth of humanity is suffering today from insufficient fresh water supplies and that this problem is anticipated to get worse over the next several decades due to population growth, especially in developing countries. The world population of over 6 billion presently is predicted to reach nine billion by 2050, while regional population growth for 2000–2020 is expected to be around 50% in Africa, 25% in Asia, 14% in the USA and –2% in Europe [3]. Water scarcity is projected to increase across much of the globe with severe water shortages predicted to affect 2.7 billion people in over 80 countries in the next century. Water is available in large quantities on Earth but only a small fraction has a low enough salinity to be fit for drinking and irrigation. The U.S. Geological Survey [4] reports that 96.5% of Earth's water is located in seas and oceans and 1.7% in ice caps. Approximately 0.8% is considered to be fresh water, while the remainder consists of brackish water, slightly salty surface waters in estuaries and groundwater in salty aquifers. With roughly 1% of fresh water available for agriculture, industrial and domestic purposes, fresh water resources are vital. Water shortages will greatly affect health, through lack of potable water. Water is likely to become the most critical natural resource issue to confront our environment and economy and may become the cause of political disputes [5].

Measures to cope with water shortages, such as water conservation and reuse and water transfer or dam construction, are not adequate to address increasing demands and, in many cases, decreasing supplies. Traditional fresh water resources such as lakes, rivers and groundwater are overused or misused, often diminishing these resources or making them saline. As countries continue to develop and cities expand, few new fresh water resources are available to meet demand. As a result, salt water desalination has emerged as necessary for sustaining future generations globally and corresponding technologies are rapidly developing. Water shortages will also likely limit the availability of water for industrial processes, such as thermochemical water splitting processes. For this reason, it has been suggested that seawater be used where possible for water-intensive industries including hydrogen production.

Nuclear-based hydrogen production by the Cu-Cl hybrid thermochemical cycle using sea or brackish water is consequently considered in this study. Various configurations for coupling the Cu-Cl cycle with a desalination plant using nuclear or renewable energy are identified and detailed thermodynamic analyses and comparisons of the configurations, as well as relevant parametric studies, are performed. The objective is to help assess the viability of such coupled systems.

## 2. Desalination

Desalination of brackish or seawater is an important process for producing fresh water. Distillation has long been used for making salt water drinkable and purifying water in remote locations, often using solar energy [6]. Thermal processes for desalination have developed over the past 60 years and membrane processes over the past 40 years.

Fresh water is defined as water containing less than 1000 mg/L of salts or total dissolved solids (TDS) [7]. Above this concentration, properties such as taste, color, corrosion propensity, and odor are negatively affected. Drinking water standards for specific contaminants and TDS vary from country to country and within countries. For example, the World Health Organization [8] has a drinking water taste threshold of 250 mg/L, and the U.S. Environmental Protection Agency (EPA) [9] has secondary (unenforceable) standards of 250 mg/L chloride and 500 mg/L TDS, but each U.S. state can set a primary enforceable standard. The European Union does not have a drinking water standard for TDS, although standards for other drinking water contaminants have been established. Most desalination facilities are designed to achieve a TDS of 500 mg/L or less. Desalinated water for other purposes, such as crop irrigation, may have a higher TDS concentration; irrigation water standards often include concentration limits for TDS, chloride, sodium and boron. Depending on the type of crop, the chloride standard can range from 350 mg/L to more than 2000 mg/L.

The feed water salinity for desalination facilities ranges from approximately 1000 mg/L TDS to 60,000 mg/L TDS, although feed waters are typically labeled as one of two types: seawater or brackish water. Although most seawater sources contain 30,000–45,000 mg/L TDS, seawater reverse osmosis membranes are used to treat waters within the TDS range 10,000–60,000 mg/L. Brackish water reverse osmosis membranes are used to treat water sources (often groundwater) within a range of 1000–10,000 mg/L TDS. The feed water type can dictate several design choices for a treatment plant, including the desalination method, pretreatment steps, waste disposal method and product recovery (fraction of influent water that becomes product) [7].

Mature seawater desalination technologies can be employed today to produce large amounts of good quality water at a competitive cost. However, desalinated water currently only supplements fresh water resources. An important drawback of all such processes is their high energy consumption. The specific energy consumption to desalinate water is 5 kWh/m<sup>3</sup> or less using the best available technology [3]. Desalination otherwise causes little environmental impact. By assessing a copper-chloride thermochemical cycle

coupled with a desalination plant for hydrogen production from nuclear energy, this investigation seeks to help solve energy and fresh water shortages as well as environmental and climate change concerns, and to identify the most advantageous coupled configuration.

## 2.1. Desalination technologies

Desalination processes fall into two main categories (Fig. 1): thermal and membrane. Membrane distillation is an emerging separation process suitable for desalination of brackish or seawater. In this technique, hydrophobic membranes allow only water vapor permeation through a porous barrier and the driving force is the transmembrane vapor pressure difference created by the difference in chemical potentials of the transported components. Reverse osmosis (RO), nanofiltration (NF) and electrodialysis (ED) are the three membrane processes available for desalination. ED membranes operate under an electric current that causes ions to move through parallel membranes and are typically only used for brackish water desalination. NF membranes are a newer technology developed in the mid-1980s and have been tested for a range of salt concentrations. Nanofiltration cannot alone reduce seawater salinity to drinking water standards, but has been used successfully to treat mildly brackish feed water. Coupled with RO, NF can treat seawater. NF membranes remove divalent ions such as calcium and magnesium that contribute to water hardness, as well as dissolved organic material. RO has recently become one of the most widely used desalination technologies.

At high salinities and high recoveries (e.g., 55,000 mg/L TDS and above 35% recovery), the pressure required for membrane desalination can be greater than the maximum allowable pressure of membrane modules, and thermal desalination must be used. High feed water temperatures and foulants can also cause problems in membrane desalination that can be avoided by using thermal desalination. Industrial-scale thermal desalination technologies are generally multi-stage flash (MSF), multiple effect evaporation (MEE) (or multiple effect desalination (MED)) and mechanical vapor compression (MVC).

Characteristics of thermal and membrane desalination processes, in terms of advantages and disadvantages, are listed in Table 1.

A breakdown of 2009 global desalination production capacity by separation technology is shown in Fig. 2. Membrane and thermal (distillation) processes are seen to share equally in production capacity, with RO dominating the membrane

processes and MSF dominating distillation. However, RO membrane plants represent 80% of the number of desalination plants worldwide, while thermal processes represent 20%. Today, over 15,000 desalination plants are in operation worldwide.

The Middle East with 2.9% of the world's population has approximately 50% of the world's desalination capacity and is a leader in large-scale seawater desalination. Israel opened the world's largest seawater RO desalination plant in 2005, with a production capacity of 330,000 m<sup>3</sup>/day (100 million m<sup>3</sup>/yr). In 2005, the United Arab Emirates (UAE) opened its Fujairah desalination plant, which combines MSF and RO technology to produce 454,000 m<sup>3</sup>/day of fresh water. Saudi Arabia is currently the world leader with approximately 26% of global desalination capacity, while the United States ranks second with 17%. Other countries also utilize desalination for drinking water production. Spain has been using desalination since 1964 to provide drinking water in the Canary Islands, the Balearic Islands and along its southern and eastern coasts. Spain and Italy have the majority of the European desalination capacity, with each country accounting for 2.6% of world production capacity; 69% of desalination plants in Spain and 20% of those in Italy use RO. Japan is responsible for 3.7% of global desalination capacity and has been using seawater RO technology since 1974. China, with its population growth and industrialization but little control over or protection of water resources, is beginning to investigate desalination; the current water transfer strategy (moving Southern water resources to water-poor Northern China) is no longer sufficient.

A feasibility study is currently underway for a thermal desalination (MED) plant coupled with a nuclear power plant in the Yantai region. Countries in North Africa and the Middle East, such as Algeria, Tunisia and Jordan, have investigated using both brackish and seawater desalination. The world's largest brackish water RO desalination plant, completed in 2006 in Wadi Ma'in in Jordan, operates at 129,000 m<sup>3</sup>/day and has a maximum capacity of over 150,000 m<sup>3</sup>/day. The largest RO desalination plant in Africa started production (200,000 m<sup>3</sup>/day) in Algiers, and Algeria plans to increase from 10 to 43 desalination plants by 2019, with a production goal of 2 million m<sup>3</sup>/day. Countries in South America, such as Chile, have recently commissioned large desalination plants, while Australia has installed RO installations from Melbourne to the Gold Coast to address fresh water shortages. England plans to construct its first desalination plant for drinking water in 2009 in East London, using the Thames Estuary as the brackish water source [7].

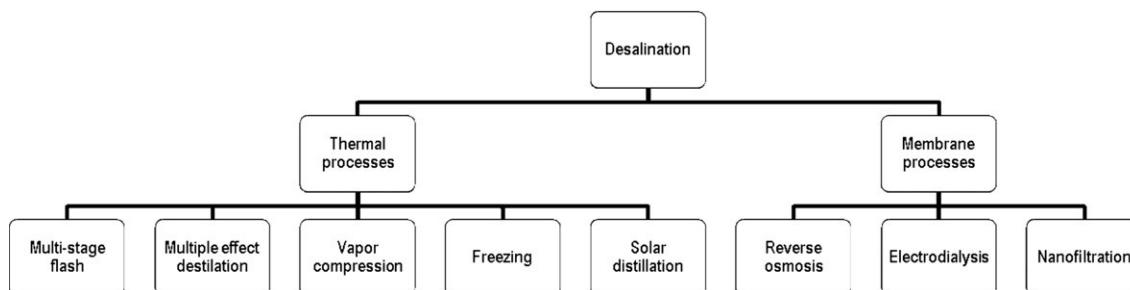


Fig. 1 – Desalination technologies.

