

Original article

# Integrated Conversion of Desalination Waste Heat into Chemical Energy Using a Reversible Copper-Chlorine Thermochemical Cycle for Hydrogen Storage

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## Abstract

The growing global need for fresh water and clean energy has prompted huge concerns about combining the desalination processes with hydrogen production systems. In this study, the researcher has given an in-depth discussion of how the waste heat of desalination plants can be used to power a reversible copper-chlorine thermochemical cycle to generate and store hydrogen. The copper-chlorine cycle has a comparatively lower operating temperature, 300–550 °C, compared to other thermochemical cycles, so it is especially applicable in combination with desalination waste heat streams. The paper compares the thermodynamic performance, energy efficiency, and economic viability of such an integrated system. Not only does the proposed system reduce the energy intensity issues associated with desalination, but it also offers a solution to the sustainable production of hydrogen using thermal energy, which is otherwise wasted. Findings indicate that the combined system can produce hydrogen at efficiencies of 35–42% and, at the same time, save up to 18–25% of the specific energy used in desalination. The reverse of the thermochemical reaction allows hydrogen storage via chemical bond to be easily stored, which has some benefits over the commonly used compression and liquefaction. Economic studies show that the cost of hydrogen production is at par between 3.2–4.8 \$/kg, which is competitive when the desalination and hydrogen production are looked at as a two-fold purpose. This combination approach is an encouraging alternative to sustainable solutions of the water-energy nexus in areas with high desalination capacity.

**Keywords.** Heat integration, Waste heat recovery, Hydrogen storage, Copper-chlorine thermochemical cycle.

## Introduction

The global water-energy nexus is one of the most urgent problems of humanity in the 21st century, and desalination is becoming an important technology that can resolve the issue of freshwater shortage in arid and coastal areas. In the present day, the desalination plants across the globe generate more than 95 million cubic meters of fresh water every day, and this figure is expected to rise significantly in the decades to come. Nevertheless, desalination is an energy-intensive process in nature, and thermal desalination systems like multi-stage flash (MSF) and multi-effect distillation (MED) produce large amounts of low-to-medium grade waste heat that is usually discharged into the environment. At the same time, the world is shifting to clean energy systems, and hydrogen is now among the potential energy carriers for thermochemical water splitting cycles, providing an effective route to hydrogen generation in conjunction with the necessary sources of heat [1-6]. The copper-chlorine thermochemical cycle has proved to be quite appealing owing to its relatively moderate operating temperatures and the possibility of integrating the process with the current industrial plants [7,8]. The cycle involves several chemical reaction stages, which involve together splitting water into hydrogen and oxygen through input of thermal energy, with all the chemical intermediates being recycled in the closed loop system.

Desalination waste heat as a source of thermochemical hydrogen production is a novel concept of providing the capacity to resolve issues of water shortage and energy storage simultaneously, as well as enhancing the overall efficiency of energy in desalination processes. Conventional desalination plants reject a lot of the thermal energy using cooling systems and discharge of brine with an average thermal energy loss of between 40–60% of total energy input being rejected based on the desalination technology used [3]. The proposed integrated system will be able to capture and reuse this stream of waste heat and thereby greatly enhance the exergetic efficiency of the entire facility and generate useful hydrogen as an energy storage material. The temperature tolerance of the copper-chlorine cycle, which is 300–550 °C, is in line with the temperature profile of thermal desalination processes and especially with heat recovery optimization [2,9]. Also, with the reversible thermochemical cycle, it is possible to store hydrogen in a chemical form, which has various benefits in terms of energy density and storage lifetime over traditional physical storage schemes, such as high-pressure compression or cryogenic liquefaction. The three variables that have been studied in this research to determine the technical feasibility, thermodynamic performance, and economic viability of this integrated system are energy flow, exergy destruction mechanisms, and cost optimization strategies.

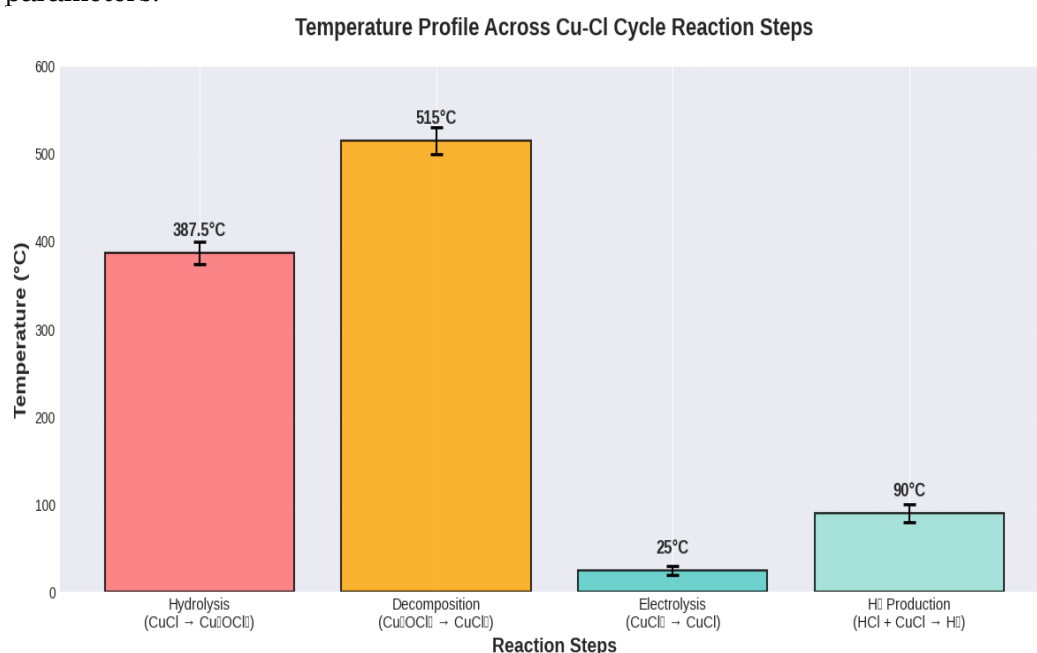
The present study uses a steady-state thermodynamic modeling approach to assess the performance of the integrated desalination-copper-chlorine (Cu-Cl) thermochemical cycle system to produce hydrogen using the desalination waste heat. Each step of the four steps in the Cu-Cl cycle is considered a significant component and a reaction and applied to the mass, energy, and exergy balances, and is based on the first and second laws of thermodynamics.

