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Review Article

A critical review on integrated system design of solar thermochemical water-splitting cycle for hydrogen production



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- Research on thermochemical cycles, solar energy, and thermal storage are reviewed.
- Combinations of thermochemical cycle, solar energy, and thermal storage are given.
- Cu–Cl and S–I cycles are suitable for hydrogen production using solar energy.
- Composition, operation, performance, and application of the system is summarized.
- Future works on the integration design of solar thermochemical cycle is reviewed.

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GRAPHICAL ABSTRACT



ABSTRACT

The development of clean hydrogen production methods is important for large-scale hydrogen production applications. The solar thermochemical water-splitting cycle is a promising method that uses the heat provided by solar collectors for clean, efficient, and large-scale hydrogen production. This review summarizes state-of-the-art concentrated solar thermal, thermal storage, and thermochemical water-splitting cycle technologies that can be used for system integration from the perspective of integrated design. Possible schemes for combining these three technologies are also presented. The key issues of the solar copper-chlorine (Cu–Cl) and sulfur-iodine (S–I) cycles, which are the most-studied cycles, have been summarized from system composition, operation strategy, thermal and economic performance, and multi-scenario applications. Moreover, existing design ideas, schemes, and performances of solar thermochemical water-splitting cycles are

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Concentrated solar power Thermal storage Integrated system design summarized. The energy efficiency of the solar thermochemical water-splitting cycle is 15 -30%. The costs of the solar Cu–Cl and S–I hydrogen production systems are 1.63–9.47 $kg H_2$ and 5.41–10.40 $kg H_2$, respectively. This work also discusses the future challenges for system integration and offers an essential reference and guidance for building a clean, efficient, and large-scale hydrogen production system.

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Abbreviations

| ANL | Argonne National Laboratory |
|-----------------------|---|
| AP | Acidification potential |
| CeO ₂ /Ce | ₂ O ₃ Cerium oxide |
| CSP | Concentrated solar thermal power |
| Cu–Cl | Copper-chlorine |
| EED | Electro-electrodialysis |
| FeO/Fe ₃ 0 | D4 Iron oxide |
| FeCl | Iron-chlorine |
| GA | General Atomics |
| GWP | Global warming potential |
| HyS | Hybrid Sulfur |
| INET | Institute of Nuclear and New Energy |
| | Technology |
| JAEA | Japan Atomic Energy Agency |
| LCA | Life cycle assessment |
| LFR | Linear Fresnel reflectors |
| L-L | Liquid-liquid |
| Symbols | |
| 1111/122 |) Higher heating value of H2 (kI/mol) |
| 07 | Every of other products (kl/mol H) |
| ex _{useful} | Exergy of other products (K)/mol H ₂) |
| exelec | Liectricity power input (k)/inor H ₂) |
| Greek sy | mbols |

Energy efficiency

 $\eta_{\rm energy}$

| $\eta_{\rm conv}$ | Efficiency of converting thermal energy into |
|--------------------------|---|
| | electric energy |
| Mg–Cl | Magnesium-chlorine |
| ODP | Ozone depletion potential |
| ORC | Organic Rankine cycle |
| PCM | Phase change material |
| PTC | Parabolic trough collectors |
| PV-EL | Photovoltaic-electrolysis |
| SCS | Solar collection system |
| SPD | Solar parabolic dishes |
| SPT | Solar power tower |
| S—I | Sulfur-iodine |
| TES | Thermal storage system |
| TRR | Total revenue requirement |
| TWSC | Thermochemical water splitting cycle |
| UOIT | University of Ontario Institute of Technology |
| V-Cl | Vanadium-chlorine |
| Zn/ZnO | Zinc oxide |
| Q _{heat} | Heat requirement of the system (kJ/mol H ₂) |
| ex_{H_2} | Exergy of H ₂ (kJ/mol) |
| ex _{in} | Heat input (kJ/mol H ₂) |
| η_{exergy} | Exergy efficiency |
| | |
| | |

Introduction

Global energy demand is steadily increasing with the industrialization and electrification of human society. Currently, 80% of the primary global-energy supply comes from fossil fuels [1]. In an effort to prevent the catastrophic consequences of global climate change, international agreements have been reached to limit carbon emissions, and a global consensus to vigorously develop renewable energy has emerged. The proportion of renewable energy in the primary energy supply is expected to reach 63% by 2050 [2], and solar energy will constitute a large proportion of renewable energy.

Hydrogen is considered a clean energy source with significant developmental potential and plays an important role in the chemical, metallurgical, and transportation industries [3]. However, on Earth, hydrogen is not a primary energy source that can be obtained directly and can only be produced by consuming other energy sources and substances [4]. Traditional hydrogen production methods include coal gasification, steam methane reforming, biomass gasification, and water electrolysis. Fossil-fuel-based hydrogen production methods usually have high carbon emissions, which contradicts the goal of carbon neutrality. Future hydrogen production should be based on renewable resources and have low carbon emissions [5–7]. The splitting of hydrogen from water using solar energy is an attractive method. Water electrolysis and the thermochemical water-splitting cycle (TWSC) are both considered potential schemes for large-scale hydrogen production above 500 t/day [8]. The technical maturity of photovoltaic-electrolysis (PV-EL) is relatively high, but the overall efficiency of this technology is limited owing to the large amount of electricity consumed. The TWSC is primarily driven by thermal energy. Therefore, the efficiency of the solar thermochemical cycle is theoretically higher than that of PV-EL. The TWSC is also suitable for large-scale hydrogen production because of its economies of scale [9]. Safari et al. [8] suggested that the solar thermochemical cycle is a long-term pathway toward green hydrogen production.

The TWSC relies on a series of chemical reactions to produce hydrogen and oxygen from water [10]. Except for water, hydrogen, and oxygen, all other substances can be recycled during the process. Dincer et al. [11] evaluated the environmental impacts of 19 hydrogen production methods using life cycle assessment (LCA). They found that TWSCs have lower global warming potential (GWP), acidification potential (AP), and cost than electrolysis-based (electrolysis, hightemperature electrolysis, or plasma-arc decomposition) hydrogen production methods. According to the form of the input energy, TWSCs can be divided into pure TWSCs that require only heat, and hybrid TWSCs that require heat and a small amount of electricity [12]. To achieve future-oriented large-scale hydrogen production and maintain the zerocarbon emission advantage of the TWSC, the primary energy source needs to provide a large amount of high-temperature heat and a small amount of electricity simultaneously. Therefore, nuclear and solar energy are considered ideal energy sources for TWSCs [13]. However, the location, quantity, safety, and disposal of nuclear waste limit the large-scale application of nuclear hydrogen production [14]. Furthermore, the heat

source for nuclear hydrogen production is waste heat, and its temperature is usually a fixed value, which limits the choice of TWSCs and scale of hydrogen production. By contrast, the integration of solar energy with TWSCs results in greater flexibility. Fig. 1 shows a schematic of the solar TWSC cycle system. The solar collection system (SCS) converts the collected solar energy into heat, then transfers the heat to the heat storage media of the thermal storage system (TES). Some of the heat storage media flows and exchanges heat in the system to meet the heat requirement of the TWSC reactions, while others can be supplied to the circulating working medium of the power generation part to generate electricity for the hybrid TWSCs or to the power grid. Under extreme weather conditions, electricity can also be provided by the power grid to ensure stable hydrogen production. The integration of solar energy and TWSCs makes the hydrogen production process flexible, efficient, and environmentally friendly [8,15], and is a large-scale hydrogen production solution toward carbon neutrality.