**Table 1 – Characteristics of desalination processes.**

Process	Advantages	Disadvantages
Multi-stage flash (MSF)	Flexibility in salinity of feed water High purity production (<30 ppm) High production capacity Low skill requirement Production of both water and electricity Low energy input	Labor-intensive Low conversion ratio (30–40%) Feed water pretreatment required High operating costs High construction requirements Limited potential for improvement
Multiple effect desalination (MED)	High production capacity Low capital costs High purity (<30 ppm) Energy input independent of purity Little skilled operator requirements	Dependence on local power availability Long construction period Difficult to control water quality Low feed water conversion (30–40%) Labor-intensive Large space and material requirements
Vapor compression (VC)	High water quality (20 ppm) High operating load Short construction period Small space requirement Operation and production flexibility	High operation costs High energy consumption Lack of water quality control
Humidification-dehumidification (HD)	Low operating temperature Low energy requirement Low operating and capital cost Little skilled operator requirements Operable on renewable or waste energy	Low production capacity Limited potential for improvement Inflexibility in water quantity and quality Dependent on feed water temperature
Reverse osmosis (RO)	Suitable for sea and brackish water Flexibility in water quantity and quality Low power requirement (compared to MED and VC) Flexibility in site location Flexible start-up and shut-down Simple operation	Low quality (250–500 ppm) High-quality feed water requirement Relatively high capital and operating costs High pressure requirements Long construction time for large plants
Electrodialysis (ED)	Low operating and capital costs Flexible energy source High conversion ratio (80%) Low energy consumption Low space and material requirements	Low to medium brackish water capability (3000 ppm) Requires careful pretreatment of feed water Low production capacity Purity affected by quality of feed water

Source: Adapted from Ref. [10].

## 2.2. Economics of desalination

The economics of obtaining fresh water by desalination depend on the initial and operating costs of the system. Desalination processes require significant quantities of energy, the amount and type of which depend on the desalination method [11]. For instance, the quantity and quality of

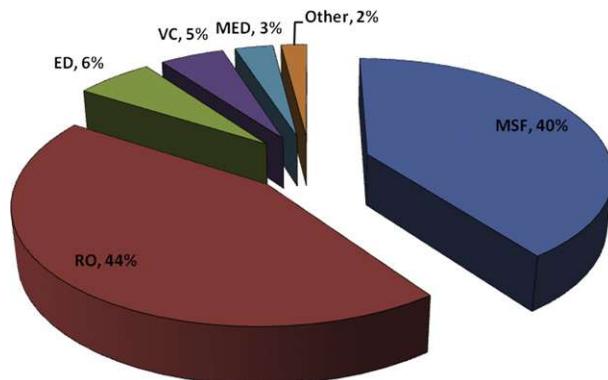
steam required to produce desired fixed amount of fresh water, depends on the seawater temperature, the maximum brine temperature and the type, design and performance of the distillation plant. The efficiency of a steam-based distillation plant is usually expressed by the gain output ratio (GOR), which is the ratio of fresh water mass produced to mass of steam used in the first effect.

Water desalination costs include the following:

- fixed charges, which are dependent on capital cost and depreciation factor (determined from plant life and financial parameters); and
- variable charges, which include the use and cost of energy, operating and maintenance costs (including labor), the use and cost of chemicals for pre- and post-treatment of water (especially in RO plants) and the rate at which membranes are replaced.

Most of these factors are site-specific and vary by country. The production costs considered here are therefore approximate and in US dollars based on 2008 currency.

Economic characteristics of various desalination technologies are shown in Table 2, where it is observed that the water



**Fig. 2 – Breakdown of global desalination production capacity by process (adopted from [6]).**

**Table 2 – Thermal and economic characteristics of selected desalination technologies.**

Characteristic	Technology			
	MSF	MED	RO	VC
Typical average capacity (m <sup>3</sup> /d)	25,000	10,000	6000	3000
Maximum average capacity (m <sup>3</sup> /d)	50,000	20,000	10,000	5000
Thermal energy consumption (kWh/m <sup>3</sup> )	80	60	–	–
Electric energy consumption (kWh/m <sup>3</sup> )	4	2	5	7
Equivalent electric energy consumption (kWh/m <sup>3</sup> )	15	7	5	7
Cost of plant (\$/(m <sup>3</sup> /day))	1300	1200	1000	1000
Production cost (\$/m <sup>3</sup> )	1.1	0.8	0.7	0.7

Source: Modified from Ref. [3].

desalination method affects significantly the desalination cost. Thermal methods are used mainly in medium and large-capacity systems, while membrane methods (mainly RO) are used by medium and small systems. Recently RO methods, which are dominant in the desalination of brackish water, have become preferred in larger units. RO has low costs, mainly due to lower energy use and technological advances in membranes. Under special conditions hybrid systems can be advantageous.

Costs for membrane water desalination methods of various capacities are shown in Table 3, where the type of feed water (seawater or brackish water) as well as the plant size and the energy source are observed to impact the unit cost of desalinated water. For example, the investment capital cost per unit of production capacity of seawater RO plants (600–800 \$/m<sup>3</sup>/day) is higher than that of brackish water RO plants (240–400 \$/m<sup>3</sup>/day). For both seawater and brackish water, small RO plants (<5000 m<sup>3</sup>/day) have higher unit water costs than medium (5000–60,000 m<sup>3</sup>/day) or large (>60,000 m<sup>3</sup>/day) plants.

For future large-scale seawater desalination, the above considerations suggest that MSF plants will continue to be preferred to treat water with high salinity. To enhance efficiency, such plants are being coupled with thermal power stations so as to generate water and electricity simultaneously. When operating conditions are not be excessively severe, RO plants are likely to occupy the market of small to medium users and for large users with single-purpose

systems (water production only). But the amount of energy needed to desalinate seawater remains high, despite progress in reducing it, limiting the diffusion of the technology. It is noted that:

- to reduce production costs, large-scale MSF and MED plants need to be coupled with thermal power stations, even though this increases investment costs, logistic problems (e.g., siting power and desalination plants in the same neighborhoods) and management complexity (e.g., electric and water load are generally out of phase); and
- large-scale RO and VC plants need to be located at a site with a sufficient supply of inexpensive electric power.

### 2.3. Desalination concentrate disposal

The concentrated residue of desalination requires disposal, and methods differ for seawater and brackish water. For seawater plants, the concentrate is usually discharged back into the same body of water. The feed water intake and the concentrate discharge are located apart, and the concentrate is diluted into the large seawater body. The primary concerns are only the pumping system and length of piping needed to reach the chosen underwater discharge point. For brackish water plants, surface water disposal is preferred if feasible due to the higher costs of other options. However, this method is often limited to coastal plants, as the extensive piping to transport concentrate to the sea is financially prohibitive. Some inland brackish water plants discharge concentrate to local lakes and rivers. Unlike seawater discharge, brackish water concentrate, if discharged to surface water, can change the salinity of the receiving water, which in turn can change the concentration of dissolved oxygen in the water and negatively affect aquatic life. The standard limit for surface water discharge is a salinity difference of less than 10% [7].

### 2.4. Desalination using renewable energy

A primary challenge with desalination remains large energy use and related environmental impacts. These and other socially negative impacts can in part be offset by using renewable energy resources for desalination. For example, nearly 3 kg of CO<sub>2</sub> generation for each m<sup>3</sup> of water produced (at an energy consumption rate of 5 kWh/m<sup>3</sup> with the best technology currently used on large-scale) can be avoided if conventional fuels are replaced with renewable energy [3].

Sometimes lack of on-site power is a major problem, e.g., one third of the world population, mainly in developing countries does not have access to an electric grid. Population growth and expanding industrialization in developing countries may intensify the problem, highlighting the need for alternative energy sources to supplement or substitute for conventional fuels, especially for remote areas with no electricity grid and which are expensive to connect [13]. Hence, efforts are being expended to find ways to use renewable energy resources for water desalination, even though these efforts are presently limited mainly due to costs (which are almost twice those of conventional systems). For instance solar energy is costly today compared to conventional energy

**Table 3 – Costs of membrane (RO) methods for water desalination.**

Type of feed water	Capacity (m <sup>3</sup> /day)	Cost (\$/m <sup>3</sup> )
Brackish	<20	5.62–12.90
	20–1200	0.78–1.33
	40,000–46,000	0.26–0.54
Seawater	<100	1.50–18.75
	250–1000	1.25–3.92
	1000–4800	0.70–1.72
	15,000–60,000	0.48–1.62
	100,000–320,000	0.45–0.66

Source: Adapted from Ref. [12].

resources, but the cost is expected to decrease significantly over the next few years while the cost of fossil fuels is anticipated to rise. Price increases for fossil fuels may be due to fiscal penalties associated with environmental impact. Geothermal and wind energy both are competitive today in terms of costs.