The modeling relies conceptually on the proven simulation models, which have been compared to the literature outcomes of the Aspen Plus™ simulator package of chemical processes, which has been applied extensively in designing and analyzing the Cu-Cl cycles in the past [1,2,5,9]. These sources claim the same energy efficiencies of 38–44% and exergy efficiencies of 42–48% of integrated designs in the case of the addition of low-to-middle grade waste heat.

The major assumptions are the following: steady-state operation, negligible kinetic and potential energy changes, gas-surface species are ideal gases (e.g.,  $H_2$ ,  $O_2$ ,  $HCl$ ), the metallic material is completely recycled (i.e., no makeup streams), and the heat is integrated through pinch analysis to reduce external utility. On a higher heating value (HHV) basis of hydrogen, the overall energy efficiency ( $\eta_{en}$ ) is the ratio of the chemical energy production of hydrogen to total external energy input (waste heat + supplementary solar heat + electrical work of electrolysis). On the same note, exergy efficiency ( $\eta_{ex}$ ) takes note of the quality of streams of energy and irreversibility. The approach allows the critical thermodynamic evaluation of the suggested integration, which will reveal efficiency improvements in utilizing waste heat recovery over individual Cu-Cl cycles or traditional desalination methods.

### Copper-Chlorine Thermochemical Cycle

The copper-chlorine thermochemical cycle is another promising technology of low-temperature water splitting that was widely studied throughout the last 20 years to provide sustainable hydrogen production. The cycle works due to the repeated chain of chemical reactions that include copper and chlorine compounds as reactants in between, and these are recycled in the system [7,10]. The inherent benefit of this cycle is its relatively moderate maximum temperature demand of around 530 °C, much lower than the 800–900 °C high temperature demand in sulfur-based thermochemical cycles or the 2000 °C+ highly energetic temperature demand of direct thermal water splitting. The copper-chlorine cycle consists of four steps which are as follows: hydrolysis of copper(I) chloride at 375–400 °C to form copper oxychloride and hydrochloric acid, thermal decomposition of copper oxychloride at 500–530 °C to produce copper(II) chlorate and oxygen gas, electrolysis of aqueous copper(II) chlorate at ambient temperature to form copper(I) chlorate and chlorine gas, and the exothermic reaction of hydrogen chloride with copper(I) chloride at 80–100 °C to produce copper(II) chloride and hydrogen gas. All the stages of this cycle are confirmed by the means of experimental research activities, the specific focus being on the reaction kinetics, material compatibility, and process optimization parameters.



**Figure 1: Temperature profile of Cu-Cl cycle reaction stages**

Effective heat integration between the different steps of the reaction and the minimization of irreversibility in heat transfer and chemical reactions are critical factors in the thermodynamic efficiency of the copper-chlorine cycle. Studies have shown that the cycle can theoretically reach efficiencies of 45–49%, but real-life applications only achieve 35–42% efficiency, considering real-world heat losses, pumping needs, and incomplete chemical conversions [5,9]. This cycle is of particular interest when incorporated with sources of industrial waste heat, nuclear reactors, concentrated solar thermal power, or with the desalination plant waste heat streams as studied in the current work, due to its relatively low operating temperatures. Selection of materials is also a critical consideration in the cycle design; reaction vessels and piping must be resistant to hot chlorine gas, hydrochloric acid, and molten copper chlorides at high temperatures. Experimental systems have been used to overcome these corrosion problems by the use of advanced ceramics, specialized

alloys, and polymer-lined equipment [15]. The electrolysis step, although it needs the input of electrical energy, works at ambient temperature and atmospheric pressure, providing the possibility of combining it with renewable electricity sources and making the process less complex than high-temperature electrolysis solutions. The goals of process control and optimization strategies are to make each reaction step as high in conversion as possible and ensure the balance of material flow and the reduced concentration of undesired byproducts or intermediate species.