This study reviews the key issues and integrated design concepts of solar thermochemical cycle hydrogen-production systems. Section 2 introduces the principles, classifications, temperature requirements, advantages, and disadvantages of the nine mainstream TWSCs. The characteristics of concentrated solar-thermal power (CSP) technology and related properties of the heat storage media are also discussed. Subsequently, the possible combinations of CSP, TES, and TWSC technology are summarized. In Section 3, the Cu-Cl and S-I cycles, which are the most studied and feasible for solar integration, are selected as typical TWSCs. The basic processes and research status of the two TWSCs are summarized. Previous studies on the design concept and performance evaluation of the integrated system are reviewed, and future research directions and prospects of the integrated system are summarized

This study aimed to determine which TWSCs have the potential to be integrated with solar thermal technology. The topics discussed in this article are nine mainstream TWSCs, four CSP technologies, TES materials, and the possibility and feasibility of their integration. This study provides a new perspective for comprehensively evaluating the integration of the TWSC and solar thermal technology from the perspective of system integration efficiency. In addition, the economics, environmental friendliness, safety, production scale, and other factors are also considered. Another innovation of this study is that it summarizes the design schemes and performances of existing solar thermochemical cycle hydrogenproduction systems. This paper offers a crucial reference and guidance for design ideas toward high-efficiency, lowcarbon emission, and large-scale solar thermochemical hydrogen production in the future.

Classification, screening, and temperature matching of solar technology and thermochemical cycles

Thermochemical cycle

Before discussing the integrated design of the TWSC and solar energy, it is necessary to explain the performance of the TWSC itself and clarify its requirements for solar technology. The following conditions need to be clarified:

- 1) The temperature requirement of each TWSC reaction and the types of energy required by the TWSC.
- 2) The indicators used to evaluate and screen the TWSC to achieve clean, efficient, and large-scale hydrogen production in an integrated system, as well as the potential of different types of TWSCs when combined with solar energy.

More than 200 TWSCs have been proposed since Funk and Reinstrom first introduced the concept of a thermochemical cycle to produce hydrogen through a multi-step thermally driven chemical reaction using water as a raw material in the 1960s [16]. In 1969, the European Community Joint Research Center compiled 24 TWSCs, known as Mark Cycles [17]. Subsequently, in 1977, General Atomics summarized more than 200 TWSCs [18]. As shown in Fig. 2, TWSCs can be classified into two, three, four, and other cycles with more steps, according to the number of reactions involved in the cycle. Twostep TWSCs typically require a reaction temperature above 2000 K. The temperature requirement can be reduced to less than 1200 K in some three-step TWSCs, and less than 800 K in some four-step TWSCs. In addition to reducing the reaction temperature by increasing the number of reaction steps [15], electricity can be used to replace high-temperature reactions. However, the addition of electricity typically complicates this process. Not all types of TWSCs are suitable for integrated design and industrialization. Scholars have conducted studies to compare and evaluate TWSCs. Fig. 3 summarizes the main evaluation indicators, including efficiency, economics, environmental friendliness, chemical reaction difficulties, safety, process complexity, production scale, and technical maturity. Some representative studies and the main conclusions obtained from them are listed in Table S1 in the supplementary information.

Based on previous TWSC comparisons and evaluation results [8,19–21], nine mainstream TWSCs were selected for this study according to their environmental friendliness, efficiency, economics, and development prospects. Publications published between 1970 and 2022 were searched using the Scopus database. The search terms and number of retrieved publications are listed in Table S2 in the supplementary information. The year distribution of publications is shown in Fig. 4. As shown in Fig. 4, the TWSC has gained increasing attention from scholars since 2005. Among the nine TWSCs, the S–I and Zn/ZnO cycles have the most publications.

Fig. 5 summarizes the chemical equations, reaction temperatures, and endothermic and exothermic properties of the selected TWSCs. It is also marked when there is a requirement for electricity. As shown in Fig. 5, the maximum reaction temperatures of the three TWSCs from the metal oxide family are all above 1000 °C. The maximum reaction temperatures of the TWSCs from the sulfur family, the V–Cl cycle, and the Fe–Cl cycle are between 500 and 1000 °C. The maximum reaction temperatures for the Cu–Cl and Mg–Cl cycles are lower than 500 °C.

Currently, TWSCs from the metal oxide family have three critical problems: excessively high-temperature requirements, poor material stability, and difficulty in practical operation of the solar furnace owing to the high temperature. The Zn/ZnO cycle has a higher oxygen exchange capacity and faster hydrolysis rate than the Ce₂O₃/CeO₂ and FeO/Fe₃O₄ cycles, making it easier to produce hydrogen [23]. However, if separation is not performed in a timely manner during the reduction process, the Zn vapor recombines with O₂, resulting in a lower conversion rate of ZnO [24,25]. Although some scholars have proposed that the product can be separated in time by quenching, use of this method results in a large energy loss. For non-volatile metal oxide cycles, such as the CeO/Ce₂O₃ cycle, the advantage is that the materials remain solid during the reaction, enhancing the sustainability of the cycle [26,27]. The use of low-valent metaloxide-doped CeO can lower the reduction temperature. However, this doping makes metal-oxide powders more likely to sinter, thereby lowering the hydrogen yield [27]. The FeO/ Fe₃O₄ cycle has a high theoretical hydrogen yield, low cost, and readily available raw materials. However, achieving a high yield requires a high temperature of up to 2200 K. This temperature exceeds the boiling point of Fe₃O₄, which can easily cause gasification and sintering of the material. Although it is suggested that the reduction temperature can be reduced by doping the reactants with Ni, Zn, and Co, sintering problems in the reaction still exist [28]. The GWP of the metal oxide family is the highest among the selected TWSCs because quenching and segregation of the products require a large amount of electrical power. The GWP of the most representative Zn/ZnO cycle is close to 12 kg CO_2 eq/kg H_2 , which is 20 times that of the S-I cycle.

TWSCs from the sulfur family are considered promising for industrialization [27] and superior to TWSCs from the chlorine family in terms of the potential for helping mitigate global warming [8]. The theoretical efficiency of the S-I cycle is 51% [29], and the raw materials of the cycle are abundant and relatively inexpensive. The main problem with the S-I cycle is that the temperature required for sulfuric acid decomposition is relatively high. At such high temperatures, the high corrosiveness of sulfuric acid poses challenges to the design of the reactor. Moreover, the two-phase separation after the Bunsen reaction and the concentration and decomposition of HI are complex. The advantages of the HyS cycle are that it has fewer reaction steps and is comparable to the S-I cycle in terms of efficiency, cost, and environmental friendliness [15]. The HyS cycle avoids HI decomposition by using an electrolyzer to generate H₂SO₄ and H₂. However, it should be noted that H₂SO₄ generation in the electrolyzer causes electrode and membrane corrosion. SO₂ from the anode chamber may pass through the membrane to reach the cathode, resulting in a decrease in electrolysis efficiency and clogging of the reaction products [30]. As for the safety of the sulfur family cycles, the HyS cycle contains two types of toxic and corrosive gases: H₂SO₄ and SO₂. If the reactor or pipelines are corroded by H₂SO₄, a large amount of high-concentration and high-temperature H₂SO₄ vapor together with toxic SO₂ will leak from the cracks and endanger worker safety. In addition to H₂SO₄ and SO₂, the HI and I₂ vapors contained in the S–I cycle are also highly toxic reactants, which makes the risk level of the S-I cycle higher than that of the HyS cycle. Some research institutes have suggested that the toxicity of reactants in the sulfur family should be seriously



Fig. 1 - Schematic diagram of solar TWSC hydrogen production system.

considered during the industrialization stage [17]. With a GWP value of nearly 0.5 kg CO_2 eq/kg H₂, the sulfur family has one of the lowest GWP values, which means that it possesses high environmental friendliness.

