

Development of a Solar-thermal ZnO/Zn Water-splitting Thermochemical Cycle

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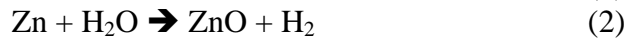
Executive Summary

The research carried out in this project involves developing an understanding of the two-step zinc oxide water splitting thermochemical cycle to produce hydrogen. Step 1 of the process is carried out using a high temperature transport tube reactor to dissociate zinc oxide. The forward zinc oxide dissociation reaction has been shown to be fast, but overall conversion is limited by the reverse-reaction of oxygen with zinc vapor near the exit portion of the reactor. Step 2 of the process to react zinc powder with steam to produce hydrogen is carried out in both a thermogravimetric analyzer and a transport tube reactor. It has been shown that this step can be driven to completion provided that enough residence time is provided (minutes required, not seconds). Each step in the process was demonstrated separately. The primary technical challenges are the materials development required to construct an 1800°C high temperature reactor tube that can withstand both thermal shock and oxygen, and the ability to properly design the reactor in order to prevent the reverse-reaction during the first step while maintaining high efficiency. The research results are summarized in detail in eight papers published in peer-reviewed research journals.

An economic evaluation of the process to produce 100,000 kg/day H₂ was done utilizing the H₂A program. Two cases were considered: (1) a 2015 case in which Step 1 was assumed to achieve 70% ZnO dissociation, where a hydrogen compressor was required to supply pipeline hydrogen and where heliostats were \$126.50/m²; and (2) a 2025 Case 2 in which Step 1 was assumed to achieve 85% dissociation, where the Step 2 operated at 300 psig to eliminate the need for downstream compressor and where heliostats were \$90/m². For Case 1, 3027 GWhr/yr energy was required to drive receivers located on fifteen 250 m tall towers. For Case 2, 2904 GWhr/yr energy was required to drive receivers located on fourteen 250 m tall towers. The LHV thermal efficiency for Case 1 is 38.2 %, while for Case 2 is 46.1%. Combining this with annual average solar efficiencies, the overall solar to hydrogen LHV efficiency for Case 1 is 17.2% and for Case 2 is 20.7%. The base case selling price of H₂ to achieve the 10% IRR for H₂A for Case 1 is \$5.58/kg, while of Case 2 is \$4.14/kg. It is believed that the zinc oxide thermochemical cycle can be developed to work. However, significant reductions in solar field costs (especially towers and heliostats) will be required to reduce the required selling price to \$3/kg (for the 10% IRR). It is recommended that research focus on developing suitable reactor materials and an efficient reactor design that reduces the tendency for reverse reaction from occurring (without inefficient quenching).

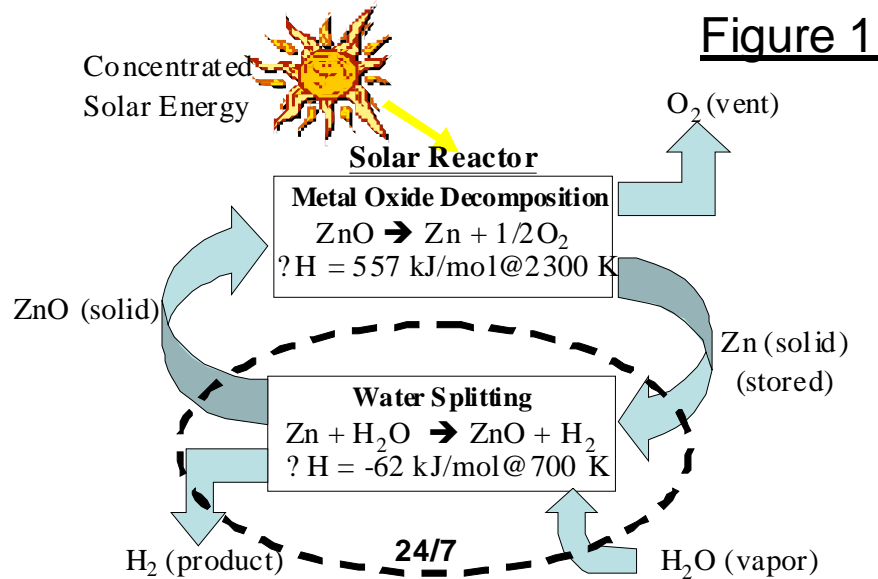
Introduction

All of the “high temperature” water splitting cycles involve thermal reduction of a metal oxide as the solar driven step of the process. In the simplest version of the cycle, the oxide is completely reduced to a lower valence state. In a subsequent, “off-sun” reaction, the reduced oxide is contacted with steam to produce hydrogen and regenerate the original oxide. This is the pattern for cycles based on the redox pairs examined most closely in the literature, i.e. Zn/ZnO. This approach to water splitting has only two steps, leading to a low potential for energy losses between cycle steps and during separations.