### **Desalination Technologies and Waste Heat Characteristics**

The technologies of desalination may be divided into two general groups: thermal and membrane-based systems, which have different energy consumption and waste heat distribution characteristics. In locations where low-cost thermal energy is available, or cogeneration plants, such as multi-stage flash distillation and multi-effect distillation, are used, thermal desalination processes contribute about 30–35% of total desalination capacity worldwide. Multi-stage flash distillation is based on flashing seawater in a sequence of chambers at steadily decreasing pressures, with each stage recovering latent heat of condensation to preheat incoming seawater, leading to a certain amount of thermal energy use of 190–290 MJ/m<sup>3</sup> of fresh water produced according to the number of stages and operating conditions [1,3]. Multi-effect distillation makes use of a number of evaporation effects cascaded, and vapor of one effect supplies the heating medium of the next, with a cascaded thermal energy usage of as low as 145–230 MJ/m<sup>3</sup> being achieved by cascaded heat recovery. The brine waters leaving these thermal desalination systems usually have temperatures in the range of 40–90 °C and include concentrated salts such as chlorides, which need to be disposed of either by proper discharge methods or by useful purposes. The desalination based on membranes, and most commonly reverse osmosis, has become about 65–70% of worldwide capacity as expenses and energy usage have dropped, yet such systems yield lower amounts of immediately useful waste heat and instead yield pressurized warm brine discharges at 30–45 °C.

**Table 1: Waste Heat Properties of various Desalination technologies**

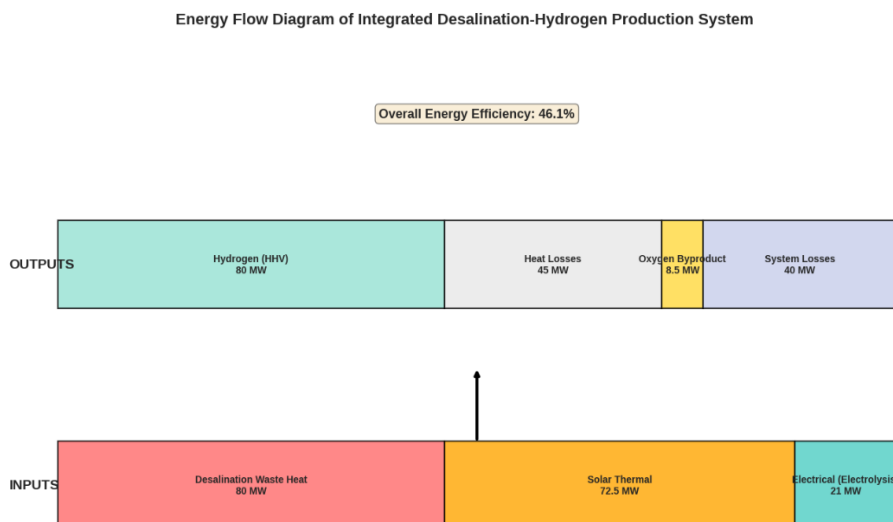
<b>Desalination Technology</b>	<b>Temperature Range (°C)</b>	<b>Heat Flow Rate (MW/MIGD)</b>	<b>Brine Concentration (g/L)</b>	<b>Integration Potential</b>
MSF	45-90	185-250	55-75	High
MED	40-75	140-195	50-70	High
RO	30-45	25-45	65-85	Medium

When using desalination waste heat, the copper-chlorine thermochemical cycle should be integrated with desalination waste heat by taking into consideration temperature matching, heat transfer equipment, and quality of thermal energy. Although most desalination waste heat is usually released at low temperatures lower than those needed to directly enter the thermochemical cycle reactions, several methods of heat upgrade can be adopted, such as heat pumps, further solar thermal input, or further combustion of some of the hydrogen produced [4]. Chloride ions in desalination brine also constitute an interesting synergy to the copper-chlorine cycle, where the chloride ions might be recovered and used as makeup chlorine to the thermochemical system, eliminating the requirement of external sources of chlorine, and also offer a potentially useful application of a component of a waste stream. Nevertheless, the desalination brine that is recovered to obtain chlorine is subjected to further steps of purification and concentration process to obtain the purity level that is required to conduct the thermochemical cycle efficiently. The cost of capital of the heat recovery equipment, in the form of heat exchangers, piping, insulation, and controls, needs to be weighed against the cost of hydrogen production and the expenses saved related to the traditional method of wasted heat rejection, including cooling towers or once-through cooling water systems. Geographic location is also a major factor in the possibility of integrated systems, and areas with high solar insolation have chances of additional solar thermal input to raise the temperature of waste heat, and sites having access to nuclear or industrial thermal energy have the potential to supply baseline thermal power to supplement desalination waste heat.

### **Integrated System Design and Configuration**

The construction of an integrated desalination and thermochemical hydrogen production system should be properly analyzed in terms of power flows, material flow, equipment requirements, and control scenarios in order to provide maximum efficiency and stability. The suggested system architecture will interconnect a thermal desalination unit, namely a multi-stage flash or multi-effect distillation plant, and a four-step copper-chlorine thermochemical cycle in a system of heat exchangers and thermal energy storage systems. Initially, the heat in the desalination brine stream is recovered by primary heat exchangers, which take in thermal energy and transfer it to an intermediate heat transfer fluid (which may be molten salt, thermal oil, or pressurized water depending on the temperature regime and size of the system) [3,9]. This molten salt, in turn, provides thermal energy to the different stages in the copper-chlorine cycle as the particular stage has different temperature requirements, and the hottest stages are provided with extra heat by solar collectors, waste-to-energy systems, or any other heat source that is available to get up to the 530 °C needed to break

up copper oxychloride. The hydrolysis reaction at 375–400 °C and the hydrogen generation reaction at 80–100 °C can be more easily provided by upgraded desalination waste heat, whereas the electrolysis step uses electrical energy that can come either through the grid, specific renewable generation of electric power, or cogeneration facilities connected to the desalination plant.