The difficulty and challenge of TWSCs from the chlorine family are that they involve the reverse Deacon reaction, that is, $Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + 1/2O_2(g)$ [31]. To prevent the occurrence of the reverse Deacon reaction, the quenching method is commonly used to separate the products in time; however, this method leads to a waste of thermal energy and reduction in energy efficiency. The raw material for the Fe-Cl cycle is relatively inexpensive, but the theoretical efficiency is only 30%, and the GWP value of this cycle is relatively high [31]. Moreover, the conversion rates are low for the hydrogengenerating and FeCl₂-generating reactions [32]. The theoretical maximum efficiency of the V-Cl cycle was calculated to be 65% using pinch analysis [29]. Many variants of this cycle have been developed [33,34]. However, the separation of products and reactants is still difficult, the yield is low, and the efficiency is only 31–46% [20]. The Cu–Cl cycle has three-, four-, and fivestep variants. The four-step Cu-Cl cycle requires less heat than the other variants and performs better in terms of acidification potential (AP), GWP, and ozone depletion potential (ODP), which means it is more environmentally friendly [35]. The maximum reaction temperature of the Cu-Cl cycle is low and the energy efficiency can reach 55% [36]. No catalyst is required for this cycle, and all steps have been demonstrated to be achievable on a laboratory scale [31]. The investigation and optimization of the hydrolysis and electrolysis reactions are current concerns of scholars. The energy efficiency of the Mg-Cl cycle is close to that of the Cu-Cl cycle. Although the reverse Deacon reaction is not present in the Mg-Cl cycle, this cycle requires a high amount of electricity, and the cost and GWP are also higher than those of the Cu-Cl cycle [8,15].

Regarding the safety of the chlorine family, the toxic and corrosive HCl gas present in these cycles is the biggest threat to the health of workers. The risk level of the chlorine family is the same as that of the HyS cycle and lower than that of the S–I cycle. The chlorine family has one of the lowest GWPs, which is nearly 0.5–2.5 kg CO₂ eq/kg H₂. It is also a family with high environmental friendliness.

In general, the nine mainstream TWSCs have unique advantages and disadvantages; not all of the TWSCs are suitable for integrated design with solar energy, which will be discussed in the following sections.

Solar thermal collection and storage

Research on solar thermal collection and storage is mainly applied to solar thermal power generation. When solar energy is used as an energy source for TWSCs, specific solar thermal collection and storage issues must be considered. Many TWSCs require higher heat-source temperatures than solar thermal power generation. Another notable difference is that the TWSC requires two or more heat sources at different temperatures. The critical issues that should be considered in the integrated design of CSP and TES technologies can be listed as follows:

- Classification and basic evaluation parameters of CSP technologies. The most suitable CSP technology for combining with the TWSC. Methods to meet the heating needs at multiple temperatures while reducing the cost and carbon emissions of the integrated system.
- The most suitable TES technologies to be combined with TWSC. Advantages and disadvantages of direct and indirect heat-storage methods. Applicability of the heat storage media.

These are our concerns in this paper.

CSP technology

As shown in Fig. 6, CSP can be divided into four types according to the solar collection methods: linear Fresnel reflector (LFR), parabolic trough collector (PTC), solar power tower (SPT), and solar parabolic dishes (SPD).

PTC and LFR are line-focus technologies with medium and high working temperatures, respectively, making them suitable for meeting the low- and mid-temperature requirements of TWSCs. PTC has a high commercial maturity, lower costs, and is more convenient for large-scale arrangements [37–39]. Considering the technical requirements for large-scale hydrogen production, PTC is more suitable than LFR for integration with TWSCs.

SPT and SPD are point-focus technologies with high and very high concentration ratios and working temperatures [40,41]. The working temperatures of the two technologies can reach above 800 °C, allowing them to satisfy the hightemperature requirements of the TWSC. SPD systems have the advantages of flexible installation and a high working temperature. The disadvantage lies in the small power capacity of a single unit [42], and the cost per unit power is higher than that of SPT systems [43]. SPD are generally used for direct power generation and are not equipped with thermal energy storage systems. Therefore, SPT is more suitable for integration with TWSCs than SPD.

The technical characteristics of the four CSP technologies are summarized in Table S3 in the supplementary information.

On the basis of meeting the temperature required for TWSC reactions, the CSP system should involve a technology that is safe, reliable, lower in cost, and more mature. Furthermore, the selected CSP technology should be combined with a heat-storage system to achieve a continuous and stable heat supply for large-scale continuous hydrogen production. Therefore, PTC and SPT are more suitable for integration with the TWSC. Nevertheless, using SPT/PTC alone to provide heat at multiple temperatures, or using SPT and PTC simultaneously, requires further discussion and evaluation according to the selected TWSC.

Thermal energy storage

The fluctuating and intermittent properties of solar energy adversely affect stable hydrogen production by TWSCs. The fluctuating heat supply leads to the disruption of flow and cycle disorder; alternation between day and night leads to repetitive starts and stops of the cycle. Stable operation of the TWSC can be maintained using TES technology. The integration of TES provides a stable heat supply for the continuous operation of TWSCs and shortens the cycle start-up period for the intermittent operation of TWSCs. Therefore, TES technology is essential for integrated design.

TES can be divided into direct and indirect heat storage systems depending on whether the heat storage media is the same as the heat transfer fluid. The structures of the two systems are shown in Fig. 7. Direct heat storage uses the same type of heat transfer fluid and heat storage media, eliminating the heat exchange process between different materials and reducing the cost of the heat exchangers [37]. However, it is necessary to install thermal insulation on the piping to prevent clogging caused by condensation of the molten salt. The direct-heat storage method is mostly used in the existing integrated designs. For indirect-heat storage, the selection of the heat-transfer fluid must be considered. Synthetic oil and water/steam can be used as heat transfer fluids for low-tomid-temperature heat requirements. For TWSCs with midto-high-temperature requirements, particles and gases (air, He, and CO₂) can be used [44], but currently, these technologies are still immature, and commercialization progress is slow.

The TES system stores heat and serves as an intermediary for heat transfer between the solar collectors and TWSC. The density, specific heat, thermal conductivity, other physical parameters, and cost of the heat storage media significantly affect the performance and operation of the integrated system. The classification of the heat storage media is shown in Fig. 8. Sensible-heat storage is currently commercialized and widely used. This storage method is convenient and easy to integrate. Moreover, there are no significant volume changes during the heat storage or release processes, but the heat storage capacity is limited. Latent-heat storage media, using the phase-change latent heat, can reduce the volume of the heat-storage tank and temperature difference between the inlet and outlet media [37,45]. Thermochemical heat storage involves the separation of substances and chemical reactions, and is a complex and costly process that is currently in the theoretical research and experimental stages.

The working temperature ranges and related parameters for some commonly used sensible-heat storage media are listed in Table S4 in the supplementary information. Typical molten salts can be classified into nitrate/nitrite, carbonate, fluoride, and chloride salts. Nitrate/nitrite salts are widely used in solar thermal power generation, but have a maximum



Fig. 2 – Classification of TWSCs based on the number of reaction steps.



Fig. 3 – Evaluation aspects and specific indicators of TWSCs.



Fig. 4 – The numbers of publications about the TWSCs selected in this paper from 1970 to 2022 (data from Ref. [22]).

working temperature of 565 °C, making them unsuitable for high-temperature reactions such as those in the S–I cycle. The maximum working temperature of the carbonate and fluoride salts can reach higher than 900 °C, but the specific heat of fluoride salts is relatively low. The chloride salts exhibit a maximum working temperature of 800 °C. Chloride salts are less expensive, but more corrosive at high temperatures, and possess a lower specific heat [46]. Based on the properties above, it is recommended to use highly commercialized nitrate/nitrite salts as the heat storage media for the low-tomid-temperature requirements of TWSCs (<500 °C). For high-temperature requirements (>500 °C), chlorides and carbonates are recommended because of their high working temperatures and relatively low prices.

Table S5 in the supplementary information lists the technical parameters of the commonly used latent-heat storage media. Latent-heat storage media can be divided into organic, inorganic, and eutectic compounds based on the composition of the substance [47]. The organic phase-change materials are generally only suitable at low temperatures (<260 °C) [48]. Salt hydrates have irreversible melting-freezing problems, which reduce the available salt hydrate in every charge-discharge cycle [49]. The problem with metallic materials is that they provide lower fusion heat per unit weight, and their working temperatures are relatively low [50]. Furthermore, considering the low maturity of latent-heat storage technology, the commonly used latent-heat storage media are unsuitable for integration with the TWSC.