Costs of fresh water from desalination using conventional and various renewable energy sources have been determined (see Table 4). The main renewable energy sources in that table are solar (photovoltaic and thermal), wind and geothermal. The thermal energy sources are most often used with distillation desalination, while wind and photovoltaic solar energy are commonly paired with RO desalination. The energy and process are often chosen to match advantageously the type of energy with the type of process (thermal versus mechanical). RO systems can use seawater or brackish water as the feed source and are typically small to medium in size. Overall, the renewable energy source most often used has been solar energy (70% of market), and RO has the majority (62%) of the renewable energy desalination market [7].

The potential of using solar energy is further explored since its features make it beneficial for desalination. Conventional desalination methods such as MSF, MED, VC and RO are suitable for large and medium capacity plants for fresh water production, but conventional thermal desalination methods are uneconomic at small capacities. Many remote arid areas need low-capacity desalination systems. Air humidification-dehumidification (HD) desalination is a suitable choice for production of fresh water when the demand is decentralized. Because of the low-temperature heat requirement of this method it is compatible with solar energy, which can be used to provide the total required thermal energy [14]. To exploit solar energy substantially, means are required for it to power medium- to large-capacity desalination plants. All desalination technologies can be coupled with solar energy, but solar thermal is most appropriate for thermal processes (MSF or MED) whereas photovoltaics can supply electric energy for processes such as VC or RO (see Table 5).

Water desalination technologies coupled with solar energy are of particular interest to countries located within the Southern Mediterranean belt, which are generally characterized by vast arid and isolated areas having little access to electric power from the national grid. Economic factors are one of the main barriers to solar device utilization. Spain, Italy, and Saudi Arabia, have successfully implemented solar photovoltaic electricity and seawater RO. A wide range of

**Table 5 – Options for coupling solar energy and desalination.**

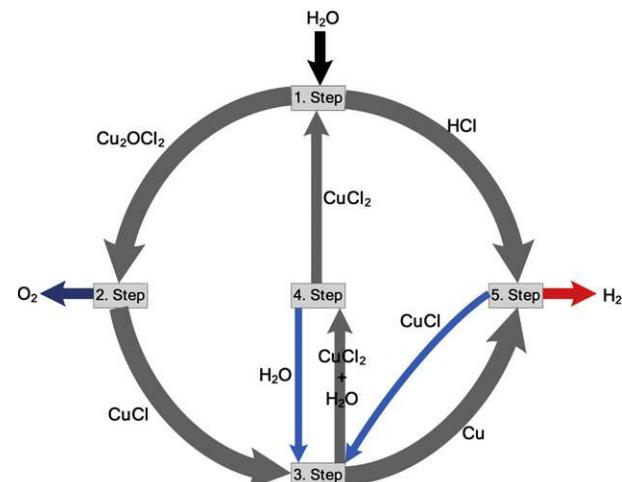
Desalination process	Possible type of solar energy supply		
	Photovoltaic	Solar thermal	Solar thermal (electric)
MSF		✓	✓
MED		✓	✓
VC	✓		✓
RO	✓		✓

permeate production capacities for solar photovoltaic-seawater RO plants, from 0.5 to 120 m<sup>3</sup>/day has been reported. Spain has also paired renewable energy from a wind farm with a seawater RO plant in Gran Canaria, Canary Islands. Four wind generators provide the main energy source for a 5000 m<sup>3</sup>/day RO permeate production facility, along with pressure exchangers and motors with variable frequency that act as an energy recovery system. The power produced by the wind generators varies throughout the year, with excess power sometimes sold to the conventional power network and the RO plant using supplementary power from the grid at other times. In 2004, the plant obtained 57% of its power from the wind generators, and sold 95% of the power produced by the wind generators to the power network [7].

### 3. The copper-chloride cycle

The Cu-Cl cycle consist of a set of reactions to achieve the overall splitting of water into its constituents, hydrogen and oxygen. The overall net reaction is H<sub>2</sub>O (g) → H<sub>2</sub> (g) + 1/2O<sub>2</sub> (g). The Cu-Cl cycle uses a series of intermediate copper and chloride compounds. These chemical reactions form a closed internal loop that recycles all chemicals on a continuous basis, without emitting any greenhouse gases.

A conceptual layout of the Cu-Cl cycle is illustrated in Fig. 3. The cycle includes three thermochemical reactions and one electrochemical reaction, and involves five steps:



**Fig. 3 – Cu-Cl thermochemical cycle for hydrogen production.**

**Table 4 – Cost of fresh water from desalination using various energy types.**

Feedstock	Type of energy used	Cost (\$/m <sup>3</sup> )
Brackish water	Conventional	0.26–1.33
	Photovoltaics	5.62–12.90
	Geothermal	2.50
Seawater	Conventional	0.43–3.37
	Wind	1.25–6.25
	Photovoltaics	3.92–11.25
	Solar collectors	4.37–10.00

Source: Adapted from Ref. [12].

**Table 6 – Main steps in the Cu–Cl cycle with their corresponding reactions.**

Step	Reaction	Temperature range (°C)	Pressure (kPa)	Feed/Output <sup>a</sup>
1	$2\text{CuCl}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CuO} \times \text{CuCl}_2(\text{s}) + 2\text{HCl}(\text{g})$	400	101	Feed: $\text{CuCl}_2(\text{s}) + \text{H}_2\text{O} + Q$ Output: $\text{CuO} \times \text{CuCl}_2(\text{s}) + \text{HCl}(\text{g})$
2	$\text{CuO} \times \text{CuCl}_2(\text{s}) \rightarrow 2\text{CuCl}(\text{l}) + 1/2\text{O}_2(\text{g})$	500	101	Feed: $\text{CuO} \times \text{CuCl}_2(\text{s}) + Q$ Output: Molten CuCl salt + $\text{O}_2$
3	$4\text{CuCl}(\text{s}) + \text{H}_2\text{O} \rightarrow 2\text{CuCl}_2(\text{aq}) + 2\text{Cu}(\text{s})$	25–80	101	Feed: $\text{CuCl}_2(\text{aq}) + \text{H}_2\text{O} + E_e$ Output: C and slurry
4	$\text{CuCl}_2(\text{aq}) \rightarrow \text{CuCl}_2(\text{s})$	>100	101	Feed: $\text{CuCl}_2(\text{aq}) + Q$ Output: $\text{CuCl}_2 + \text{H}_2\text{O}$ vapor
5	$2\text{Cu}(\text{s}) + 2\text{HCl}(\text{g}) \rightarrow 2\text{CuCl}(\text{l}) + \text{H}_2(\text{g})$	430–475	101	Feed: $\text{Cu} + \text{HCl}$ Output: $\text{H}_2 + \text{CuCl}(\text{l})$ salt + $Q$

<sup>a</sup> Q denotes thermal energy and  $E_e$  electrical energy.

1. HCl(g) production, using such equipment as a fluidized bed,
2. oxygen production,
3. copper (Cu) production,
4. drying, and
5. hydrogen production.

A chemical reaction takes place in each step, except drying (see Table 6).

The Cu–Cl cycle has been shown to be a potentially attractive option for generating hydrogen from nuclear energy [15–19]. Compared with other hydrogen production options, the thermochemical Cu–Cl cycle is expected to have a higher efficiency [20–23], to produce hydrogen at a lower cost, and to have a smaller impact on the environment by reducing airborne emissions, solid wastes and energy requirements.

#### 4. Coupling of the Cu–Cl cycle with a desalination plant

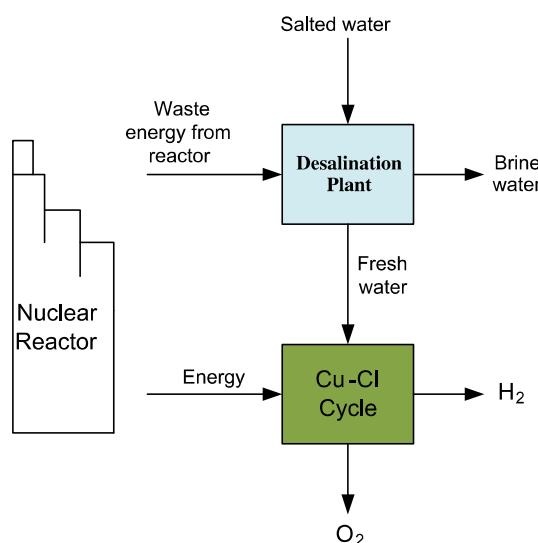
The main objective of a plant designer is to determine the optimal plant configuration and operative conditions to satisfy requirements according to specified constraints (environmental and otherwise). The most efficient configuration is not always the optimal one in terms of economics, since capital, labor and energy costs vary differently with increasing efficiency [24]. Here we consider five configurations, in hopes of determining or helping to determine an optimum option to couple the Cu–Cl cycle with a desalination plant.