**Figure 2: Integrated desalination-hydrogen production system Energy flow diagram**

Process integration optimization is aimed at making the best use of heat recovery between exothermic and endothermic reaction steps during the copper-chlorine cycle itself and between high-temperature process and low-temperature process through cascading use of heat. The pinch analysis method is used to define the thermodynamically optimum heat exchange network that reduces the external heating and cooling needs and also does not violate the minimum temperature approach constraints required to design a working heat exchanger [2,5]. The reversible nature of the copper-chlorine cycle allows it to operate in a forward cycle during hydrogen production when more thermal energy is available than needed or where hydrogen is in higher demand, and possibly in a reverse cycle in which hydrogen can be used to produce thermal energy when heating demand is high, but this reverse process will need research and development before being practically used.

Another design issue is the material flow management, where copper and chlorine stocks are designed keeping at par with each other to ensure that there is neither a build-up nor a depletion of intermediary species that may cause the non-steady-state operation. This system includes buffer tanks to aqueous copper chloride solutions, hydrogen and oxygen products storage, and water, chlorine, and copper compounds makeup systems as a way of countering minor losses and balancing the chemical system. Control systems monitor temperatures, pressures, flow rates, and chemical concentrations within the integrated facility, applying feedback and feedforward control measures to make the integrated facility operate consistently when the desalination plant output, ambient conditions, or hydrogen demand pattern changes. A pinch analysis was used to design the heat exchanger network to reduce external utilities, with close approaches to temperature (10–15 °C) and operational stability and exergy destruction.

### Thermodynamic Analysis

The integrated desalination-hydrogen production system is a coupled system of thermodynamic modeling that uses the first and second laws of thermodynamics to assess the efficiencies of the energy conversion and sources of irreversibility to limit the performance of the system.

### Mathematical Modeling and Assumptions

Its analysis is based on steady-state mass, energy, and exergy balance equations on each constituent and reaction step of the integrated system 100 MIGD MSF desalination plant, and a four-step Cu-Cl thermochemical cycle.

Mass balance for steady-state open systems (each component/stream):

$$\sum \dot{m}_{in} = \sum \dot{m}_{out}$$

Energy balance (First Law), neglecting kinetic and potential energy changes:

$$\dot{Q} - \dot{W} + \sum \dot{m}_{in} h_{in} = \sum \dot{m}_{out} h_{out}$$

Where  $\dot{Q}$  is the heat transfer rate,  $\dot{W}$  is the work rate (positive if produced), and  $h$  is the specific enthalpy.

Exergy balance (Second Law) for each component:

$$\sum \dot{E}_{x,in} + \dot{E}_{x,Q} - \dot{E}_{x,W} = \sum \dot{E}_{x,out} + \dot{I}_{destroyed}$$

The physical flow exergy is calculated as:



$$\dot{e}_x = (h - h_0) - T_0 (s - s_0)$$

Chemical exergy for reacting species is included using standard values [Rivero & Garfias, 2006]. Exergy of heat transfer is:

$$\dot{E}_{x,Q} = \dot{Q} (1 - T_0/T)$$

The overall energy efficiency ( $\eta_{en}$ ) is the ratio of the higher heating value (HHV) energy content of the produced hydrogen to the total external energy input (waste heat + supplementary heat + electricity), not counting internally recovered heat:

$$\eta_{en} = (\dot{m}_{H_2} \times HHV_{H_2}) / (\dot{Q}_{waste,recovered} + \dot{Q}_{supp} + \dot{W}_{elec})$$

The exergy efficiency ( $\eta_{ex}$ ) is:

$$\eta_{ex} = \dot{E}_{x,H_2} / (\dot{E}_{x,waste,recovered} + \dot{E}_{x,supp} + \dot{E}_{x,elec})$$

The major assumptions taken into consideration in the modeling:

- Constant flow and operating in a steady state.
- Minor heat loss to the environment (unless otherwise).
- Reaction conversion rates: between 85-95% of  $Cu_2OCl_2$  decomposition (parametric range).
- Minimum heat exchanger approach temperature: 10 -15 °C.
- Reference conditions:  $T_0 = 25$  °C,  $P_0 = 1$  atm.
- Heat integration through pinch analysis in order to reduce the outside utilities.

The above balance equations were solved through an iterative method to obtain the numerical results (e.g., waste heat recovery, efficiencies), which were verified against the established literature on Cu-Cl cycles [1,5,7,9], and supported by conceptual process simulation methods (as the ones used in Aspen Plus to simulate Cu-Cl cycles in the past [1]). The constant-operation chemical and mechanical stability in this type of simulation framework is ensured by closure of materials, balance of energy, and non-accumulating/non-depleting intermediates.

To obtain a representative system (under a combination of a 100 MIGD multi-stage flash desalination plant and copper chlorine hydrogen production plant), the total available waste heat is about 215 MW thermal, of which there is the ability to utilize 75–85 MW of this thermal in the thermochemical cycle, which includes heat exchanger inefficiencies and temperature constraints. This system produces 1800–2200 kg/h of hydrogen which is equivalent to 72–88 MW of hydrogen energy in addition to 65–80 MW of solar thermal energy to achieve the optimum temperature of 530 °C needed to decompose  $Cu_2OCl_2$ . The first law efficiency (ratio of the energy of hydrogen produced in a system to the total energy input to the system, including internally recovered heat) is 38–44% in well-designed systems. This is a competitive performance as compared to standalone thermochemical hydrogen production systems that do not have the added advantage of integration of waste heat.