Possibility of integrating solar energy with the TWSC

The ability of the working temperatures of the solar collector and storage system to meet the requirements of each TWSC step is the essential factor that determines whether they can be integrated with the TWSC. Therefore, the suitability of the three technologies for an integrated system can be screened based on the working temperature. With the working temperature as the key parameter, Fig. 9 summarizes the commonly used CSP technologies, heat storage media, and TWSC methods.

As can be seen from Fig. 9, the reaction temperatures of the three metal oxide cycles are all above 1600 °C, while the highest temperature provided by the four CSP technologies was the 1500 °C provided by the SPD. Moreover, the working temperatures of commonly used heat storage media cannot meet these temperature requirements. These results indicate that metal oxide cycles are not currently suitable for large-scale thermochemical-cycle hydrogen production using solar energy as the heat source [51,52], while the reaction heat required by the other six TWSCs can be provided by solar energy.



Fig. 5 – Basic information for the TWSCs selected in this paper.

It can also be seen from Fig. 9 that a TWSC generally involves multiple reactions, and some of the reaction temperature differences are large, whereas some are small. To avoid the extremely large exergy loss caused by the large temperature difference, multiple CSP systems should be considered when integrating with the TWSC. Reactions with small temperature differences can be heated using a single CSP system, whereas those with large temperature

established in the United Sta

differences can be heated separately using multiple CSP systems at different working temperatures. Owing to system complexity and area limitations, it is not recommended to use more than two CSP technologies. Because some hightemperature reaction products are reactants for lowtemperature reactions, the heat released from the cooling process of the high-temperature products can be recovered to supply heat for the subsequent low-temperature reaction, and the low-temperature heat (below 200 °C) should preferably be provided by process waste heat.

The energy flow for the integrated solar TWSC is shown in Fig. 10, and the main energy losses in the entire process from solar energy to hydrogen are estimated. The energy loss in the TWSC section was the highest, accounting for nearly half of the total energy loss.

Most existing research studies calculate energy efficiency only starting from the receiver part. The energy efficiency of the solar TWSC from the receiver to hydrogen can reach up to 52.6%. When considering the loss of solar energy from the atmosphere to the receiver, approximately 15–30% of the solar energy is converted into H_2 energy.

To make full use of the heat from the heat storage media, cascade heat utilization should employed. The highest-grade heat is first supplied to the high-temperature reaction, and the lower-grade heat after cooling is supplied to the subsequent low-temperature reactions in turn. Based on the above considerations, we summarized the feasible integration schemes of the TWSC, CSP, and TES sensible-heat storage in Table 1.

Integration of solar energy with typical TWSCs

Among the nine mainstream TWSCs discussed in Section 2, the Cu–Cl and S–I cycles have received extensive attention from scholars. Demonstration projects for the two cycles were

established in the United States, Japan, South Korea, and China. These are the most promising TWSCs for industrialization. Therefore, this section uses Cu–Cl and S–I cycles to represent hybrid and pure thermochemical cycles, respectively, to review related studies on the integrated design of solar TWSC systems.

Integration of solar energy with Cu–Cl cycle

Basic introduction to the Cu–Cl cycle

The highest reaction temperature in the Cu–Cl cycle is only 500 °C. Therefore, commercialized solar-heat collection and storage technologies can be used to meet the heat requirements. Thus, the Cu–Cl cycle has the potential to be integrated with solar energy. According to the number of reaction steps, the Cu–Cl cycle can be divided into three-, four, and five-step methods. The four-step Cu–Cl cycle has the highest theoretical efficiency and the lowest GWP and AP [53]. It also has the largest number of studies on its combination with solar energy. A simplified four-step Cu–Cl cycle is shown in Fig. 11.

The Cu–Cl cycle consists of four steps: hydrolysis, thermolysis, electrolysis, and drying. The feed water is heated to 400 °C and undergoes a gas-solid hydrolysis reaction with the dried CuCl₂ solid. CuO·CuCl₂ is formed, with the simultaneous generation of HCl gas. After gas-solid separation, the two products are subjected to thermolysis and electrolysis reactions. Before participating in the thermolysis reaction, the CuO·CuCl₂ should meet the heating demand from 400 to 500 °C. This heating demand is also the highest grade requirement in the Cu–Cl cycle. After the thermolysis reaction, the heat of the 500 °C liquid CuCl and O₂ products are recovered. The HCl generated at 400 °C undergoes exothermic cooling to 25 °C before participating in the electrolysis reaction. The released heat is often used for heating the dried CuCl₂ from 100 to 400 °C. HCl and CuCl are electrolyzed together to produce H₂ gas and



Fig. 6 - Four CSP technologies, along with their capacity range.

CuCl₂ solution at room temperature. After passing through the gas-liquid separation device, H_2 is purified and collected, and the CuCl₂ solution is dried and placed back into the hydrolysis reactor to complete a cycle.

The University of Ontario Institute of Technology (UOIT) in Canada and the Argonne National Laboratory (ANL) of the United States have carried out many studies on the Cu–Cl cycle. Fig. 12 summarizes the main research status of the Cu–Cl cycle. The research institutions investigating the 4-step Cu–Cl cycle and the focused issues are summarized according to the reaction steps. The hydrolysis reaction is an endothermic non-catalytic gas-solid reaction at 350–400 °C. Daggupati et al. [54] reported that the influencing factors of this reaction can be summarized from three aspects: (1) the kinetics of the gas-solid reaction, (2) the size distribution of the solid particles, and (3) the flow pattern of solids and gases in the reactor. The temperature, pressure, and concentration of the reactants significantly affect the gas-solid reaction [55]. Particle size also has an important effect. Oversized particles can interfere with gas-solid mass transfer and increase side reactions [56]. Pope et al. developed a fluidized bed reactor for the hydrolysis of CuCl₂ solid particles at high temperatures, and attempted to add excess steam to the reactor to increase the conversion and reaction rate [57]. Ferrandon et al. indicated that a spray reactor increased the yield of CuCl₂ to 95% [58]. To simplify reaction operation, the hydrolysis and drying processes can be integrated into one step, which also makes the size of the CuCl₂ particles more uniform and controllable [59]. To study the thermolysis reaction, Ferrandon et al. [56] calculated the decomposition rate of CuO·CuCl₂. UOIT is developing oxygen production reactors that can be integrated with solar energy [60]. The development of membrane and electrode materials is a major constraint for the electrolysis reactions. The membrane materials used in the Cu-Cl cycle must be highly corrosion-resistant. The drying process can involve either spray- or crystallization-drying.



Fig. 7 - Schematic diagram of direct (a) and indirect (b) heat storage.



The studies above mainly focused on improving a specific process or reaction, but their impact on the overall performance of the Cu–Cl cycle has not been extensively investigated.

Integration design of Cu-Cl cycle and solar energy

The Cu–Cl cycle has low reaction temperatures and small reaction temperature differences, and is suitable for use with solar energy as an energy source. In addition to heat, the Cu–Cl cycle requires electricity. The following problems should be considered when the S–I cycle is integrated with solar energy: (1) The method for using CSP to heat the Cu–Cl cycle should be clarified. (2) The electricity requirements of the Cu–Cl cycle should be met. (3) The efficiency and economic performance of solar Cu–Cl cycle systems should be evaluated. Studies for solar Cu–Cl cycle systems are summarized in Table 2.

The energy efficiency of the overall system is defined in Table 2 as the energy output divided by the energy input. Based on the higher heating value (HHV) of hydrogen, the efficiency of the system is given by

$$\eta_{\text{energy}} = \frac{\text{HHV}(\text{H}_2)}{\text{Q}_{\text{heat}} + \frac{W_{\text{elec}}}{\eta_{\text{prove}}}}$$
(1)

where η_{energy} represents the energy efficiency of the entire system; HHV(H₂) (kJ/mol H₂) represents the higher heating value of hydrogen; Q_{heat} (kJ/mol H₂) represents the heat requirement of the system; W_{elec} (kJ/mol H₂) represents the overall electricity requirements of the system; and η_{conv} is the heat to power conversion efficiency.