##### 4.1. Case I: Using waste energy from nuclear reactor to operate desalination plant

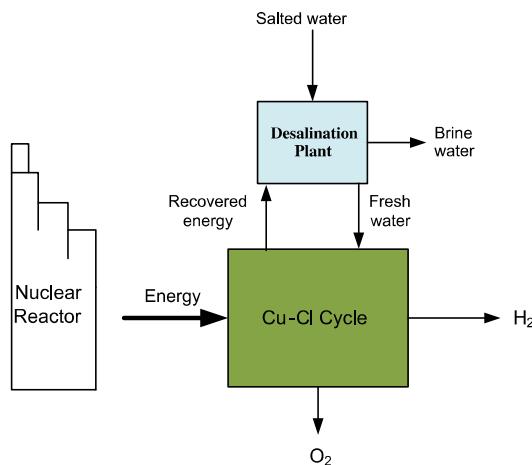
Case I is a configuration that couples the Cu–Cl cycle and a desalination plant using nuclear energy, as shown in Fig. 4. In this case, salty water is input to the desalination plant and salt is removed from the water using waste energy from the nuclear reactor. In this case a low-temperature desalination process is used since waste energy from a nuclear reactor is often near 70–80 °C. Fresh water supplied by the desalination plant is decomposed into hydrogen and oxygen by the Cu–Cl cycle driven by nuclear energy.

##### 4.2. Case II: Using recovered energy from Cu–Cl cycle to operate desalination plant

In Case II, energy recovered from the Cu–Cl cycle is transferred to the desalination plant to remove salt from fresh water (see Fig. 5). As illustrated in the figure, the desalination plant operates as a sub-system of the Cu–Cl cycle. Considering the overall system, only process/waste energy from the nuclear reactor and salty water enter the system. Hydrogen is produced, and oxygen and salt are byproducts. In Case II, a desalination method with low process energy needs is used since the recovered energy from the Cu–Cl cycle may not otherwise be sufficient for distillation. A drawback to this case is the efficiency decrease (~3–5%) incurred by the Cu–Cl cycle since the recovered energy is used for the desalination process rather than within the cycle itself. But the Cu–Cl cycle is a subsection of the plant and, when the desalination plant and the Cu–Cl cycle are considered as a combined system, the efficiency is not affected significantly since the recovered energy is used within the overall system. The efficiency of the combined system (desalination plant and copper chlorine cycle) is about 0.4.



**Fig. 4 – Case I: Using waste energy from nuclear reactor for desalination process.**



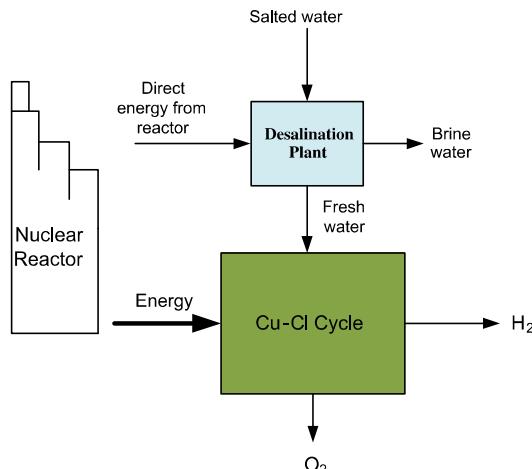
**Fig. 5 – Case II: Using recovered energy from Cu-Cl cycle for desalination process.**

#### 4.3. Case III: Using process energy from nuclear reactor to operate desalination plant

Process nuclear energy is used directly in the desalination plant in Case III (see Fig. 6). As fresh water is supplied to the Cu-Cl cycle, process (and some waste) energy from the nuclear reactor is used to produce hydrogen. Also, energy recovered in the Cu-Cl cycle is used within that cycle. In Case III, a desalination method with high capacity and low production cost is used since high-grade energy is available.

#### 4.4. Case IV: Using solar energy to operate desalination plant

The main rationale for using nuclear energy and the Cu-Cl cycle for hydrogen production is to address environmental and climate change problems. The configuration in Case IV supports this objective further by not only producing hydrogen in an environmentally benign way from seawater,



**Fig. 6 – Case III: Using direct (process) energy from nuclear reactor for desalination process.**

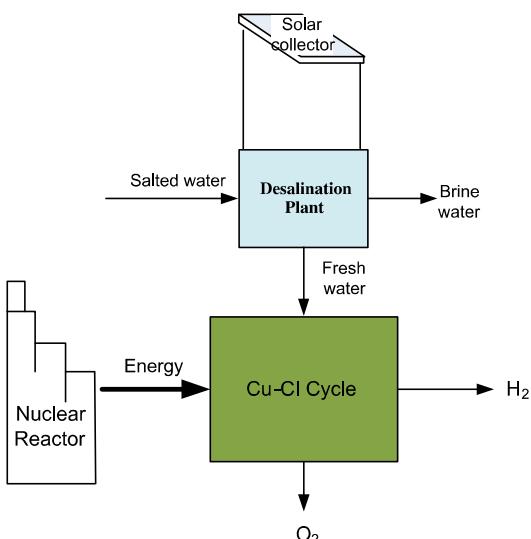
but also by using renewable energy in the form of solar energy to drive desalination (see Fig. 7). Although solar thermal energy is used by the desalination process, process and waste energy from a nuclear plant is used in the Cu-Cl cycle. A drawback of this configuration is its dependence on the availability of solar energy, which is intermittent. Since the capacity of the desalination plant and hence the Cu-Cl cycle determines the required capacity of the solar collectors, the site for the Cu-Cl cycle and desalination plant are chosen carefully. However, since constraints likely exist regarding siting of the nuclear reactor, this configuration is likely advantageous if the nuclear reactor is located in an area with high solar insolation. Otherwise, a desalination process with low-capacity and low inlet energy requirements is used.

#### 4.5. Case V: Using off-peak electricity from nuclear reactor to operate desalination plant

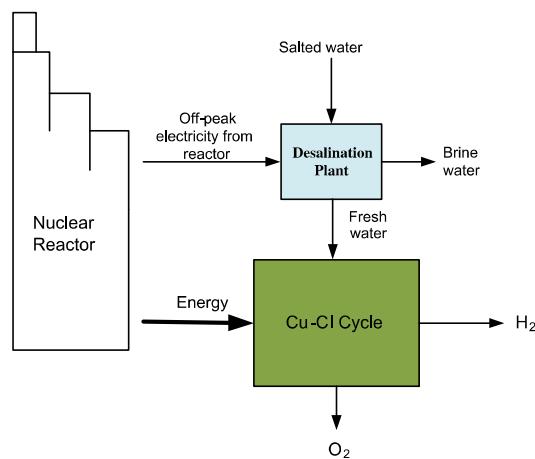
When off-peak electricity is available, it is usually less expensive than peak electricity and thus is used by many industrial processes. Off-peak electricity can also be used to desalinate seawater and to produce hydrogen, and could be beneficial for the same reason. Case V includes a Cu-Cl cycle coupled with a desalination plant driven by off-electricity (see Fig. 8). In this case, efficient membrane processes such as RO are used since electrical energy is supplied.

### 5. Analysis of heat transfer and system efficiency

An example of a coupling of a desalination plant with the Cu-Cl cycle is shown in Fig. 9. In the figure, a humidification-dehumidification (HD) desalination unit has been integrated with the cycle and the recovered energy from the Cu-Cl cycle is reused within the cycle. The HD desalination plant is driven by nuclear energy or other sources.



**Fig. 7 – Case IV: Using solar energy for desalination process.**



**Fig. 8 – Case V: Using off-peak electricity from nuclear reactor for desalination process.**

It can be observed in Fig. 9 that only water and nuclear-derived heat enter the Cu-Cl cycle and only  $H_2$  and  $O_2$  are produced, while greenhouse gas emissions are avoided. In the first step of the cycle (S1), steam at  $400^\circ C$  and solid copper chloride ( $CuCl_2$ ) at  $400^\circ C$  from the dryer enter the fluidized bed, where an endothermic chemical reaction occurs that yields hydrochloric gas ( $HCl$ ) and  $Cu_2OCl_2$ . The hydrochloric gas is compressed and the  $Cu_2OCl_2$  is transferred to another process step after its temperature is increased to the oxygen production reaction temperature of  $500^\circ C$ . In the second (oxygen production) step (S2) an endothermic chemical reaction takes place in which  $Cu_2OCl_2$  is heated and  $O_2$  and copper monochloride ( $CuCl$ ) are produced. Liquid copper monochloride is solidified by cooling it to  $20^\circ C$ , after which it enters the third (copper production) step (S3) together with the solid copper monochloride from the fifth step (S5). In the third step, solid copper monochloride and water interact endothermically at  $20^\circ C$ . The water acts as a catalyst in this reaction, and does not react with the other elements or compounds. The third reaction involves an electrolysis step, which makes it the most expensive step depending on the price of electricity. In this reaction, solid copper and copper chloride–water solution are produced. A mixture of copper chloride and water is

transferred to the dryer (S4), and solid copper enters the fifth step after its temperature is increased to that step's operating temperature. In the fifth (hydrogen production) step, hydrochloric gas and copper enter and are converted to hydrogen gas ( $H_2$ ) and solid copper monochloride ( $Cu-Cl$ ) in a steady-state reaction at  $450^\circ C$ .