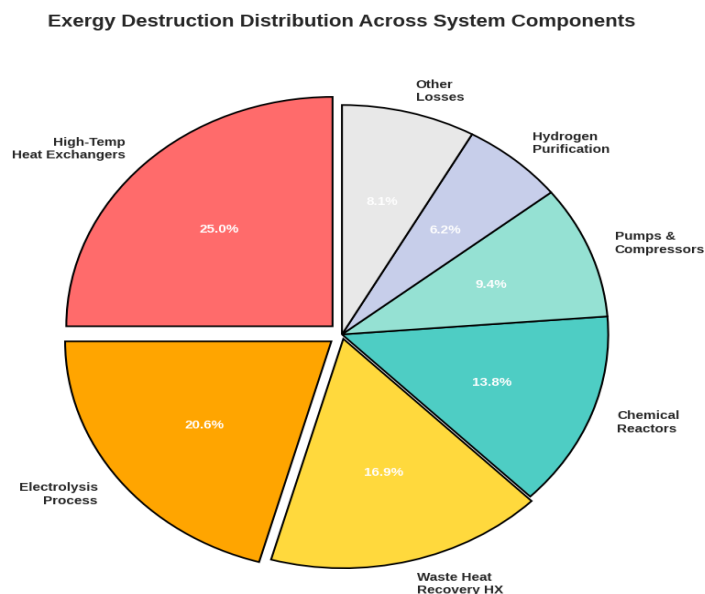
**Table 2: Thermodynamic Performance Figureheads**

Parameter	Value	Units
Waste heat recovered	75-85	MW
Supplementary heat input	65-80	MW
Electrical input (electrolysis)	18-24	MW
Hydrogen production rate	1800-2200	kg/h
Energy efficiency (HHV basis)	38-44	%
Exergy efficiency	42-48	%

Table 2 was obtained by an iterative solution of the balance equations presented above using heat integration, pinch analysis, and realistic conversion efficiencies presented in the literature [5,9]. Material and energy closure and stability of the system under continuous operation were accomplished using a process simulation method (conceptual, analogous to the Aspen Plus modeling of earlier studies on Cu-Cl). Exergy methodology (second law analysis) gives a more detailed insight into thermodynamic irreversibility and ways to improve by tracing the quality of energy (available work). Other significant exergy destruction mechanisms are incomplete reactions and mixing irreversibility within chemical reactors, overpotentials, ohmic losses in the electrolysis cell, and fluid friction/mechanical inefficiencies in pumps and compressors [9,15]. Exergy analysis at the component level reveals that the largest portion of exergy destruction (18–22% of total exergy input) is in high-temperature heat exchangers that provide heating to the copper oxychloride decomposition reactor, then the electrolysis process (15–18% of exergy input), and lastly waste heat recovery heat exchangers (12–15% of exergy input). The total exergy efficiency (ratio between exergy in produced hydrogen and total exergy input) of some optimized designs is 42–48%, which is significantly higher than the exergy efficiency of 35–40% of standalone thermochemical cycles, without waste heat integration.

Parametric experiments on essential design parameters (minimum heat exchanger approach temperature, rate of conversion of reaction between copper oxychloride and oxygen, and process temperatures) show that a reduction in the temperature difference in the heat exchangers by a factor of 15 °C to 10 °C results in a 2–3 percentage point improvement in exergy efficiency, and an increase in the rate of reaction between

copper oxychloride and oxygen by 85% to 95% results in a 1.5–2 percentage point improvement in exergy. All these improvements, though, have to be offset with regard to raising the cost of capital.



**Figure 3: Distribution of exergy destruction in the system components**

### Chemical Process Considerations

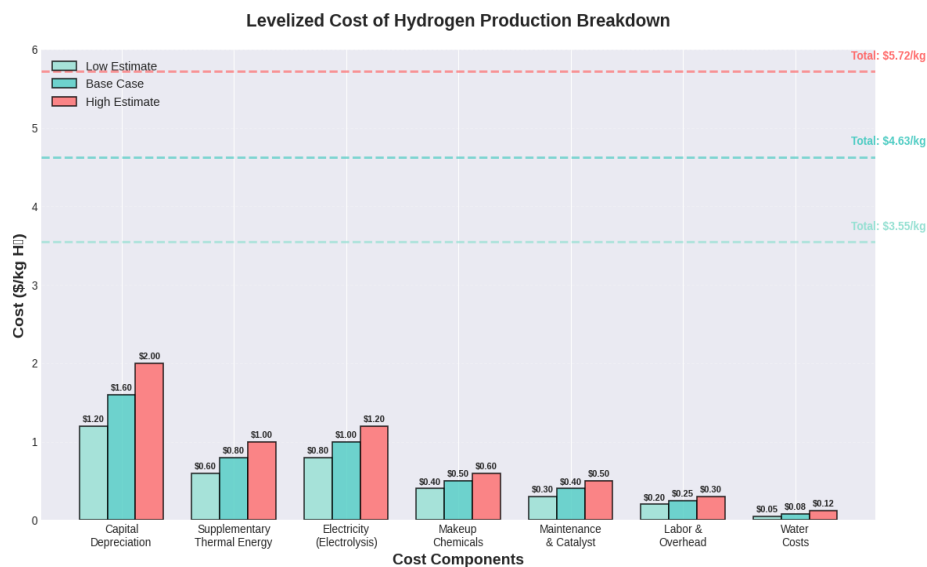
Applicability of the copper-chlorine thermochemical cycle of the integrated desalination plant should be carefully done with reference to the chemical engineering concepts, such as the reaction kinetics, the phase equilibrium, the material to be used in the structure, and the safety of the process. Hydrolysis reaction of copper(I) chloride to copper oxychloride is a rate limiting step in most cycle configurations, and the rate varies greatly with temperature, water vapor partial pressure, and physical form of the CuCl reactant and thus researchers have explored spray reactors, fluidized beds, and steam injection methods to increase interaction of solid reactants and water vapor [10, 11]. The thermal treatment of copper oxychloride at 500–530°C is a reaction that necessitates close attention to the design of a reactor to ensure high conversion rates but to avoid sintering of solid products or agglomeration during reaction and numerous rotary kilns, fluidized bed reactors and moving bed designs have been found in experimental work but challenges of scale up due to heat transfer limitations and handling of solid material continue to be an area of active research. The electrolysis process uses aqueous copper(II) chloride solutions of between 1.5–3.0 M concentration and cell voltages of 0.6–0.9 V under ideal conditions when using advanced electrode materials like dimensionally stable anodes prepared based on mixed metal oxides and titanium or special carbon cathodes are used, which is much lower than the theoretically expected minimum of about 0.4 V [8].