The exergy efficiency of the overall system is defined as the energy divided by the exergy input and exergy output, and is given by

$$\eta_{\text{exergy}} = \frac{\mathbf{e}\mathbf{x}_{H_2} + \mathbf{e}\mathbf{x}_{\text{useful}}}{\mathbf{e}\mathbf{x}_{\text{in}} + \mathbf{e}\mathbf{x}_{\text{elec}}}$$
(2)

where η_{exergy} represents the exergy efficiency of the entire system; e_{H_2} (kJ/mol H₂) represents the exergy of the produced

hydrogen; ex_{useful} (kJ/mol H₂) represents the exergy of other products of the system such as oxygen, heating, and electricity; ex_{in} (kJ/mol H₂) represents the heat input; and ex_{elec} (kJ/mol H₂) represents the electricity power input.

As can be seen from Table 2, the CSP technologies commonly used for the solar Cu–Cl cycle are SPT and PTC. Molten salts are usually chosen as TES materials, and in recent years, some studies have used phase-change materials as TES materials. In addition to solar energy, various renewable energy sources are used to meet the electricity requirements of the Cu–Cl cycle in the integration schemes, and the corresponding power generation technologies and efficiencies are also different.

First, because the two reaction temperatures with the greatest heat demand in the Cu-Cl cycle are between 400 and 550 °C, the Cu–Cl cycle is a low-temperature cycle, and only one CSP technology is needed to meet the heating demand. The existing design concept involves heat cascade utilization to make full use of the solar energy. Because the electrolysis reaction is performed at room temperature, no heat supply is required in this step. Therefore, the ideal heat-exchange sequence is thermolysis, hydrolysis, and drying. In terms of the heat supply, molten salts can directly supply heat to the reactor and heat exchanger [60,67,68,73]. Furthermore, because the water needs to participate in the reaction at 400 °C, there is another concept to first transfer heat to the water (which has an extremely high specific heat value) and then use the water as a medium to supply heat to the Cu–Cl cycle [61,63,66]. This method can reduce the piping and heat exchangers required for molten salts and avoid clogging and corrosion problems caused by the solidification of molten salt in long lengths of pipe. Heated vapor can also drive the turbine to generate electricity.

The electrolysis reaction is considered the key to the Cu–Cl cycle [64] and greatly impacts the performance of the integrated system. Table 3 lists the heat and electricity requirements of the Cu–Cl cycle. The energy consumed by



Fig. 9 – Summary of the operating temperatures of CSP, TES, and TWSC technologies.

electrolysis accounts for approximately 15% of the total energy consumption. Wang et al. [60] found that the solar energy required for the electrolysis reaction accounts for nearly 60% of the total energy requirement when the electricity is provided by solar energy (energy efficiency 30–35%), and the efficiency of the electrolyzer (energy efficiency 80%) is also considered. This result shows that the power generation process requires more attention in the integrated design.

Based on ensuring the solar energy can supply heat for the Cu–Cl cycle, in order to generate electricity, many scholars have proposed different integrated designs. Some scholars have considered using other power sources directly: Ishaq et al. [63,65] used wind turbines to generate electricity; Sayyaadi et al. [77] directly drew electricity from the grid to maintain a continuous and reliable supply of electricity. Another design concept is using renewable energy such as



Fig. 10 - Energy flow of the integrated solar TWSC system.

| Table 1 — Feasible integration schemes for TWSC, CSP, and TES technologies. | | | | | | | | |
|---|-----------------------|-------------|----------------------|---------------------------|-----|----------|------|------------------------|
| TWSC | Reaction | Temperature | Heat source | Heat source arrangement | | technolo | gies | Suitable sensible heat |
| | steps requirement (°C | | Outer heat source | Internal heat recovery | LFR | PTC | SPT | storage materials |
| S—I | 1 | 120 | | 1 | | | | / |
| | 2 | 850 | 1 | | | | 1 | Chloride salts |
| | 3 | 450 | 1 | | 1 | 1 | 1 | Nitrate/Nitrite salts |
| HyS | 1 | 100 | | ✓ | | | | / |
| | 2 | 850 | 1 | | | | 1 | Chloride salts |
| Cu-Cl | 1 | 400 | 1 | | 1 | 1 | 1 | Nitrate/Nitrite salts |
| | 2 | 500 | 1 | | 1 | 1 | 1 | Nitrate/Nitrite salts |
| | 3 | 100 | | 1 | | | | / |
| | 4 | 25 | | 1 | | | | / |
| V-Cl | 1 | 25 | | 1 | | | | / |
| | 2 | 750 | 1 | | | | 1 | Chloride salts |
| | 3 | 200 | | 1 | | | | / |
| | 4 | 850 | 1 | | | | 1 | / |
| Fe-Cl | 1 | 450 | 1 | | 1 | 1 | 1 | Nitrate/Nitrite salts |
| | 2 | 100 | | 1 | | | | / |
| | 3 | 300 | | 1 | | | | / |
| | 4 | 800 | 1 | | | | 1 | Chloride salts |
| Mg–Cl | 1 | 450 | 1 | | 1 | 1 | 1 | Nitrate/Nitrite salts |
| | 2 | 400 | 1 | | 1 | 1 | 1 | Nitrate/Nitrite salts |
| | 3 | 70 | | 1 | | | | / |

solar, biomass, and geothermal energy to drive turbines for electricity generation (Rankine cycle or Kalina cycle). Wang et al. [60] and Sadeghi et al. [67,73,75] designed integrated systems with solar energy as the only energy source. Solar heat was used to produce steam to drive steam turbines for electricity generation. Ishaq et al. [66] used a biomass combustion-driven gas-steam combined cycle power generation; Siddiqui et al. [64] and Temiz et al. [70,71] used a steam turbine power generation system driven by geothermal energy to provide electricity. The most commonly used integration scheme in the papers above is a renewable energydriven turbine to generate electricity for the Cu–Cl cycle.

The efficiency and economic performance of the solar Cu–Cl cycle varies under different system-design schemes. From Table 2, it can be seen that the energy efficiency of the solar Cu–Cl cycle calculated in existing studies varies from 19.6 to 52.6%. The design schemes and energy-efficiency calculation methods were carefully examined in this study. It was found that some scholars used only the heating value of H_2 , as shown in Eq. (1); however, some have also considered the enthalpy of



by-product O₂. Some studies used the enthalpy of the produced t steam as a benefit rather than the exergy of the steam, which leads to a higher efficiency than those of the other studies. In moreover, some researchers used the heat received by the TWSC, and some used solar energy as the inlet of the system. According to the above considerations, the energy efficiency of a

system using solar energy as the only energy source and pro-

ducing hydrogen as the only product is approximately 15–30%. The hydrogen production costs of the integrated system are listed in Table 4. Sadeghi designed a Cu–Cl cycle entirely powered by solar energy with a hydrogen production scale of 0.1 kg/s. The cost of hydrogen production was calculated to be 1.63 \$/kg H₂ after considering equipment purchase, operation, and maintenance costs, as well as other factors [68]. Temiz et al. [71] designed a system for solar heating coupled with geothermal electricity generation, with a hydrogen production scale of 296.9 t/year. The cost was evaluated to be 2.84 \$/kg H₂ after considering replacement, operation, and maintenance costs, along with other costs in the future. The system was also integrated with a water purification system that supplied fresh water and electricity as outputs. Sadeghi and Ghandehariun [75] designed a system powered only by solar energy with an overall energy efficiency of 28.77% and hydrogen production scale of 1530.4 kg/h. After considering capital recovery, debt investment return, and operation and maintenance costs, the cost of hydrogen production was calculated to be 7.58-9.47 \$/kg H₂ because there are no other products available for sale. Sadeghi et al. [68] calculated the purchase cost of an integrated system and found that 76.72% of the purchase cost of the entire system is related to the solar field, including the solar heliostat field and receiver system. From the perspective of energy flow, Sadeghi and Ghandehariun [75] calculated and found that the largest energy loss of an integrated system is in the solar-energy-related part, accounting for 32.54% of the total energy demand. Some scholars have also concluded that the highest exergy loss of

the system occurs in the solar subsystem [67,73]. All of the above results indicate that the solar subsystem has a significant impact on the efficiency and cost of the integrated system. With the development of solar technology, the efficiency and economic performance of the solar Cu–Cl cycle system can be further improved.