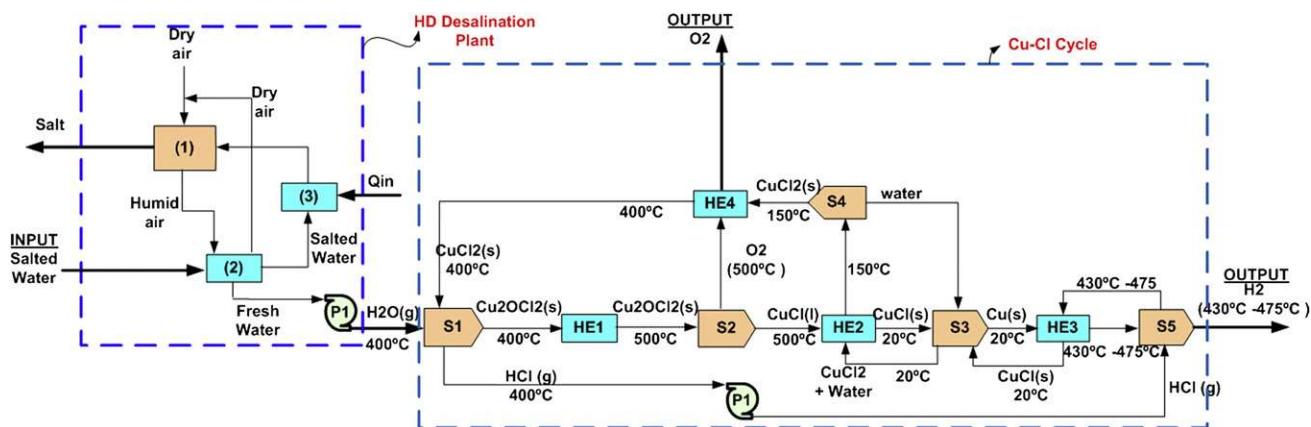
The HD desalination process utilizes the fact that air can be mixed with water vapor and the amount of water vapor that can be mixed with air increases with the temperature. For instance, 1 kg of dry air can carry 0.5 kg of water vapor and about 670 kcal when its temperature increases from  $30^\circ C$  to  $80^\circ C$  [25]. When an air flow is in contact with salt water, the air extracts a certain quantity of water vapor at the expense of sensible heat of salt water, inducing cooling. Distilled water is recovered by bringing humid air near or into contact with a cooling surface, causing condensation of part of the water vapor mixed with air. Generally the condensation occurs in another heat exchanger in which salty water is preheated through latent heat recovery. An external heat contribution is thus necessary to compensate for the sensible heat loss. The heat exchangers are often constructed of tubes placed on perforated plates.

The operating principle of the HD process is illustrated in Fig. 9. Air is preheating at the same location where salty water preheating occurs. The process consists of a heat source, air humidifiers (labeled 1) and dehumidifiers (2). The brine passes through a heater (3) where its temperature rises, and then through packed towers where water vapor and heat are released to the counter-current air stream, reducing the brine temperature. One packed tower, or several in series, may be used as the humidifier depending on desired results and design conditions. Some air is bled into the dehumidifier at various points for efficient operation.

At a temperature between  $70$  and  $95^\circ C$ , heat has to be supplied to the brackish water in circulation by an external energy supply. This need can be met using renewable energy or low-temperature waste energy from various industries.

Salinity is represented as mass fraction  $m_f_s$  and often expressed in units of ppm [26]. The mole fraction of salt  $x_s$  can be related to the mass fraction as follows:

$$m_f_s = \frac{m_s}{m_m} = \frac{N_s M_s}{N_m M_m} = x_s \frac{M_s}{M_m} \text{ and } Mf_w = \frac{M_w}{M_m} \quad (1)$$



**Fig. 9 – Coupling of the Cu-Cl cycle with an HD desalination plant.**

where  $m$  denotes mass,  $M$  molar mass,  $N$  number of moles and  $x$  mole fraction, while the subscripts  $s$ ,  $w$  and  $m$  represent salt, water and saline water, respectively. The molar mass of the saline water can be written as

$$M_m = \frac{m_m}{N_m} = \frac{N_s M_s + N_w M_w}{N_m} = x_s M_s + x_w M_w \quad (2)$$

The molar masses of salt ( $\text{NaCl}$ ) and water ( $\text{H}_2\text{O}$ ) are 58.5 kg/kmol and 18.0 kg/kmol, respectively. Combining Eqs. (1) and (2) and noting that  $x_s + x_w = 1$  yields the following relations between mass and mole fractions:

$$x_s = \frac{M_w}{M_s \left( \frac{1}{mf_s} - 1 \right) + M_w} \quad \text{and} \quad x_w = \frac{M_s}{M_w \left( \frac{1}{mf_w} - 1 \right) + M_s} \quad (3)$$

The flow rates are generally given as volume flow rates in  $\text{m}^3/\text{s}$  or gallons/min, and can be converted to mass flow rates by multiplying them by density. The total mass flow rate can thus be determined as:

$$\dot{m}_{\text{total}} = (1 + mf_s) \rho_w \dot{V} \quad (4)$$

where  $\rho_w$  denotes the density of water (1 kg/L),  $mf_s$  the mass fraction of salt (concentration in  $\text{ppm} \times 10^{-6}$ ) and  $\dot{V}$  the volume flow rate. When the salinities and flow rates of feed water and permeate are known, the salinity of brine is determined from a mass balance for salt as follows:

$$\dot{m}_{s,\text{feedwater}} = \dot{m}_{s,\text{permeate}} + \dot{m}_{s,\text{brine}} \quad (5)$$

Since desalination plants generally involve two-stage desalination in which the brine output from the first stage is further separated into permeate and more concentrated brine in the second stage, we can write:

$$mf_s = \frac{\dot{m}_{s,\text{brine}}}{\dot{m}_{\text{total, brine}}} \quad (6)$$

We now consider mass balances for the Cu–Cl cycle, accounting for chemical reactions. A general steady-state mass rate balance can be expressed as follows:

$$\dot{m}_{\text{in}} = \dot{m}_{\text{out}} \quad \text{or} \quad \dot{m}_R = \dot{m}_P \quad (7)$$

Thus, the mass balance of the reaction in any step in the cycle can be written as:

$$\sum_{\text{reactants}} n_i \bar{m}_i = \sum_{\text{products}} n_k \bar{m}_k \quad (8)$$

where  $\bar{m}$  and  $n$  are the molar mass and the mole number of the compound per cycle, respectively. Also, subscripts  $i$  and  $k$  represent reactants (or inputs) and products (or outputs), respectively. To relate capacities of the Cu–Cl cycle and desalination plant, we note that 1 kmol of fresh water is needed to produce 1 kmol of hydrogen, according to the water splitting reaction:



Saline water can be considered as an “ideal solution” with little error since the effect of dissimilar molecules (molecules of salt and water) on each other is negligible. Extensive properties of a mixture can be determined as the sum of the extensive properties of its components. The enthalpy of a salt–water mixture, for example, can be determined as

$$H = \sum m_i h_i = m_s h_s + m_w h_w \quad (10)$$

while the specific enthalpy (per unit mass) can be found by dividing the enthalpy by the total mass of the mixture:

$$h = \sum m f_i h_i = m f_s h_s + m f_w h_w \quad (11)$$

A typical value for the specific heat of salt is  $c_{ps} = 0.8368 \text{ kJ/kg K}$ , and is used here. Also for consistency with prior work, we take the enthalpy of salt at  $T_0 = 15^\circ\text{C}$  to be  $h_{s0} = 12.552 \text{ kJ/kg}$  [26]. Noting that enthalpy is independent of pressure for incompressible substances, the enthalpy of salt at temperature  $T$  can be expressed as

$$h_s = h_{s0} + c_{ps}(T - T_0) \quad (12)$$

The heat transfer of any component in the system is determined using the energy balance  $\dot{E}_{\text{in}} - \dot{E}_{\text{out}} = \Delta \dot{E}_{\text{system}}$ . For a chemical process with no work interaction,  $W=0$  and for a steady-state reaction process,  $\Delta \dot{E}_{\text{system}} = 0$ , so the energy balance simplifies to:

$$Q = H_p - H_R = \sum n_p (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p - \sum n_R (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_R \quad (13)$$

The overall energy efficiency of the coupled system,  $\eta_{\text{overall}}$ , represents the fraction of energy supplied to produce hydrogen from salted water that is recovered in the energy content of  $\text{H}_2$  based on its lower heating value. The total energy required to produce hydrogen from salty water can be written as

$$\bar{Q}_{\text{in,Total}} = \bar{Q}_{\text{in,Cu-Cl cycle}} + \bar{Q}_{\text{in,desalination plant}} \quad (14)$$

The overall efficiency can be expressed as

$$\eta_{\text{overall}} = \frac{\text{LHV}_{\text{H}_2}}{\bar{Q}_{\text{in, Total}}} \quad (15)$$

where  $\text{LHV}_{\text{H}_2}$  is the lower heating value per kilomole of hydrogen and  $\bar{Q}_{\text{in, Total}}$  is the total energy demand by the process to produce a unit amount of hydrogen. This total energy demand of the coupled system is the summation of the energies needed by the Cu–Cl cycle ( $\bar{Q}_{\text{in,Cu-Cl cycle}}$ ) and the desalination plant ( $\bar{Q}_{\text{in,desalination plant}}$ ). Note that the energy recovered from the Cu–Cl cycle is assessed assuming this energy can be used for the desalination process or within the cycle. A typical lower heating value for hydrogen is 242,400 kJ/kmol  $\text{H}_2$ .