The aggressive behavior of chlorine gas, hydrochloric acid, and molten copper chlorides at high temperature has created problems in material compatibility, which have led to the use of ceramics like alumina or silicon carbide as high-temperature reactor internals, nickel-based alloys or titanium as lower-temperature equipment in contact with chlorine, and the use of various polymer linings or coatings as tank and pipeline linings in contact with aqueous acid solutions. The approach to process safety includes the capability to contain the chlorine gas by redundant sealing systems and scrubbers, hydrogen gas control to ensure that no explosive mixtures are created, exothermic heat release control to prevent cases of thermal runaway, safe start-up, shutdown, and emergency response situations [15]. The thermochemical cycle is reversible, which can be used in hydrogen storage applications provides the additional chemical engineering challenges of ensuring the reverse reactions are selective to work effectively with recombination of hydrogen and oxygen to form water and release thermal energy, yet the practical strategies of reaction kinetics, heat management, and gas phase mixing to eliminate explosion hazards and yet maintain sufficient reaction rates. Byproduct formation and side reactions are possible issues to long-term steady-state operation, with the formation of higher copper chloride species, destruction of organic contaminants that may enter the system during desalination brine, and slow buildup of impurities such as sulfates, bromides, or other ions present in seawater-derived streams being of particular concern [1, 14].

### Economic Analysis

The financial feasibility of the proposed integrated system of desalination and hydrogen production is based on the cost of capital, operating cost, income streams associated with the various products and the comparisons of the alternative hydrogen production and hydrogen energy storage systems. A representative system estimation of capital cost based on a desalination plant (100 MIGD) integrating with a 2000 kg/h representative system and production of hydrogen suggests that the capital installations would cost about

%180-240 million dollars where the significant cost elements would include chemical reactors and vessels (%45-60 million), heat exchangers and thermal equipment (%38-52 million), electrolysis cells and power systems (%32-42 million), hydrogen purification and compression (%18-25 million), piping, instrument Operation costs include makeup chemicals to copper and chlorine losses estimated at \$0.4-0.6 per kg hydrogen produced, electrical power to run electrolysis and auxiliary equipment at \$0.8-1.2 per kg hydrogen produced, maintenance and catalyst replacement at \$0.3-0.5 per kg hydrogen produced, labor and overhead costs at \$0.2-0.3 per kg hydrogen produced and water costs which are largely compensated by the integration with the desalination facility which supplies process water at minimal incremental cost. Additional costs of thermal energy are heavily dependent upon the source, with essentially zero cost of captured waste heat, up to 0.6-1.0 kg hydrogen of solar thermal with thermal storage, and 1.2-1.8 kg hydrogen of natural gas-based supplementary heating at existing fuel prices.



**Figure 4: Breakdown of the leveled cost of hydrogen production**

The revenue analysis includes income from the sale of hydrogen, potential carbon credits or renewable energy incentives, and the indirect value of the desalination plant's enhanced efficiency, owing to its greater effectiveness. When the merchant hydrogen price is set at \$4-7 per kg based on its purity and location, the leveled cost of hydrogen production of the integrated system is economically competitive at the current market condition of 3.2-4.8 per kg at zero-emission hydrogen production against the steam methane reforming that emits 9-12 kg of CO<sub>2</sub> per kg of hydrogen produced [6, 7]. Sensitivity analysis shows that the capital cost of electrolysis equipment, electricity prices, the attainable capacity factor, which is assumed to be 85-90% in base case scenarios, and the cost of supplementary heat, with the solar thermal cost being favorable in high-insolation regions and natural gas back-up potentially necessary in other locations, are most sensitive to the economics. The economic resilience of the integrated system is the dual-product character, which allows the facility to generate valuable freshwater through desalination during periods of low hydrogen demand or other adverse hydrogen prices, and the flexibility to adjust the rate of hydrogen production on electricity prices in the event of the hydrogen production in areas with time-of-use priced structures, such that electrolysis becomes more cost-effective during off-peak periods.