Since 2007, many investigators have proposed integrated designs for solar Cu–Cl cycle hydrogen production systems. A summary of the system composition design for the solar Cu–Cl cycle is presented in Fig. 13. Scholars have used solar energy and various renewable energy sources for hydrogen production. Hydrogen is produced along with electricity, heating, and cooling, and desalination technology is used to produce fresh water. The integrated systems are different; therefore, the performance of these systems cannot be directly compared. However, studies have shown that the solar Cu–Cl cycle is a promising hydrogen production solution with wide application scenarios and prospects.

There are many related studies on the integration scheme and performance analysis of the solar Cu-Cl cycle hydrogenproduction system. To improve the system efficiency and reduce the cost of hydrogen production, progress can be made in the following three aspects: (1) further research on the Cu-Cl cycle and solar subsystems, (2) designing a clean, stable, and efficient heat and electricity supply, and (3) increasing the product output of the system while producing hydrogen. For example, the performance of the Cu-Cl cycle can be improved by using a spray reactor to simplify the process, identifying reasonable electrolysis reaction parameters, and designing the Cu-Cl cycle with an optimal technology combination. The efficiency can be improved by cascade utilization of solar energy and the use of wind turbines, steam turbines, ocean thermoelectric power generation, and other technologies to generate electricity. Furthermore, economic performance can be improved by introducing renewable energy sources such as



Fig. 12 – Summary of research progress for the Cu-Cl cycle.

wind and geothermal energy into the system and adding subsystems to produce electricity, steam, fresh water, and other commodities. These measures can help achieve a clean, efficient, and economical hydrogen production system.

Integration of solar energy with S-I cycle

Basic introduction to the S–I cycle

The S–I cycle was proposed by General Atomics (GA) in the 1970s [78] and proved to be one of the most promising TWSC technologies. The S–I cycle has the advantages of high theoretical efficiency and large-scale application potential and is suitable for integration with solar energy. The general schematic of the S–I cycle is shown in Fig. 14.

The S–I cycle consists of three sections: Bunsen reaction, sulfuric acid decomposition, and HI decomposition. First, sulfuric acid and hydroiodic acid are produced by H_2O , I_2 , and SO_2 in a low-temperature exothermic Bunsen reaction. These two acids are separated and then enter the decomposition sections. The sulfuric acid absorbs heat and decomposes at approximately 850 °C, producing SO_2 , O_2 , and H_2O . The sulfuric acid decomposition section is the highest-temperature part of the S–I cycle. The hydroiodic acid decomposes at approximately 400 °C, to produce H_2 and I_2 . Finally, SO_2 and I_2 produced from sulfuric acid decomposition and hydroiodic acid decomposition, respectively, are recycled and sent back to the Bunsen reaction.

The S–I cycle is theoretically highly efficient and has potential for large-scale applications. However, there are still many problems with the S–I cycle, such as complex separation processes, high reaction temperatures, unclear thermodynamic properties, and difficult concentration processes. Currently, the S–I cycle is mainly studied in the United States, Germany, China, Japan, and South Korea. The current research institutes for each process are summarized in Fig. 15. The research institutions studying the S–I cycle and the focused issues are summarized according to the reaction

steps. Hydroiodic and sulfuric acid are produced by the Bunsen reaction. For the acid separation unit, the most commonly used method is liquid-liquid separation (L-L separation), which was proposed by GA [78]. In the L-L separation method, the sulfuric and hydriodic acid phases separate spontaneously when excess I₂ and H₂O are added to the Bunsen reaction. However, recycling excess I2 and H2O increases the energy consumption of the system. Lee et al. [79] proposed optimal operating conditions for the Bunsen process, and Zhang et al. [80] studied the optimization of Bunsen reaction conditions and phase separation characteristics of a complex system. Nomura et al. [81], Zhang et al. [82], and Ying et al. [83] introduced electrochemical Bunsen reactions to increase the reaction rate and efficiency. The sulfuric acid decomposition unit had the highest temperature in the S-I cycle. The design of the reactor is particularly important because the high temperature and concentration of sulfuric acid often corrode the reaction vessel [84]. Furthermore, the catalyst selection for the sulfuric acid decomposition unit has been studied by GA and other institutions [85]. After separation from the Bunsen reaction, purified hydriodic acid forms a strong non-ideal ternary mixture with I2 and H2O. In the HI-I2-H2O ternary system, there are many problems, such as the HI-H₂O azeotrope, L-L equilibrium, immiscibility of I2-H2O, and multiiodine ion combinations, making it difficult to predict the complex thermodynamic properties of the system. Furthermore, because of the azeotrope problem, hydroiodic acid cannot be extracted using the ordinary distillation method. O'Keefe et al. [86] proposed the use of phosphoric acid to extract hydroiodic acid in the S-I cycle, Engels and Roth et al. [87] proposed a reaction distillation flowsheet that concentrated and decomposed the hydroiodic acid at the same time, and JAEA and INET proposed the use of the EED method to concentrate the hydroiodic acid [88].

GA, JAEA, and other institutions have proposed different methods for various sections to improve the efficiency of the S-I cycle. Table 5 lists the energy requirements of the

| Table 2 - Summary of research on Cu-Cl cycle and solar energy integration. | | | | | | | | |
|--|------------|-------------|--|----------|--|----------------|----------------|--|
| Authors | CSP | External | Electricity | Heat | TES materials | Energy | Exergy | |
| | technology | energies | - | recovery | | efficiency (%) | efficiency (%) | |
| Wang et al. [60] | SPT | No | Solar-thermal driven turbine | Yes | Molten salt (HiTEC) | / | / | |
| Ratlamwala and Dincer [61] | SPT | Electricity | Solar-thermal Kalina cycle + grid power | Yes | Molten salt | 40.0 | 49.2 | |
| Ouagued et al. [62] | PTC | Electricity | Not mentioned | Yes | Molten salt | / | / | |
| Ishaq et al. [63] | SPT | Wind energy | Wind turbine | Yes | Molten salt | 49 | 48.2 | |
| Siddiqui et al. [64] | SPT | Geothermal | Geothermal Rankine cycle | Yes | LiF/BaF(67/33) ^a | 19.6 | 19.1 | |
| Ishaq et al. [65] | SPT | Wind energy | Wind turbine | Yes | LiF/BaF(67/33) ^a | 45.3 | 44.9 | |
| Ishaq and Dincer [66] | SPT | Biomass | Reheat Rankine cycle | Yes | Molten salt | 29.9 | 31.5 | |
| Sadeghi and Ghandehariun [67] | SPT | No | Solar-thermal Rankine cycle | Yes | Air + PCM: Molten salt CaF ₂ /CaSO ₄ /CaMoO ₄ (49/41.1/9.6) ^a | 45.07 | 49.04 | |
| Sadeghi et al. [68] | SPT | No | Solar-thermal Rankine cycle | Yes | Air + PCM: Molten salt CaF ₂ /CaSO ₄ /CaMoO ₄ (49/41.1/9.6) ^a | 48.2 | 45 | |
| Ishaq and Dincer [69] | SPT | Electricity | Not mentioned | Yes | Not mentioned | 32.7 | 33.2 | |
| Temiz and Dincer [70] | PTC | Geothermal | Solar-thermal Rankine cycle | Yes | Solar salt | 52.6 | 47.1 | |
| Temiz and Dincer [71] | PTC | Geothermal | Geothermal Rankine cycle | Yes | Molten salt (HiTEC) | 27.4 | 17.3 | |
| Temiz and Dincer [72] | BiPV | Geothermal | PV | Yes | No | 22.8 | 18.2 | |
| Sadeghi et al. [73] | SPT | No | Solar-thermal Rankine cycle | Yes | Air +PCM: Molten salt CaF2/CaSO4/CaMoO4(49/41.1/9.6) ^a | 49.9 | 44.9 | |
| Dincer and Ishaq [74] | SPT | Electricity | Not mentioned | Yes | Molten salt | / | / | |
| Sadeghi and Ghandehariun [75] | SPT | No | Solar-thermal Rankine cycle | Yes | Carbonate salt Li ₂ CO ₃ /Na ₂ CO ₃ /K ₂ CO ₃ (32.1/33.4/34.5) ^b | 28.77 | / | |
| ^a mol. %. | | | | | | | | |