Note that in the cost analysis for producing hydrogen from sea or brackish water, the cost of desalination given in Section 2 is used. Also, energy, exergy [23–31] and cost [32–34] analyses by authors of the Cu–Cl cycle have been reported elsewhere.

## 6. Results and discussion

**Table 7** lists the cases considered here, which are explained in Section 4. In Case I waste energy from the nuclear reactor is used for desalination. As previously mentioned, the temperature of waste heat from the nuclear reactor is between 70 °C and 80 °C. Thus, the humidification-dehumidification (HD) process, which operates at 70–90 °C, is the suitable for this case.

**Table 7 – Configured cases for hydrogen production from salty water.**

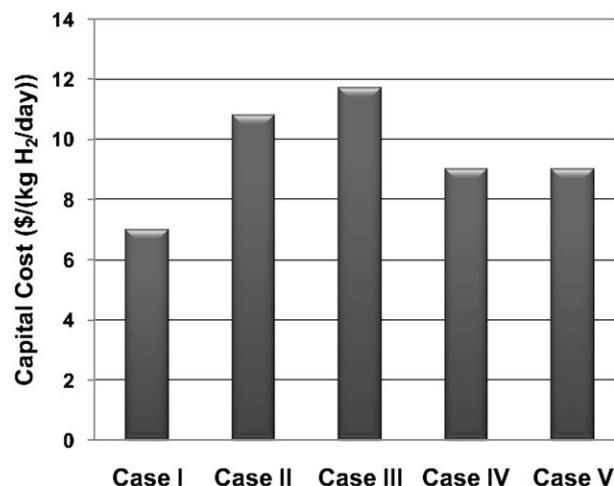
Case	Desalination method selected
I	HD
II	MED
III	MSF
IV	VC
V	RO

Case II assumes that the recovered energy from the Cu–Cl cycle can be used for distillation of water. As explained earlier, this recovered energy is not large in quantity and some may be used in the Cu–Cl cycle. Thus, a desalination process that operates with little energy and has a small capacity appears most suitable for this case. As can be seen in Fig. 16, MED (Case II in the figure) and VC (Case IV in the figure) are the two options that operate with the least energy for small capacities. However, VC is an electrical process and not applicable to Case II. Thus, MED is chosen for this case.

Direct energy from the nuclear reactor, which is large in quantity and of high quality, is used for desalination in Case III. The commonly used and mature multi-stage flash (MSF) desalination, which is applicable to large-capacity production, is chosen for this case. MSF also has other advantages (see Table 1).

Vapor compression (VC) desalination technology is chosen for Case IV since it operates with solar energy. For areas with short summer seasons with relatively low temperatures, like Canada, photovoltaic solar collectors operate more efficiently. As seen in Table 5, only two options operate with photovoltaic solar energy, VC and RO. In Table 1, RO is shown to have a long construction time as well as high operating and capital costs for small capacities. Thus VC is considered the most suitable option for this case.

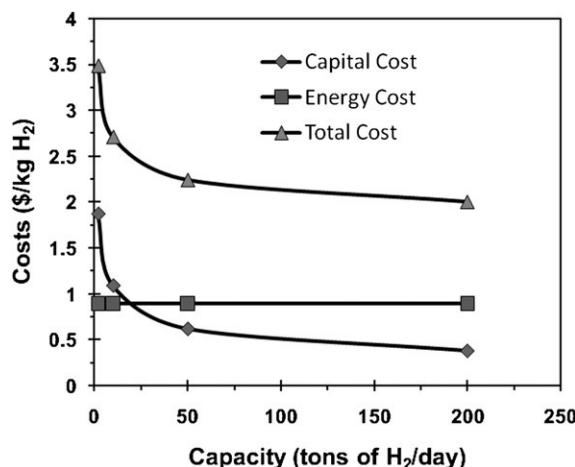
In Case V, off-peak electricity is used for distillation. When large quantities of inexpensive electricity are available, reverse osmosis (RO) appears to be the advantageous option since it has a low production cost along with the



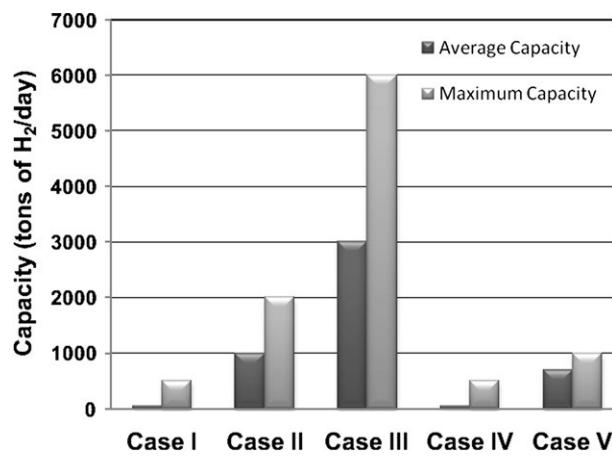
**Fig. 11 – Capital cost of desalination plant.**

capability of large-scale production. Thus, RO is chosen for Case V.

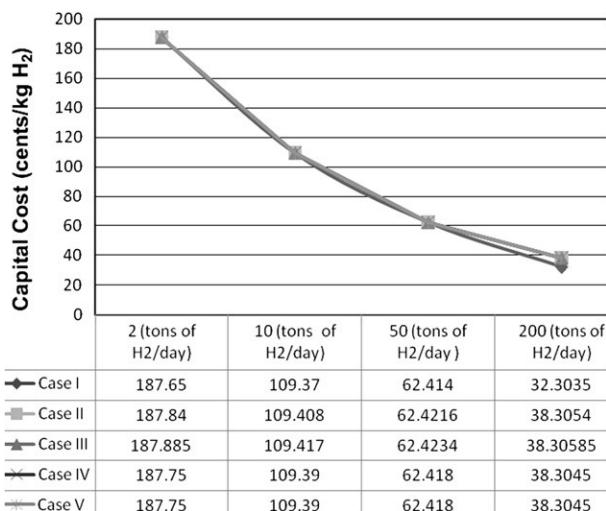
The variation of costs with hydrogen production capacity of a Cu–Cl thermochemical plant is shown in Fig. 10. These costs are based on producing hydrogen from fresh water and do not include costs associated with desalination. As can be observed, the capital cost of the Cu–Cl cycle varies from 1.8 to 0.3 \$/kg H<sub>2</sub> based on the capacity of the cycle. The capital cost of the cycle per unit hydrogen output is less for a larger capacity plant while the production cost (energy cost) remains constant at around 0.9 \$/kg H<sub>2</sub>, mainly because the reaction energy (per unit hydrogen produced) of any chemical or physical reaction occurring in the Cu–Cl cycle does not change based on plant capacity. The total cost of hydrogen production is the sum of the capital cost, energy cost and also some additional costs such as operating, storage and distributions costs. In Fig. 10, two main cost items (capital and energy costs) are given along with the total cost to build a pilot plant of the Cu–Cl cycle, presumably at the commercialization stage of the cycle. The total cost varies from 3.5 to 2 \$/kg H<sub>2</sub> in an inversely proportional relationship with plant capacity.



**Fig. 10 – Variation of costs with hydrogen production capacity of a Cu–Cl thermochemical water decomposition plant (using fresh water).**



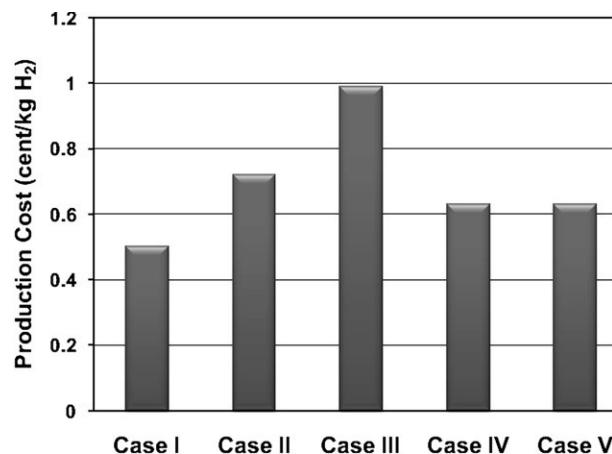
**Fig. 12 – Capacities of desalination plant.**



**Fig. 13 – Capital cost of overall system (Cu-Cl cycle and desalination plant).**

The capital cost of the desalination plant is shown in Fig. 11 for each case in Table 7. The least expensive desalination method is humidification-dehumidification (HD) at 7 \$/(kg H<sub>2</sub>/day), which is considered in Case 1, and the technology with the highest initial cost (11.7 \$/(kg H<sub>2</sub>/day)) is multi-stage flash desalination, which is used in Case III. The capital costs of vapor compression (VC) in Case IV and reverse osmosis (RO) in Case V appear to be the same at 9 \$/(kg H<sub>2</sub>/day) while the capital cost of multiple effect desalination (Case II) is 10.8 \$/(kg H<sub>2</sub>/day). Note that these capital costs vary based on capacity and that the capacity of the desalination method for each case differs, as shown in Fig. 12. It can be seen there that MSF has the highest capacity while the DS and VC have lowest. Capacities are expressed in tons of hydrogen per day and both average and maximum capacities for each case are given.