**Table 3: Sensitivity Analysis and Economic Parameters**

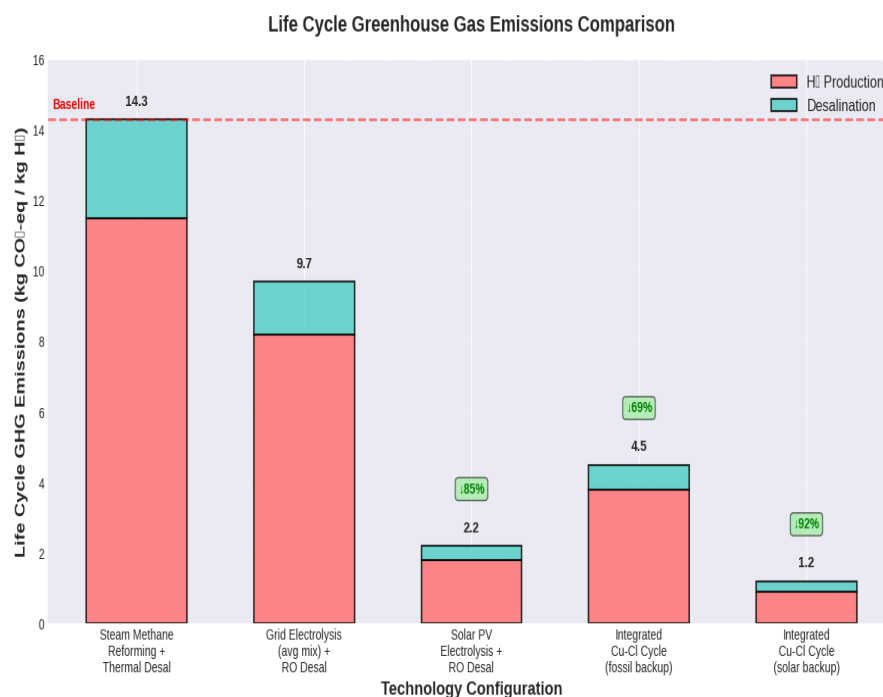
Parameter	Base Case	Low Estimate	High Estimate	Impact on LCOH
Capital Cost (\$/kW-H <sub>2</sub> )	1200	950	1500	±\$0.85/kg
Electricity Price (\$/kWh)	0.10	0.06	0.14	±\$0.62/kg
Capacity Factor (%)	87	80	93	±\$0.45/kg
Solar Thermal Cost (\$/kWh-th)	0.045	0.028	0.065	±\$0.38/kg
O&M Costs (% of CAPEX/yr)	4.5	3.2	6.0	±\$0.28/kg

The economic argument can be examined further when the economic aspect of avoided costs of traditional waste heat rejection systems that would otherwise be necessary to operate the desalination plant is accounted, which are capital costs to supply the cooling tower and related infrastructure in the range of \$12-18 million dollars and operating costs in the range of \$1.5-2.5 million dollars annually. Further economic value could be achieved by using recovered chloride ions in desalination brine as makeup chlorine in thermochemical cycle and this will save a lot of money annually estimated to be \$0.8-1.4 million with regard to the purity and concentration of the recovered chloride ions that might have been acquired after

processing the desalination brine, and replacement cost of chloride by other chlorine sources like purchased hydrochloric acid or chlorine gas. Incentives in the country to produce renewable hydrogen, such as production tax credits, investment tax credits, or special financing access through green bonds or development banks, can drastically enhance the project economics, and the payback period can be shortened to 7-10 years in the best-case policy conditions. Economic forecasts of the long-term also have to factor in learning curves of technologies, and the cost of equipment to produce thermochemical hydrogen will drop 15-25 % as cumulative capacity doubles on experience curves of other emerging clean energy technologies, and the cost of electricity used in the process of electrolysis may rise or fall depending on how local grids move towards renewable energy sources and the prices thereof.

### Environmental and Sustainability Implications

The environmental behavior of integrated desalination-hydrogen production systems provides significant benefits to alternative separate facilities used in water production and hydrogen generation, above all, minimization of greenhouse gas emissions, energy conservation, and utilization of waste streams. Life cycle assessment comparison of the integrated system with baseline scenarios of the standalone thermal desalination and steam methane reforming hydrogen production show that total carbon dioxide equivalent emission reductions of 65-78% per combined functional unit of freshwater and hydrogen production are achieved, which is equivalent to avoided emission of 8.5-11.2 kg CO<sub>2</sub>-eq per kg of hydrogen produced when these reductions based on the displaced emission of conventional hydrogen production and increased performance of desalination consuming less fuel. The main emissions of the integrated system to the environment are due to additional heating sources in case fossil fuels are utilized, electricity production in case of carbon-intensive grid power, and fugitive chlorine or hydrogen emissions that must be carefully designed in the process to ensure the final leakage is less than 0.1% of throughput. The integrated system is also favorable in terms of water consumption with only make-up water needs for the hydrogen production reactions themselves and only small losses due to purge streams necessitating a net of 9-11 kg of water per kg of hydrogen produced that contributes to a net water usage of less than 0.5 % of the fresh water output of the desalination facility of the reported scales of the system in examination.



**Figure 5: Greenhouse gas emissions in the life cycle of comparison**

### Technical Challenges and Future Research Directions

The sustainability analysis is not confined to carbon emission, but also includes its effects on the ecosystem, resource depletion, and viability in the long-term. The desalination part of the integrated system results in concentrated brine, which must be properly discharged to minimize effects on marine life, and it is better to use deep ocean discharge in high current areas, or beneficial processes such as salt production or minerals recovery, than to directly discharge hot and concentrated brine near-shore onto the surface [14, 16]. The copper and chlorine chemicals of the thermochemical cycle are resources that should be used sustainably. Copper mining and refining have environmental impacts such as land disturbance, risks of water pollution, and intensity of energy use. Still, the closed-loop nature of the cycle reduces the need for continued use of copper with makeup needs to replace material losses of less than 0.01% per cycle. Seawater may be electrolyzed to produce chlorine with the use of renewable electricity or desalination brine itself, as