^b wt. %.

| Table 3 – Heat and electricity requirements of the Cu–Cl cycle. | | | | | |
|---|--|--|--|--|--|
| Authors | Heat requirement (kJ/mol H ₂) | Electricity requirement (kJ/mol H ₂) | | | |
| Wang et al. [60] | 499.5 | 52.3 | | | |
| Temiz and Dincer [70] | 473.4 | 142.9 | | | |
| Temiz and Dincer [71] | 473 | 130 | | | |
| Temiz and Dincer [72] | 473 | 156 | | | |
| Orhan et al. [76] | 505.88 | 88.2 | | | |

different sections of the improved S-I cycle. The main heat demand in the S-I cycle is from the high-temperature sulfuric acid decomposition section and mid-temperature hydroiodic acid decomposition section. As shown in Table 5, the decomposition of high-temperature sulfuric acid is carried out at approximately 850 °C, which requires heat absorption of 321–452 kJ/mol H₂, and the HI decomposition is carried out at approximately 300 °C in the heat absorption range 119.5-237 kJ/mol H₂. Although the Bunsen reaction is exothermic, it can only provide low-grade heat below 120 °C, which can only be used for heat recovery, and cannot be used in the two high-temperature reactions. Therefore, when solar energy is used to provide heat for the S-I cycle, it should be carefully considered how to satisfy the different requirements of temperature and heat in the sulfuric acid decomposition and HI decomposition units.

S—I cycle integration with CSP

The S–I cycle is suitable for integration with solar thermal technology to achieve large-scale hydrogen production using renewable energy. To meet the high reaction temperature and large reaction temperature difference requirements of the S–I cycle, these problems should be considered when integrating the S–I cycle with the solar system: (1) The manner in which the CSP system powers the S–I cycle should be clarified. (2) The operation strategies between the stable S–I cycle part and intermittent solar part should be coordinated. (3) The efficiency and economic performance of the solar S–I cycle system should be evaluated. Studies on the integration of the S–I cycle and the solar system are summarized in Table 6.

A thermodynamic performance assessment of the S–I cycle powered by a solar tower was performed by Yilmaz et al. The thermal and entropy efficiencies of the S–I cycle were 43.85% and 62.39%, respectively. After incorporating the solar tower, the overall thermal and extropy efficiencies decreased to 32.76 and 34.56%, respectively. An integrated system including solar dish technology, the S–I cycle, and ORC was proposed by Mehrpooya et al. The overall system efficiency was 36.3% and the entropy efficiency was 56.33%. This high efficiency is due to the high energy conversion ratio of the ORC. Giaconia, Liberatore, and Cumpston et al. proposed the overall structure of an integrated solar thermal S–I thermochemical cycle system and focused on process design, system simulation, and system performance assessment. The studies of these three scholars were analyzed as follows.

First, different heat-providing modes were proposed considering the different temperature requirements and heat demands of the sulfuric and hydriodic acid decomposition

| | thods Other productions | | sis Electricity: 50.49 MW | Blectricity: 47.6 GWh/yea Heat: 452.8 GWh/year | Freshwater: 160392.1 t/y ent (TRR) method Hydrogen only |
|-------------------------------|--------------------------|-------------|---------------------------|---|--|
| | Costing met | | Exergoeconomics analys | Present value method | Total revenue requireme |
| | Costs ($^{\rm K}$ | | 1.63 | 2.84 | 7.58-9.47 |
| | Production scales (kg/h) | | 360 | 33.9 | 1530.4 |
| -Cl cycle. | supplies | Electricity | Solar thermal | Geothermal | Solar thermal |
| or the solar Cu- | Energy : | Heat | Solar thermal | Solar thermal | Solar thermal |
| Table 4 – Cost calculations f | Authors | | Sadeghi et al. [68] | Temiz and Dincer [71] | Sadeghi and Ghandehariun [75] |

sections. Giaconia used methane combustion to heat the hightemperature sulfuric acid decomposition section and parabolic troughs to heat the medium-temperature hydriodic acid decomposition section. This system achieved progress in that 70% of the entire required system energy was provided by solar energy. Liberatore used a solar tower to supply heat for the high-temperature sulfuric acid decomposition section and parabolic troughs for the medium-temperature hydriodic acid decomposition section. To overcome the problem of intermittency of solar energy, the system uses fossil fuels as a backup heat source for energy supplementation, and 80% of the required system energy is supplied by solar energy. Cumpston proposed a 100% solar-heated solar S-I thermochemical cycle system, which used a solar tower to supply heat for high-temperature sulfuric acid decomposition and solar parabolic troughs to supply heat for mediumtemperature hydriodic acid decomposition.

Moreover, owing to the intermittence of solar energy and the stable heat demand of the chemical part, the matching of the energy demand and supply and the operation mode of these two parts must be considered. Giaconia proposed a feasible operation model to maintain a steady S-I cycle by adding a fossil fuel supply. The system also reduced solar energy requirement in the summer, and shut down the solar part in the winter, when there was little solar energy. In the one-day operation mode, the high-temperature part continued using the heat supplied by methane combustion. The medium-temperature part used molten salt to store heat and stabilize the chemical reactions. Considering the distribution of solar energy throughout the year, Liberatore controlled the S-I cycle to produce hydrogen from February to November, and fossil fuels were used as a backup energy supply when solar energy was insufficient. In a one-day operation, there were two modes: (1) During the day, the system used a solar tower to supply high-temperature sulfuric acid decomposition, and parabolic troughs were used to supply medium-temperature hydriodic acid decomposition. (2) During the night, the high-temperature sulfuric acid decomposition section stopped, whereas the parabolic troughs continued to supply heat using two molten salt storage tanks. The integration system of Cumpston uses 100% solar energy. During the day, the system kept the solar tower and parabolic troughs running to meet the heat demand of sulfuric acid and hydriodic decomposition, respectively, and used molten salts and chemical storage tanks for heat and chemical substance storage. At night, the system continuously maintained the S-I cycle by consuming the heat in the molten salts and chemical substances in the chemical storage tanks. Storing molten salts and chemical substances enabled stable operation of the solar S-I cycle, and greatly improved the flexibility of the entire system.

In addition, under different system structures and operating strategies, the thermal and economic performances of the solar thermal S-I cycle system were different. Thermal and economic performance is usually evaluated by the S-I cycle efficiency, overall efficiency, and hydrogen production costs. The Giaconia system produced hydrogen at a rate of 25,920 tons/year, and the S-I cycle efficiency was 37.3%. Because of the benefits from the income related to methanol production and the subsidies of renewable energy electricity, the hydrogen production cost of the system was 5.408–7.531 $kg H_2$. The hydrogen production scale in the Liberatore system reached 100 tons/day. The S-I cycle efficiency was 34%, and the overall efficiency was 21%. By considering the power generation benefits, the hydrogen production cost was 8.3-11.7 euro/kg H₂. The integrated system designed by Cumpston produced hydrogen at a rate of 5500 tons/year, with an efficiency of 38%. The hydrogen



Fig. 13 – Summary of the system composition design for the solar Cu-Cl cycle.



production cost of the system was 10.2-10.4 \$/kg H₂ after selling oxygen as a product. These three scholars calculated the cost of the solar part and other components, such as the S–I cycle and material storage. The solar power system accounted for 54.8%, 57.0%, and 58.6% of the total annual cost of the three systems, respectively. According to the economic performance assessment by Cumpston [93], the total investment cost of the solar tower accounts for 69.5% of the solar part. The studies above indicate that the economic performance of the integrated system has the potential to improve with the development of solar technologies, especially SPT technology.