The overall unit capital cost of the coupled system is given in Fig. 13 in terms of unit H<sub>2</sub> product. This unit cost includes capital costs of both the Cu-Cl cycle and the desalination plant and, as shown in the figure, varies with production capacity but not with choice of desalination method. The unit capital cost of the overall system is similar for every case since the

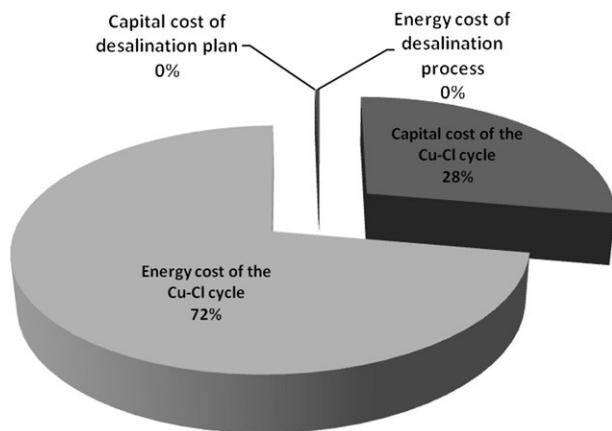


**Fig. 15 – Production cost of desalination process.**

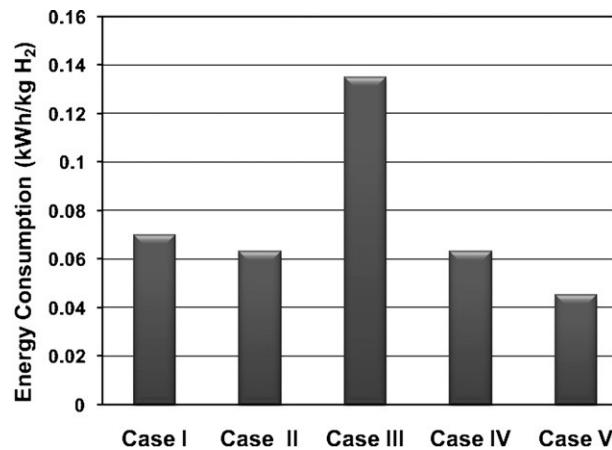
cost contribution of the desalination plant is small compared to that of the Cu-Cl cycle (see Fig. 14). The overall unit capital cost varies between 187 and 38 cents/kg H<sub>2</sub> depending on the capacity.

The unit production cost of the desalination process for each case is given in Fig. 15. This cost includes the cost of energy and processing. Case I has the lowest unit production cost (0.50 cents/kg H<sub>2</sub>) while Case III has the highest (0.99 cents/kg H<sub>2</sub>). Cases IV and V both have a unit production cost of 0.63 cent/kg H<sub>2</sub>, while that for Case II is 0.72 cent/kg H<sub>2</sub>. The unit energy consumed for each case is illustrated in Fig. 16 in terms of unit H<sub>2</sub> product. Case III consumes the highest amount energy (0.135 kWh/kg H<sub>2</sub>) for desalination and Case V the lowest (0.045 kWh/kg H<sub>2</sub>). Cases II and IV both have a unit energy consumption of 0.063 kWh/kg H<sub>2</sub> and that for Case I is 0.070 kWh/kg H<sub>2</sub>.

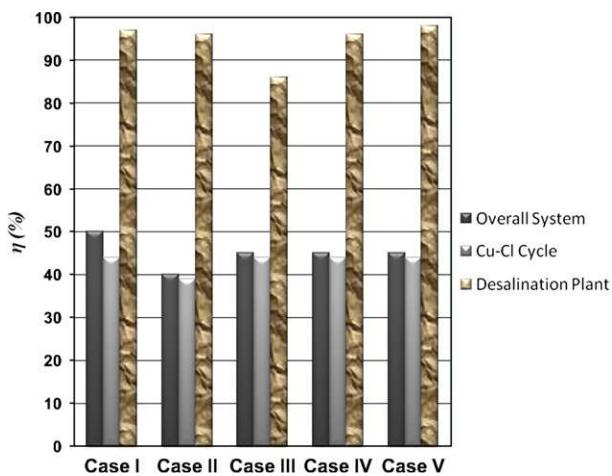
The energy efficiencies of the Cu-Cl cycle, desalination plant, and the overall system, including the Cu-Cl cycle and the desalination plant, are shown in Fig. 17. The efficiency of the desalination plant for each case is evaluated based on the energy consumptions given in Fig. 16. As observed earlier, the effect of the Cu-Cl cycle on the overall system is dominant as the desalination plant uses much less energy than the Cu-Cl cycle. Thus, the efficiency of the Cu-Cl cycle and the overall



**Fig. 14 – Breakdown of costs associated with H<sub>2</sub> production using salted water based on 50 tons/day capacity.**



**Fig. 16 – Energy use of desalination process.**



**Fig. 17 – Efficiency of the Cu-Cl cycle, desalination plant and overall (Cu-Cl cycle and desalination plant) system.**

system are very similar for each case. For the overall system, Case I exhibits a higher efficiency, since waste heat from the nuclear reactor (which is assumed to be “free”) is utilized in this option. In Case II, recovered heat from the Cu-Cl cycle is used for desalination instead of internally, within the cycle. Thus, the Cu-Cl cycle and the overall system operate at lower efficiencies, since the effect of the cycle is very important on the overall system.

About 71% of the earth’s surface is covered by water, in the form of oceans, seas and the ice in the north and south poles. However, only about 3% of water is fresh and suitable for drinking. The water in the oceans and seas is saline, and thus not directly available for hydrogen production by water splitting. Therefore, special processes are needed to desalinate these waters. Today, the production of potable water has become a worldwide concern; for many countries, projected population growth and demand exceed conventional available water supplies. Over 1 billion people are without clean drinking water and approximately 2.3 billion people (41% of the world population) live in regions with water shortages. A looming water crisis is mainly due to mismanagement of existing water resources, population growth and climate change. It is therefore necessary that major efforts are made to address the looming water crisis and conserve shrinking water supplies amidst the rising demand. Seawater desalination can resolve the fresh water problem in numerous countries in both the Near East and Mediterranean region. Despite its reliability, the relatively high energy consumption still remains to be resolved. Since areas largely exposed to water scarcity are characterized by high levels of solar radiation, consideration should be given to the opportunity of using solar energy, coupled to desalination processes. This is particularly true in isolated and far remote areas, having no access to the electric grid.

## 7. Conclusions

Coupling of the Cu-Cl thermochemical cycle with a desalination plant for nuclear-based hydrogen production has been studied.

Several configurations for integrating the cycle with a desalination plant have been identified, and then evaluated and compared, to aid efforts to determine optimum options for the cycle. Thermodynamic and cost analyses of the coupled system provide useful insights into processes for producing hydrogen from seawater. The results are expected to assist the design, improvement and optimization of the Cu-Cl cycle for hydrogen production from sea or brackish water. More generally, the results support the notion that hydrogen production from salted water can help address problems associated with fresh water supplies, environmental impact and climate change.

The following concluding remarks can be drawn from this study.

- Desalination costs have decreased over the past few years due to technical improvements and adapting to a world of increasing fossil fuel prices. For conventional systems, the cost for seawater ranges from 0.5 \$/m<sup>3</sup> to more than 4 \$/m<sup>3</sup>, while for brackish water the desalination cost is almost half. When renewable energy sources are used, the cost is much higher, and in some cases can reach up to 19 \$/m<sup>3</sup>, due to expensive energy supply systems. However, this cost is counter-balanced by the environmental benefits.
- MSF plants are expected to continue to be preferred to treat water with high salinity concentration. In order to enhance the energy efficiency, such plants are coupled with thermoelectric power stations, according to a dual purpose scheme (generation of both water and electricity). If operating conditions are not excessively severe, RO plants will occupy the market of small to medium users, or even large users in a single-purpose system (water production only).
- The capital cost of the Cu-Cl cycle per unit of hydrogen output is less for a larger capacity plant.
- The production cost (energy cost) remains constant, mainly because the reaction energy (per unit hydrogen produced) of any chemical or physical reaction occurring in the Cu-Cl cycle does not change based on plant capacity.
- The total cost of hydrogen production (which is the sum of the capital cost, energy cost and also additional costs such as operating, storage and distributions costs) varies from 3.5 to 2 \$/kg H<sub>2</sub> in an inversely proportional relationship with plant capacity.
- The least expensive desalination method is HD at 7 \$(kg H<sub>2</sub>/day) and the technology with the highest initial cost (11.7 \$(kg H<sub>2</sub>/day)) is MSF. The capital costs of VC and RO appear to be similar at 9 \$(kg H<sub>2</sub>/day), while the capital cost of MED is 10.8 \$(kg H<sub>2</sub>/day).
- The capital cost of desalination technologies varies, based on the capacity. The capacity of the desalination method differs for each case.
- MSF has the highest capacity, while DS and VC have the lowest.
- The overall unit capital cost of the coupled system, which includes capital costs of both the Cu-Cl cycle and the desalination plant, varies with production capacity, but not with the type of desalination method. The unit capital cost of the overall system is similar for every case, since the cost contribution of the desalination plant is small compared to that of the Cu-Cl cycle. The overall unit capital cost varies between 187 and 38 cents/kg H<sub>2</sub> depending on the capacity.