Second, process separations are relatively simple, involving only a solid phase and a gas phase. The hydrogen and oxygen are conveniently produced in separate reaction steps, eliminating the chance of explosive mixtures being formed. Finally, the solar step of the process is simple and easy to interface with intermittent solar energy. Solar energy is stored in the chemical bonds of solids, which are easy to store overnight. Hydrogen could be produced continuously simply by operating the hydrolysis reaction so that the solar reduced oxides are just used up over the

**Two step ZnO/Zn Process to split water
(both steps demonstrated)**



night (Figure 1). As a result, startup and shutdown of the solar portion of the plant would not severely affect the hydrolysis portion of the plant.

The Zn/ZnO cycle has been well studied, and its characteristics are helpful in understanding the potential for progress in operation of high temperature cycles in general. The ZnO dissociation reaction occurs at hot exposed surfaces, so that the kinetics are strongly dictated by diffusion away from the particle surface. It has been shown that if small ZnO particles are incorporated into an inert gas as an aerosol and irradiated, dissociation will be up to three orders of magnitude faster. For the high temperature cycles, receiver/reactors should be designed to maximize available area for reaction. Available surface area also plays a key role in determining kinetics and extent of reaction in the hydrolysis portion of the cycle. As Zn particles react with water, a layer of ZnO forms on the outside of the particles, forming a diffusion barrier and effectively passivating the rest of the particle. This has been observed with other cycles' hydrolysis steps as well. Zn particles should have very high specific surface areas to maximize conversion and cycle efficiency.

One of the key challenges to implementation of the Zn/ZnO process has been the propensity of Zn vapor and O₂ to recombine during cooling after the solar step. During the cooling process, there is a temperature regime the products must pass through in which this recombination is both thermodynamically and kinetically favored. The Zn and O₂ exist in a metastable state, with recombination kinetics requiring nucleation sites to proceed. As Zn particulates form, they provide excellent sites for recombination. It has been shown that by quenching the exit gas stream, high yields of Zn can be obtained. Experimental results using a water cooled copper tube achieved rapid cooling rates (~1000 K s⁻¹) and 18% total yield of Zn, with the added benefit that the particles were of extremely small size (10 nm – 30 nm). Such particles are more reactive in the hydrolysis step of the reaction, improving overall hydrogen yields. The main disadvantage of quenching is that most of the sensible and latent heats of the product streams are lost, decreasing efficiency and increasing overall required capital investment for the solar components. Currently, though, it is the only proven method of achieving high zinc yields.

A second difficulty in execution of the ZnO dissociation reaction is finding materials that are tolerant of oxidizing environments, maintain chemical integrity at high temperatures, and are resistant to thermal shock and stress. At the temperature of operation of all of the “high temperature” cycles, the list of materials is extremely limited.

Reviews of various solar-thermal water splitting technologies have been published as part of this work:

- Perkins, C. and A.W. Weimer, “Likely Near Term Solar-thermal Water Splitting Technologies,” International Journal of Hydrogen Energy, 29 (15), 1587-1599 (2004).
Perkins, C. and A.W. Weimer, “Solar-thermal Production of Renewable Hydrogen,” AICHE Journal, 55 (2), 286-293(2009).

Strengths of ZnO/Zn Cycle

1. Two-step simple cycle involving a high temperature endothermic Reaction (1) followed by an exothermic Reaction (2) that can be operated autothermally and at low temperature (~400°C);

2. Solar energy can be easily stored as Zn metal powder, using a storage tank padded with inert gas; the quantity of Zn metal powder simply increases when on-sun driving Reaction (1) and simply decreases during off-sun hours while Reaction (2) is consuming Zn.
3. Zinc is highly abundant, non-toxic and relatively inexpensive. It is one of the most common elements in the Earth's crust and is contained in common vitamins. Zinc oxide is used in sunscreens.

Challenges and Weaknesses

1. The reverse reaction of Zn(g) with O₂ limits overall conversion of Reaction (1); Using a gas quench to "freeze" Zn prior to reaction with O₂ poses major challenges with regard to recovery of sensible heat out of the solar reactor; It may be possible to use Zn metal powder to provide the quench, but development of this process is very challenging and would result in growth of particle size, thus reducing reactivity of Zn in Reaction (2).
2. The ultra-high 1800°C temperature with O₂ present required to drive Reaction (1) results in significant materials challenges regarding reactor design and a large heliostat/multiple tower requirement and the use of secondary concentrators to deliver the required solar power at concentrations of ~ 7,000X. Alumina and zirconia cannot be used due to thermal shock concerns.
3. Since inert gas is used to reduce the partial pressure of Zn(g) in the system so as to reduce the required reaction temperature (i.e. ~ 1750°C), it must be separated from produced O₂ and recycled.
4. It may be possible to develop a high temperature O₂ transport membrane for use within the reactor, but this is particularly difficult due to the presence of Zn vapor.