The solar S–I cycle system is feasible for clean, efficient, and large-scale hydrogen production. The addition of other heat sources can increase the stability and reliability of the integrated systems. Liberatore improved the system performance by using fossil fuels as a backup heat supplement for insufficient solar energy. However, adding fossil fuels to the solar TWSC system reduces its environmental friendliness. Other clean energy sources, such as nuclear, geothermal, and biomass energy can be considered as future energy inputs. The generated hydrogen can be used directly, stored, transported, or converted to other products. However, there are still some technical and economic problems associated with hydrogen storage. There are good application prospects for the conversion of H₂ to methane, methanol, ammonia, and other chemical products that can be easily stored, transported, and utilized. Giaconia proposed a system that can generate methanol using hydrogen and CO_x produced by a solar S–I cycle system and fossil fuel combustion, respectively. Thus, the integrated system simultaneously reduced fossil fuel pollution, with an improved economic performance. Fig. 16 shows the possible routes of the solar S-I cycle system for poly-generation, which introduces other clean energy sources. The integrated system can produce hydrogen and other chemical products in a clean, efficient, and stable manner. The products can eventually be used in combustion, hydrogen batteries, chemical synthesis, steel smelting, cement preparation, and other fields. Therefore, the solar S-I cycle has promising application prospects.

The feasibility of the solar S-I cycle system was verified, and the thermal and economic performances of the system were evaluated. There are four pathways for improving the efficiency and lowering the cost of the system in the future: (1) improvement of the solar thermal technologies and S-I cycle, (2) design and parameter optimization of the integrated system, (3) optimization of the operating strategies, and (4) exploration of the application in multi-scenario and polygeneration systems. For example, the application of technologies such as the EED method, electrochemical Bunsen reaction, and efficient catalysis for sulfuric acid decomposition can improve the performance of the S-I cycle. The solar part can be optimized using advanced solar concentrating and heat storage technologies, such as high-temperature solar tower receivers and heat transfer using particles or air media. In addition, the improvement of the thermal performance,



Fig. 15 – Summary of research progress for the S–I cycle.

| Table 5 – Energy requirements of different processes in the S–I cycle. | | | | | | | | |
|--|--|---|----------------|-----------------------------------|--|--|--|--|
| Authors | HI decomposition (kJ/mol H ₂) | Sulfur acid decomposition (kJ/mol H ₂) | Efficiency (%) | Methods or conditions | | | | |
| Norman et al. [78] | 148 | 460 | 47 | Phosphoric extraction | | | | |
| Brown et al. [33] | 237 | 409 | 44 | Reaction distillation | | | | |
| Roth and Knoche [87] | 237 | 411.4 | / | Reaction distillation | | | | |
| Kasahara et al. [88] | 119.5-166.7 | 411.4 | 34–57 | EED | | | | |
| Lee et al. [89] | 167 | 411-420 | 47–48 | Optimized on operating conditions | | | | |

| Table 6 — Summary of solar thermal S—I thermochemical cycle system. | | | | | | | | |
|---|----------------------------------|---------------------------------|---|--------------------------|--------------------------|--------------------------|--|--|
| Authors | High-temperature requirements | Low-temperature requirements | TES materials | S—I efficiency (%) | Energy efficiency (%) | Exergy efficiency (%) | | |
| Giaconia et al. [90] | Fossil fuel | PTC | Molten salt NaNO3/KNO3 (60/40) ^a | 37.3 | / | / | | |
| Liberatore et al. [91] | SPT + Fossil fuel backup | PTC + Fossil fuel backup | SPT: Air PTC: KNO2–NaNO2 | 34 | 21 | / | | |
| Yilmaz and Selbaş [92] | SPT | SPT | Molten salt (solar salt) | 43.85 | 32.76 | 34.56 | | |
| Cumpston et al. [93] | SPT | PTC | Molten salt (HiTEC) | 38 | / | / | | |
| Mehrpooya et al. [94] | SPD | SPD | Oil (75.38% DiPHEther +24.62% BiPhenyl) ^b | / | 36.3 | 56.33 | | |
| ^a wt. %. ^b mol. %. | | | | | | | | |



Fig. 16 - Application scenario diagram of solar S-I cycle.

reduction of hydrogen production costs, and ultimately clean, efficient, stable, and large-scale energy supply can be achieved by designing a reliable energy supply structure, optimizing the operating parameters and strategies of the integrated system, introducing other energy sources, and producing other chemicals such as methanol to achieve polygeneration.

Conclusions and outlook

This paper reviews state-of-the-art mainstream thermochemical water-splitting cycle, concentrating solar thermal, and heat storage technologies. The three technologies were screened to be feasibly integrated into solar thermochemical cycle systems. From the perspectives of system compositions, operation strategies, thermal and economic performances, and multi-scenario applications, this work summarizes integrated systems that combine solar energy with two typical thermochemical cycles (the Cu–Cl and S–I cycles). Therefore, this study provides possible future research directions for integrated system design.

- These nine mainstream thermochemical cycles have unique advantages and disadvantages when combined with solar energy. The high reaction temperature of TWSCs from the metal oxide family results in excessively high temperature requirements for solar thermal collection and storage; therefore, they are unsuitable for integration with solar energy. The Cu-Cl and S-I cycles have proven to be advantageous in terms of efficiency, environmental friendliness, and production scale. The Cu-Cl and S-I cycles are thermochemical cycles with practical development potential for large-scale hydrogen production combined with solar energy. Among the CSP technologies, PTC and SPT are suitable for integration with TWSCs owing to their appropriate working temperatures, safety, reliability, low cost, and technical maturity. Sensible-heat storage is widely used among heat-storage technologies, and has heat-storage media that correspond to different temperature requirements. The commonly used latentheat storage media are unsuitable for integration with TWSCs.
- The energy efficiency of the solar TWSC was 15–30%. The Cu-Cl and S-I cycles are currently the most studied TWSC cycles. Some studies have been conducted on the integrated design of these two cycles combined with solar energy. The costs of the solar Cu-Cl and S-I hydrogen production systems are 1.63–9.47 Jkg H_2 and 5.4–10.40 \$/kg H₂, respectively. In terms of system composition, because the Cu-Cl cycle requires electricity to produce hydrogen, the source and production of electricity are key to the integrated design. Although the S-I cycle does not require electricity, it has high reaction temperatures and large temperature differences. Therefore, it is necessary to consider various concentrating solar technologies for heating at different temperatures when the S-I cycle is combined with solar energy. In terms of operation strategy, to coordinate the intermittent solar energy supply and stable hydrogen production, integrated systems use methods including backup heat sources, material storage, and intermittent operation, which are rarely seen in studies of the Cu-Cl cycle. In terms of broadening application scenarios, other renewable energy sources or technologies, including geothermal, wind power, and seawater desalination, are often introduced into the integrated design of the Cu-Cl cycle combined with solar energy to explore multi-scenario application solutions. This also brings a wealth of products to improve overall economic performance.
- In-depth research on solar technology, TWSC technology, and integrated designs is required to improve the thermal and economic performances of these systems in the future. In addition, the costs of solar-related components account for more than 50% of the total spending, and these

components are the major contributors to energy and exergy losses of the solar TWSC integrated system. This indicates that the thermal and economic performance of the integrated system has the potential to improve with the development of solar technology. Therefore, the integrated solar TWSC system using renewable energy is expected to be a clean, efficient, and large-scale pathway toward green hydrogen production.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2022.07.249.

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