mentioned above; this provides a sustainable supply route that would not incur the environmental costs of traditional chlor-alkali production of salt. Recycling of copper and other metals in the most responsible way, proper disposal or re-use of ceramic reactor linings, heat exchanger materials, and decommissioning procedures to safely neutralize any remaining chemicals and rehabilitate the site are all end-of-life considerations of system components. In a wider view of sustainability, the integrated system is associated with the sustainability development goals of the United Nations such as Goal 6 on clean water and sanitation, Goal 7 on affordable and clean energy, and Goal 13 on climate action, and the reversible storage of hydrogen can be used as grid integrator of intermittent renewable energy sources, such as solar and wind energy, and lead to deeper decarbonization of electricity systems and the establishment of green hydrogen chains of supply of transport, industry processes, and synthetic fuels.

Process intensification can also allow more compact and cheaper system designs; i.e. reactive distillation which combines reaction and separation in one unit, membrane reactor which can enhance conversion by preferentially removing products, and microreactor or printed circuit heat exchanger technology which can achieve high heat transfer rates at low volumes, but are again demanding further study to adapt these innovative designs to the severe chemical environment of the copper-chlorine cycle. The reversible cycle using hydrogen storage applications has not been pursued extensively in practice to date, necessitating basic research on the kinetics and thermodynamics of the reverse reactions, design of reactor configurations that re-combine hydrogen and oxygen at safe rates and controllable rates and control the exothermic heat release and system level to analyze the round trip efficiency, response time, and cycling stability of thousands of charge-discharge cycles in order to prove the viability of the strategy relative to other chemical hydrogen storage models, like ammonia synthesis or liquid organic hydrogen carriers [4,5]. The combination of copper-chlorine hydrogen production with other sources of heat other than desalination waste heat serves prospects of greatly expanded practice of the production of copper-chlorine hydrogen, whether coupled with concentrated solar power systems by direct solar heating of reactors, coupled with nuclear reactors which can supply steady baseload thermal energy at suitable temperatures, or coupled with industrial waste heat such as steel mills, chemical plants or refineries that presently discard much thermal energy that could be used in thermochemical applications.

The digitalization and next-level control provide opportunities to enhance operational performance due to real-time optimization, predictive maintenance, and autonomous operation. Machine learning software can be used to examine the data recorded in the operation to find the best setpoints of reaction temperatures, flow rates, and recycle ratios that result in the highest rate of hydrogen production with the least energy use and minimal chemical losses, and it is possible to develop digital twins that allow testing control strategies and predicting the behavior of the system under different conditions. Condition-based predictive maintenance can help reduce unplanned downtime and extend the lifetime of equipment by means of condition-based maintenance interventions by predicting failures before they happen, as well as autonomous control systems using model predictive control and optimization can allow lights-out mode operation with very little human intervention, minimizing labor expenses and enhancing safety due to reduced worker exposure to dangerous chemicals and high-temperature equipment. Lastly, the policy and regulatory environment will have to evolve to facilitate implementation of integrated systems, such as creation of relevant safety standards of thermochemical hydrogen plants, interconnection standards of systems to supply water and hydrogen products to various distribution systems, and the development of incentive schemes to acknowledge a multiplicity of environmental and energy security advantages of integrated waste heat deployment schemes over single plants.

## Conclusion

This study has provided an impartial analysis of integrated desalination-hydrogen production systems based on waste heat recovery and copper-chlorine thermochemical cycles and proven the existence of a great potential to enhance the energy efficiency, greenhouse gas reduction, and offer sustainable solutions to interrelated water and energy issues. Moderate temperature demands of the copper-chlorine cycle are also compatible with the waste heat of thermal desalination processes, making it practical to integrate and deploy it with efficiencies of 38-44 % of the hydrogen produced and lowering the overall energy intensity of the water produced. Thermodynamic performance shows the exergy efficiency is 42-48% in optimized configurations, which is a significant improvement over standalone systems due to efficient use of waste heat and the use of a heat integration method. Economic analysis suggests that the cost of producing hydrogen is at the level of 3.2-4.8% per kilogram at a dual objective of desalination and hydrogen production, and is competitive with the conventional hydrogen sources, especially in a comparative analysis with environmental externalities and carbon price. Environmental and sustainability tests reveal a 65-78 % decrease in carbon emissions in contrast to the base situation of standalone plants, which contribute to global decarbonization goals in addition to managing water shortage issues in arid and coastal areas of the globe. Technical issues are still present in the scaling up of the components of the thermochemical cycle, materials technology, heat integration networks, and the reversible hydrogen storage capacities that may offer an added value in the form of energy storage services. The future research should look at demonstration projects at the industrially-relevant scales, long-period testing to confirm that the business can run, and look at alternative configurations that can bring in concentrated solar thermal heat sources, nuclear heat

sources, or other industrial streams of waste heat to increase the number of applications of this technology platform beyond desalination integration. Integrated approach is a paradigm shift between the concept of desalination and hydrogen production as different and independent processes to the realization of the opportunity to couple them synergistically, achieving better performance, economics, and sustainability. With freshwater, clean energy needs increasing worldwide, especially in water-stressed areas with strong access to solar energy and expanding hydrogen economies, the integrated desalination-hydrogen systems with the use of reversible thermochemical cycles become an attractive target to creating sustainable water-energy nexus solutions to help face simultaneously the many challenges confronting human civilization in the low-carbon future.

**Conflict of interest.** Nil

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