Status of Research

Both steps in the cycle, Reactions (1) and (2), have been demonstrated in the lab. Work has also progressed with solar-reactor engineering and an understanding of heat transfer for a multiple reaction tube receiver. However, residence times have been too limited in the solar reactor at this small scale to demonstrate anything worthwhile on-sun.

Step 1: Demonstrated Elements of Reaction (1)

Reaction (1) has been demonstrated and a mechanism and reaction kinetics rate expression have been identified. Forward reactions with conversions near 60% have been demonstrated based on the fact that the resulting powder is nanosized, indicative of the product powder resulting from precipitation in space from a vapor (Figure 2). Clearly, the fact that a vapor was present indicates the formation of Zn. Any subsequent ZnO resulted from back reaction. It is anticipated that 100% forward conversion could be obtained if fine ZnO feed could be dispersed as a dust cloud entering the solar reactor. A maximum of 18% overall conversion was demonstrated for Reaction (1). The limitation was both reverse reaction and the fact that some agglomerates were fed to the transport tube. Four peer-reviewed publications are available describing the results for Reaction (1):

Perkins, C., P.R. Lichty, and A.W. Weimer, "Thermal ZnO Dissociation in a Rapid Aerosol Reactor as part of a Solar Hydrogen Production Cycle," Int.J. of Hydrogen Energy, 33 (2), 499-510 (2008).

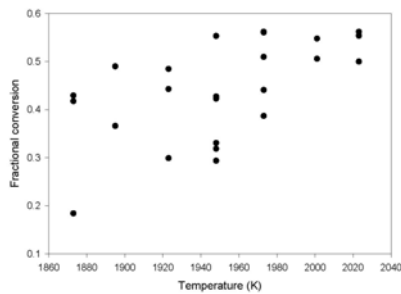
Perkins, C. and A.W. Weimer, “Computational Fluid Dynamics Simulation of a Tubular Aerosol Reactor for Solar-thermal ZnO Decomposition,” Journal of Solar Energy Engineering, **129**, 391-404 (2007).

Perkins, C., P.R. Lichty, and A.W. Weimer, “Determination of Aerosol Kinetics of Thermal ZnO Dissociation by Thermogravimetry,” Chemical Engineering Science **62**, 5952-962 (2007).

Perkins, C., P.R. Lichty, C. Bingham, and A.W. Weimer, “Effectiveness of a Fluid-wall for Preventing Oxidation in Solar-thermal Dissociation of ZnO,” AIChE Journal, **53** (7), 1830 (2007).

Aerosol Dissociation of ZnO

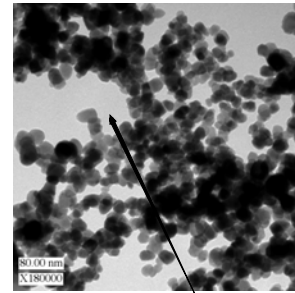
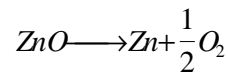
Figure 2



Forward conversions > 55% in less than 1s residence time
 Net conversions ~40% - highest ever achieved
 Aerosol rates 3-4 orders of magnitude greater than stationary configurations
 Rapid quench mitigates recombination



9 cm ID x 117 cm Al₂O₃ tube



Extremely small product particles (>50 nm) give fast rates in H₂ generation step

Aerosol processing can give fast rates for many high temperature cycles

Unproven Elements

1. Demonstration of overall conversions exceeding 18%
2. Demonstration of an efficient heat recovery step that also significantly reduces back reaction of Zn vapor and O₂.
3. Demonstration of suitable materials of construction for the reactor tube on-sun at 1750°C and with rapid temperature changes.

Step 2: Demonstrated Elements of Reaction (2)

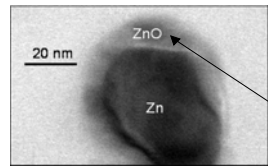
Reaction (2) has been demonstrated and a mechanism and reaction kinetics rate expression have been developed. It has been demonstrated that complete conversion can be achieved, but requires longer residence time and reaction at a temperature below the melting point of Zn in order to reduce solids handling complications (Figure 3). The reaction of Zn powder with

steam results in a Zn core/ZnO shell reacting particle. One peer-reviewed publication is available describing the results from these studies for Reaction (2);

Funke, H.H., H. Diaz, X. Liang, C.S. Carney, and A.W. Weimer, "Hydrogen Generation by Hydrolysis of Zinc Powder Aerosol," *Int. J. of Hydrogen Energy*, 33, 1127-1134 (2008).