- The unit production cost of the desalination process includes the cost of energy and processing. Case I has the lowest unit production cost (0.50 cents/kg H<sub>2</sub>) while Case III has the highest (0.99 cents/kg H<sub>2</sub>). Cases IV and V both have a unit production cost of 0.63 cents/kg H<sub>2</sub>, while that for Case II is 0.72 cents/kg H<sub>2</sub>.
- Case III consumes the highest amount of energy (0.135 kWh/kg H<sub>2</sub>) for desalination and Case V has the lowest (0.045 kWh/kg H<sub>2</sub>). Cases II and IV both have a unit energy consumption of 0.063 kWh/kg H<sub>2</sub> and that for Case I is 0.070 kWh/kg H<sub>2</sub>.
- The effect of the Cu–Cl cycle is dominant on the energy efficiency of the overall system, including the Cu–Cl cycle and desalination plant, as the desalination plant uses much less energy than the Cu–Cl cycle.
- Case I exhibits a higher efficiency since waste energy from the nuclear reactor (which is assumed to be “free”) is utilized in this option.
- In Case II, recovered heat from the Cu–Cl cycle is used for desalination instead of internally within the cycle. Thus, the Cu–Cl cycle and overall system operate at lower efficiencies, since the effect of the cycle is very important for the overall system.

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## Nomenclature

<i>c</i>	Specific heat, kJ/kg K
<i>E</i>	Energy rate, kJ/s
<i>H</i>	Total enthalpy, kJ
<i>h</i>	Specific enthalpy, kJ/kg
$\bar{h}$	Molar enthalpy, kJ/kmol
$\bar{h}^0$	Molar enthalpy at reference state, kJ/kmol
$\bar{h}_f^0$	Molar enthalpy of formation, kJ/kmol
<i>M</i>	Molar mass, kg/kmol
<i>mf</i>	Mass fraction
<i>Mf</i>	Molar mass fraction
<i>ṁ</i>	Mass flow rate, kg/s
<i>N</i>	Number of moles
<i>n</i>	Number of moles per cycle, kmol/kmol H <sub>2</sub>
<i>T<sub>0</sub></i>	Reference-environment temperature, K
<i>V̇</i>	Volume flow rate, m <sup>3</sup> /s
<i>W</i>	Work, kJ
<i>x</i>	Mole fraction

### Subscripts

<i>m</i>	Incoming saline water
<i>s</i>	Salt
<i>P</i>	Product
<i>R</i>	Reactant
<i>w</i>	Pure water

## REFERENCES

- [1] Ponomarev-Stepnoi NN. Nuclear-hydrogen power. *Atomic Energy* 2004;96:375–85.
- [2] Forsberg CW, Peterson PF, Pickard PS. Molten salt – cooled advanced high temperature reactor for production of hydrogen and electricity. *Nuclear Technology* 2003; 144:289–302.
- [3] Fiorenza G, Sharma VK, Braccio G. Techno-economic evaluation of a solar powered water desalination plant. *Energy Conversion and Management* 2003;44:2217–40.
- [4] United States Geological Survey (USGS), <http://www.usgs.gov/> [accessed 26.08.09].
- [5] Dupavillon JL, Gillanders BM. Impacts of seawater desalination on the giant Australian cuttlefish Sepia apama in the upper Spencer Gulf, South Australia. *Marine Environmental Research* 2009;67:207–18.
- [6] Arjunan TV, Aybar HS, Nedunchezhian N. Status of solar desalination in India. *Renewable and Sustainable Energy Reviews* 2009;13:2408–18.
- [7] Greenlee LF, Lawler DF, Freeman BD, Marrot B, Moulin P. Reverse osmosis desalination: water sources, technology, and today's challenges. *Water Research* 2009;43:2317–48.
- [8] World Health Organization (WHO), <http://www.who.int/en/> [accessed 26.08.09].
- [9] United States Environmental Protection Agency (EPA), <http://www.epa.gov/> [accessed 26.08.09].
- [10] Mohsen MS, Al-Jayyousi OR. Brackish water desalination: an alternative for water supply enhancement in Jordan. *Desalination* 1999;124:163–74.
- [11] Ahmad GE, Schmid J. Feasibility study of brackish water desalination in the Egyptian deserts and rural regions using PV systems. *Energy Conversion and Management* 2002;43: 2641–9.
- [12] Karagiannis IC, Soldatos PG. Water desalination cost literature: review and assessment. *Desalination* 2008;223: 448–56.
- [13] Hrayshat ES. A wind-powered system for water desalination. *International Journal of Green Energy* 2007;4:471–81.
- [14] Zamen M, Amidpour M, Soufari SM. Cost optimization of a solar humidification-dehumidification desalination unit using mathematical programming. *Desalination* 2009;239: 92–9.
- [15] Lewis MA, Masin JG, Vilim RB, Serban M. Development of the low temperature Cu–Cl cycle. In: Proceedings 2005 International Congress on advances in nuclear power plants, May 15–19, 2005. Seoul, Korea: American Nuclear Society; May 2005.
- [16] Serban M, Lewis MA, Basco JK. Kinetic study for the hydrogen and oxygen production reactions in the copper–chloride thermochemical cycle. In: Proceedings AIChE Spring National Meeting, New Orleans, LA, April 25–29; 2004. p. 2690–98.
- [17] Wang ZL, Naterer GF, Gabriel KS, Gravelsins R, Daggupati VN. Comparison of different copper–chloride thermochemical cycles for hydrogen production. *International Journal of Hydrogen Energy* 2009;34:3267–76.
- [18] Wang ZL, Naterer GF, Gabriel KS. Multiphase reactor scale-up for Cu–Cl thermochemical hydrogen production. *International Journal of Hydrogen Energy* 2008;33:6934–46.
- [19] Orhan MF, Dincer I, Rosen MA. Efficiency analysis of a hybrid copper–chloride (Cu–Cl) cycle for nuclear-based hydrogen production. *Chemical Engineering Journal* 2009;155:132–7.
- [20] Yildiz B, Kazimi MS. Efficiency of hydrogen production systems using alternative nuclear energy technologies. *International Journal of Hydrogen Energy* 2006;31:77–92.
- [21] Balta MT, Dincer I, Hepbasli A. Potential methods for geothermal-based hydrogen production. *International*

- Journal of Hydrogen Energy, in press, Corrected Proof, Available online 12 October 2009, doi:10.1016/j.ijhydene.2009.09.040.
- [22] Orhan MF, Dincer I, Rosen MA. Environmentally-benign nuclear-based hydrogen production through a copper-chloride thermochemical cycle. In: Global Conference on Global Warming 2008 (GCGW-08), Istanbul, Turkey; 2008.
- [23] Lewis MA, Masin JG. The evaluation of alternative thermochemical cycles – part II: the down-selection process. International Journal of Hydrogen Energy 2009;34:4125–35.
- [24] Fiorini P, Sciubba E. Thermo-economic analysis of a MSF desalination plant. Desalination 2005;182:39–51.
- [25] Bourouni K, Chaibi MT, Tadrist L. Water desalination by humidification and dehumidification of air: state of the art. Desalination 2001;137:167–76.
- [26] Kahraman N, Cengel YA, Wood B, Cerci Y. Exergy analysis of a combined RO, NF, and EDR desalination plant. Desalination 2004;171:217–32.
- [27] Orhan MF, Dincer I, Rosen MA. The oxygen production step of a copper-chloride thermochemical water decomposition cycle for hydrogen production: energy and exergy analyses. Chemical Engineering Science 2009;64:860–9.
- [28] Orhan MF, Dincer I, Rosen MA. Energy and exergy analyses of the fluidized bed of a copper-chloride cycle for nuclear-based hydrogen production via thermochemical water decomposition. Chemical Engineering Research and Design 2009;87:684–94.
- [29] Orhan MF, Dincer I, Rosen MA. Thermodynamic analysis of the copper production step in a copper–chloride cycle for hydrogen production. Thermochimica Acta 2008;480: 22–9.
- [30] Orhan MF, Dincer I, Rosen MA. Energy and exergy assessments of the hydrogen production step of a copper–chloride thermochemical water splitting cycle driven by nuclear-based heat. International Journal of Hydrogen Energy 2008;33:6456–66.
- [31] Orhan MF, Dincer I, Rosen MA. Energy and exergy analyses of the drying step of a copper–chloride thermochemical cycle for hydrogen production. International Journal of Exergy 2009;6:793–808. pp. 793–808.
- [32] Naterer G, Suppiah S, Lewis M, Gabriel K, Dincer I, Rosen MA, et al. Recent Canadian advances in nuclear-based hydrogen production and the thermochemical Cu–Cl cycle. International Journal of Hydrogen Energy 2009;34: 2901–17.
- [33] Orhan MF, Dincer I, Rosen MA. An exergy-cost-energy-mass analysis of a hybrid copper-chloride thermochemical cycle for hydrogen production. In: Proceeding of International Conference on Hydrogen Production, Oshawa, Ontario, Canada, 3–6, May 2009, p. 106–17.
- [34] Orhan MF, Dincer I, Naterer GF. Cost analysis of a thermochemical Cu–Cl pilot plant for nuclear-based hydrogen production. International Journal of Hydrogen Energy 2008;33:6006–20.