Figure 3

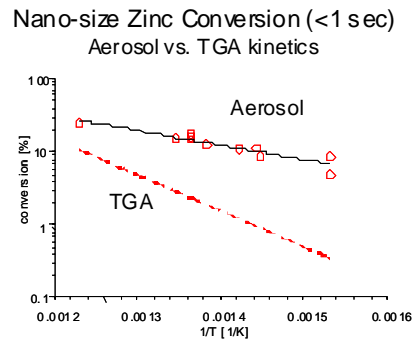
Production of hydrogen from Zn/H₂O



Reacted particle

- Successful generation of hydrogen
- Reaction is mass transfer limited – small particles are better
- Aerosol rates much faster than stationary configurations

Passivating ZnO film



Aerosol Kinetics >> TGA Kinetics

100% conversion demonstrated in TGA

Unproven Elements

1. Although complete conversion has been demonstrated using a thermogravimetric analyzer (TGA), no process demonstration has been made in larger scale research equipment.
2. Overall, the cycle has not been closed whereby product from Reaction (2) is used in Step (1) and vice versa.

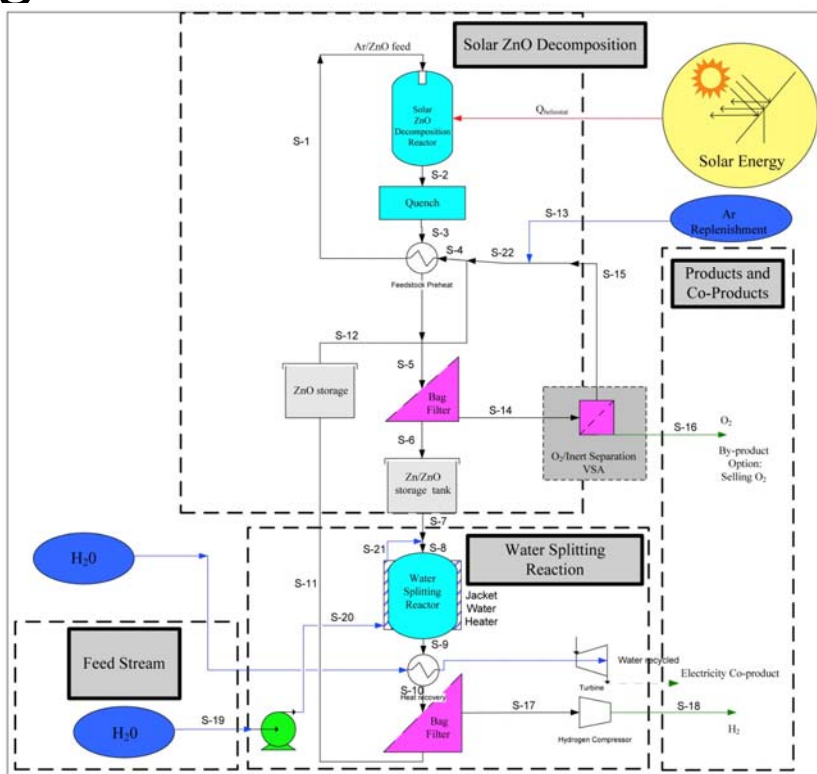
Plant Design for H₂A Analysis

The process flow diagram for a 3:1 molar flow rate of Argon:ZnO is shown in Figure 4. The thermal process is sized for producing 133,000 kg H₂/day and a 13 hr ZnO storage is used to operate at a plant capacity of 75%. The solar field design has been carried out by Al Lewandowski and is based on annual average insolation in Daggett, CA over the last 46 years. The annual average solar efficiency (sun to receiver/reactor) at 1800°C is 44.9%.

Reaction (1) is assumed to take place at ~1750°C with an external reaction tube/receiver temperature of 1800°C (reactor wall fixed at 1800°C). A vacuum swing adsorber (VSA) is used to separate O₂ from Ar so the Ar can be recycled to the process. Reaction (2) is assumed to be at 100% conversion. It is assumed that all sensible heat between 1800°C and 907°C is lost to some sort of quench. Likewise, it is assumed that all sensible heat between 907°C and a recovery temperature can be recovered.

For the 2015 case study, it is assumed that a fluid-wall two tube multi-tube transport reactor system is used and that the VSA is 3-stage. The reactor tubes are comprised of siliconized graphite. Also, Reaction (1) is assumed to occur at 70% conversion. Reaction (2) is assumed to occur at near atmospheric pressure so that a compressor is needed to supply H₂ at 300 psig to a H₂ pipeline.

Figure 4. Process Flowsheet



For the 2025 case study, it is assumed that a single tube multi-tube reactor system is used and that the VSA is single stage (less argon being recycled since the fluid-wall reaction process of the 2015 case is not being used). Reaction (1) is assumed to occur at 85% conversion. The Reaction (2) is assumed to occur at 300 psig so that a H₂ compressor is not required to supply a pipeline.

Details of Solar Process Design

Solar Heliostats/Towers designed per annual average sunlight, Daggett, CA for 100,000 kg/H₂/day. Chemical process designed for 133,000 kg H₂/day with 13 hr of storage for operation at 75% plant capacity.

2015 Case: 70% conversion for ZnO dissociation; 250 m towers; 3027 GWhr/yr needed to receiver

Each Receiver: 112 MW_{th}

3 Fields per receiver: each field is 35.9 acres of land; 73.3 % field efficiency to aperture
 358 heliostats (each 156 m²) per field; 55,938 m²/field; 41 MW_{th} each field

Secondary Concentrators: 90.8% efficiency; 106.8 m² surface area each CPC; 7414 suns concentration; of the 40.9 MW_{th} to CPC from one field, 37.2 MW_{th} is delivered to the receiver from one field; 112 MW_{th} supplied to each receiver by 3 secondary concentrators

Towers: 250 m tall (15 towers)

Overall Annual Average Efficiency (sun to receiver/reactors): 44.9%

30 tubes/receiver; each tube is 24 inches in diameter; semi-circle is about 35 ft in diameter

70% conversion requires 1.74 s residence time (TGA experimental); 8.49 m long

Reactor Temperature: 1800 °C (2173 K); ΔT = 104 K

Ar/ZnO: 3/1

2025 Case: 85% conversion for ZnO dissociation; 250 m towers; 2904 GWhr/day needed to receiver

Each Receiver: 112 MW_{th}

3 Fields per receiver: each field is 35.9 acres of land; 73.3 % field efficiency to aperture

358 heliostats (each 156 m²) per field; 55,938 m²/field; 41 MW_{th} from each field

Secondary Concentrators: 90.8% efficiency; 106.8 m² each CPC; 7414 suns concentration; of the 40.9 MW_{th} to CPC from one field, 37.2 MW_{th} is delivered to the receiver from one field; 112 MW_{th} supplied to each receiver by 3 secondary concentrators

Towers: 250 m tall (14 towers)

Overall Annual Average Efficiency (sun to receiver/reactors): 44.9%

30 tubes/receiver; each tube is 24 inches in diameter;

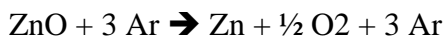
85% conversion requires 2.74 s residence time (TGA experimental); 14.9 m long

Reactor Temperature: 1800 °C (2173 K); Δ= 67 K

Ar/ZnO: 3/1

Reactor Energy Requirements Calculations

Energy Available per location in Daggett, CA (2787 kW-h/m²/yr in Mohave Desert)



$$\Delta H = 4.54 \times 10^5 \text{ J/mole (FACT at 100% conversion 2100 K)}$$



To produce 100,000 kg H₂/day requires

$$(100,000 \text{ kg H}_2/\text{day})(65.37 \text{ kg Zn}/ 2 \text{ kg H}_2) = 3.2685 \times 10^6 \text{ kg Zn/day}$$

$$(3.2685 \times 10^6 \text{ kg Zn/day})(81.37 \text{ kg ZnO}/65.37 \text{ kg Zn}) = 4.0685 \times 10^6 \text{ kg ZnO/day}$$

Determine kg ZnO required/day

If HT reactor is operating at 70% conversion,

Requires $(4.0685 \times 10^6 \text{ kg ZnO/day}) / (.7) = 5.812 \times 10^6 \text{ kg ZnO/day}$

If HT reactor operating at 85% conversion,

Requires $(4.0685 \times 10^6 \text{ kg ZnO/day}) / (.85) = 4.7865 \times 10^6 \text{ kg ZnO/day}$

Determine Q reactor for 70% conversion

Heat of Reaction

$(4.0685 \times 10^6 \text{ kg ZnO/day}) (1 \text{ mole}/0.08137 \text{ kg ZnO}) (4.54 \times 10^5 \text{ J/mole}) = 2.27 \times 10^{13} \text{ J/day}$
 $(2.27 \times 10^{13} \text{ J/day}) (1 \text{ hr}/3600 \text{ s}) (1 \text{ W}/1\text{J/s}) (1 \text{ GW}/1 \times 10^9 \text{ W}) = 6.3056 \text{ GWhr/day}$

Sensible Heat - ZnO

$(5.812 \times 10^6 \text{ kg ZnO/day}) (1 \text{ mole}/0.08137 \text{ kg ZnO}) (40.3 \text{ J/mol-K}) (2073 - 298 \text{ K}) = 5.11 \times 10^{12} \text{ J/d}$
 $(5.11 \times 10^{12} \text{ J/day}) (1 \text{ hr}/3600 \text{ s}) (1\text{W} / 1\text{J/s}) (1 \text{ GW}/1 \times 10^9 \text{ W}) = 1.4194 \text{ GWhr/day}$

Sensible Heat – Ar (3:1 Ar:ZnO ratio)

$(5.812 \times 10^6 \text{ kg ZnO/day}) (1 \text{ mol}/0.08137 \text{ kg ZnO}) (3 \text{ mol Ar}/1\text{mol ZnO}) (20.786 \text{ J/mol-K}) (2073-298 \text{ K}) = 7.906 \times 10^{12} \text{ J/day}$
 $(7.906 \times 10^{12} \text{ J/day}) (1 \text{ hr}/3600\text{s}) (1\text{W}/1\text{J/s}) (1 \text{ GW}/1 \times 10^9 \text{ W}) = 2.1961 \text{ GWhr/day}$

Determine Q reactor for 85% conversion

Heat of Reaction

$(4.0685 \times 10^6 \text{ kg ZnO/day}) (1 \text{ mole}/0.08137 \text{ kg ZO}) (4.54 \times 10^5 \text{ J/mole}) = 2.27 \times 10^{13} \text{ J/day}$
 $(2.27 \times 10^{13} \text{ J/day}) (1 \text{ hr}/3600 \text{ s}) (1 \text{ W}/1\text{J/s}) (1 \text{ GW}/1 \times 10^9 \text{ W}) = 6.3056 \text{ GWhr/day}$

Sensible Heat

$(4.7865 \times 10^6 \text{ kg ZnO/day}) (1 \text{ mole}/0.08137 \text{ kg ZnO}) (40.3 \text{ J/mol-K}) (2073 - 298 \text{ K}) = 4.208 \times 10^{12} \text{ J/d}$
 $(4.208 \times 10^{12} \text{ J/day}) (1 \text{ hr}/3600 \text{ s}) (1\text{W} / 1\text{J/s}) (1 \text{ GW}/1 \times 10^9 \text{ W}) = 1.1689 \text{ GWhr/day}$

Sensible Heat – Ar (3:1 Ar:ZnO ratio)

$(4.7865 \times 10^6 \text{ kg ZnO/day}) (1 \text{ mol}/0.08137 \text{ kg ZnO}) (3 \text{ mol Ar}/1\text{mol ZnO}) (20.786 \text{ J/mol-K}) (2073-298 \text{ K}) = 6.511 \times 10^{12} \text{ J/day}$
 $(6.511 \times 10^{12} \text{ J/day}) (1 \text{ hr}/3600\text{s}) (1\text{W}/1\text{J/s}) (1 \text{ GW}/1 \times 10^9 \text{ W}) = 1.8086 \text{ GWhr/day}$

Sensible Heat Recovery

After quenching products below the nucleation point for the particles (1180 K), sensible heat can be recovered from the process. This sensible heat can be used to preheat the argon and ZnO, reducing the overall thermal load for the process. This heat includes the sensible heat of the argon, the sensible heat of the unreacted ZnO, and the sensible heat/heat of fusion for the Zn products.

For the 70% conversion case:

$$(5.812 \times 10^6 \text{ kg ZnO/day})(1 \text{ mol}/0.08137 \text{ kg ZnO})(0.3 \text{ unconverted})(40.3 \text{ J/mol-K})(1180-350 \text{ K}) = 7.37 \times 10^{11} \text{ J/day}$$

$$(5.812 \times 10^6 \text{ kg ZnO/day})(1 \text{ mol}/0.08137 \text{ kg ZnO})(3 \text{ mol Ar/mol ZnO})(20.786 \text{ J/mol-K})(1180-350 \text{ K}) = 3.70 \times 10^{12} \text{ J/day}$$

For the 85% conversion case:

$$(4.7865 \times 10^6 \text{ kg ZnO/day})(1 \text{ mol}/0.08137 \text{ kg ZnO})(0.15 \text{ unconverted})(40.3 \text{ J/mol-K})(1180-350 \text{ K}) = 2.95 \times 10^{11} \text{ J/day}$$

$$(4.7865 \times 10^6 \text{ kg ZnO/day})(1 \text{ mol}/0.08137 \text{ kg ZnO})(3 \text{ mol Ar/mol ZnO})(20.786 \text{ J/mol-K})(1180-350 \text{ K}) = 3.07 \times 10^{12} \text{ J/day}$$

The Zn recovery is the same for both cases:

$$(3.2685 \times 10^6 \text{ kg Zn/day})(1 \text{ mol}/0.06537 \text{ mol Zn})(7320 \text{ J/mol}_{\text{fusion}} + (25.390 \text{ J/mol-K})(1180-350 \text{ K})) = 1.42 \times 10^{12} \text{ J/day}$$

The thermal load can be reduced, then, by the following amounts for each of the cases:

70% Conversion:

$$(7.37 \times 10^{11} + 3.70 \times 10^{12} + 1.42 \times 10^{12})(\text{J/day})(1 \text{ hour}/3600\text{s})(1\text{W}/1\text{J/s}) (1 \text{ GW}/10^9 \text{ W}) = 1.6269 \text{ GWhr/day}$$

85% Conversion:

$$(2.95 \times 10^{11} + 3.068 \times 10^{12} + 1.42 \times 10^{12})(\text{J/day})(1 \text{ hour}/3600\text{s})(1\text{W}/1\text{J/s}) (1 \text{ GW}/10^9 \text{ W}) = 1.3286 \text{ GWhr/day}$$

Examining the 70% conversion case:

$$(7.37 \times 10^{11} + 3.70 \times 10^{12} + 1.42 \times 10^{12})(\text{J/day}) / ((5.812 \times 10^6 \text{ kg ZnO})(1 \text{ mol}/0.08137 \text{ kg ZnO})(40.3 \text{ J/mol-K}) + (5.812 \times 10^6 \text{ kg ZnO/day})(1 \text{ mol}/0.08137 \text{ kg ZnO})(3 \text{ mol Ar/mol ZnO})(20.786 \text{ J/mol-K})) = 799 \text{ K}$$

Examining the 85% conversion case:

$$(2.95 \times 10^{11} + 3.07 \times 10^{12} + 1.42 \times 10^{12})(\text{J/day}) / ((4.7865 \times 10^6 \text{ kg ZnO})(1 \text{ mol}/0.08137 \text{ kg ZnO})(40.3 \text{ J/mol-K}) + (4.7865 \times 10^6 \text{ kg ZnO/day})(1 \text{ mol}/0.08137 \text{ kg ZnO})(3 \text{ mol Ar/mol ZnO})(20.786 \text{ J/mol-K})) = 792 \text{ K}$$

Using this amount of heat for preheat is feasible because the resulting temperature increases in the feedstocks do not exceed $1180 - 298 = 882 \text{ K}$.

The overall thermal load for the process is then:

70% Conversion:

$$6.306 + 1.419 + 2.196 - 1.627 = 8.295 \text{ GWhr/day} = 3,027 \text{ GWhr/yr}$$

85% Conversion:

$$6.306 + 1.169 + 1.809 - 1.329 = 7.955 \text{ GWhr/day} = 2,904 \text{ GWhr/yr}$$

2015 Case Study

Total Heliostat Field Size

For 70% conversion,

3,027 GWhr/yr required to reactor

15 receivers required (using 250 m towers)

Each field is 35.9 acres of land and supplies $55,938 \text{ m}^2$ of heliostat and we have 3 fields per reactor, then each reactor requires $167,813 \text{ m}^2$ of heliostat (each 156 m^2); this requires 15 receivers

Thus, the entire plant requires $2.517 \times 10^6 \text{ m}^2$ of heliostat. Total land area is 1620 acres. Total CPC area is 4800 m^2 . Each CPC (3 per receiver) is 106.8 m^2 .

A schematic of the design for a single tower/3 field system is shown in Figure 5.

Field Design for an 1800°C Receiver for a Mohave Desert Location (1 Tower; 3 Fields)

Basis

Daggett, CA TMY

Annual Energy

- 2787 kWhr/m²

- 2679 kWhr/m² when sun > 10°

Field	West	North	East
Field ?	.531	.563	.531
Receiver ?	.796	.815	.796
Net ?	.437	.469	.437

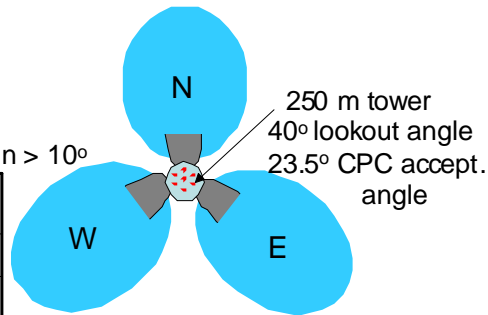


Figure 5

Annual Weighted ? = 0.449 (TMY)

Yearly Delivered Daggett (@ 45%), 1252 kWhr/m²

Annual Energy Delivered (to drive process): 202 GWhr/tower

167,814m² of total heliostat area (3 fields); 156 m² heliostats

108 acres total (3 fields)

CPC Concentration = 6.08x; Net Concentration = 7414 suns

Total Power to Receiver: 112 MW_{thermal}

2025 Case Study

For 85% conversion,

2,904 GWhr/yr required to reactor

14 receivers required (using 250 m towers)

Each field is 35.9 acres of land and supplies 55,938 m² of heliostat and we have 3 fields per reactor, then each reactor requires 167,813 m² of heliostat (each 156 m²); this requires 14 receivers

Thus, the entire plant requires 2.349×10^6 m² of heliostat. Total land area is 1512 acres. Total CPC area is 4480 m². Each CPC (3 per receiver) is 106.8 m².

H2A Analysis

Heliostat Costs

2015 Case: heliostat cost is \$126.5/m² installed

2025 Case: heliostat cost is \$90/m² installed

For 2015 case, $(2.517 \times 10^6 \text{ m}^2/\text{total system})(\$126.5/\text{m}^2) = \$318.4 \text{ M}$

For the 2025 case, the total heliostat cost at \$90/m² is \$211.4 M for the 85 % conversion.

Secondary Concentrator Costs

For the 2015 case, we have 4,800 m² of CPC. Assuming a cost per m² of 10 X that of the heliostats ($10 \times \$126.53/\text{m}^2 = \$1,265/\text{m}^2$), purchased, we have $(\$1,265/\text{m}^2)(4,800 \text{ m}^2/\text{total system}) = \6.07 M purchased

For the 2025 case, we have 4480 m² of CPC at $10 \times \$90/\text{m}^2 = \$900/\text{m}^2$, purchased. The total CPC cost for 2025 is \$4.03 M purchased.

Tower Cost

According to Sargent and Lundy (cost consistent with Greg Kolb of Sandia), cost of a 250 m tower/piping is \$14.447 M. This is calculated from $[600,000 + 17.72 (\text{m})^{2.392}] \times 1.41$ where the factor 1.41 accounts for inflation.

2015 Case

One tower is 250 m (\$14.447 M). We need 15 towers for the 2015 case, so the total tower/piping cost is \$216.7 M for towers.

2025 Case

One tower is 250 m (\$14.447 M). We need 14 towers for the 2025 case, so the total tower/piping cost is \$202.3 M for towers.

Receiver Cost

The cost of graphite tubes is \$13.68/linear inch for a 6" ID tube. Scaling capacity (area) by the 0.6 rule to a 24" ID tube:

$$(\$13.68/\text{linear inch})(16)^{0.6} = \$72.20/\text{linear inch} = \$2842/\text{linear m}$$

2015 Case

For 70% conversion, 1.74 s residence time is required, requiring 8.49m of tube length for 30 tubes per receiver:

The temperature drop across the tube is 104 K in this situation.

$(8.49 \text{ m})(\$2842/\text{linear m}) = \$24,129/\text{tube}$

With 30 tubes/receiver, 15 receivers, 450 tubes are required:

$(450 \text{ tubes})(\$24,129/\text{tube}) = \$10.86 \text{ M purchased}$

2025 Case

For 85% conversion, 2.74 s residence time is required, requiring 14.9 m of tube length:

The temperature drop across the tube is 67 K in this situation.

$(14.9 \text{ m})(\$2842/\text{linear m}) = \$43,346/\text{tube}$

With 30 tubes/receiver, 14 receivers, 420 tubes are required:

$(420 \text{ tubes})(\$42,346/\text{tube}) = \17.79 M

Two Scenarios

In both cases, equipment costs based on 2005 simulations to size and either vendor quotes or tables/figures from textbooks

2015 Case

Fluid-wall Reactor (outside siliconized graphite; inside graphite); 70% conversion; Ar inert gas; 3 stage Vacuum Swing Adsorbers; 2nd step at atmospheric pressure; \$126.5/m² heliostats

Zn/H₂O reactor cost is estimated for fluidized bed reactor at pressure. For batch turnover every 30 minutes and a reactor volume 5 times that of the stationary bed, the necessary reactor volume is 17,336 gal. An estimate for glass-lined steel (Peters & Timmerhaus) is \$308,000, and for high pressure stainless steel is \$560,000. To be conservative, these estimates have been doubled to \$616,000 for the 2015 case and \$1,120,000 for the 2025 case.

First Step

Heliostats (\$126.5/m ² installed);	\$ 318.4 M installed
Receiver Costs (15 receivers)	
Reactor (2 X \$10.86 M; double tubes)	\$ 21.72 M purchased
- Secondary concentrators	\$ 6.07 M purchased
Towers/Piping (15)	\$ 216.7 M installed
Preheater/Recovery Heater	\$ 5.00 M purchased
Bag Filter/Tanks	\$ 0.69 M purchased
Structures/Improvements (\$3/m ² from Sargent and Lundy)	\$ 7.55 M
Zinc oxide (45.7 kg ZnO/kg H ₂ ; assuming Need for 13 hr inventory; inventory is 2.48 x 10 ⁶ kg ZnO); cost of Zn metal is \$1,650/mt, assuming ZnO similar, then @ 80% Zn in ZnO (cost is \$1.33/kg)	\$ 3.30 M installed

Second Step

Steam Generation	\$ 2.09 M purchased
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Power Recovery Turbines	\$ 1.56 M purchased
Zn/H ₂ O Reactor	\$ 0.655 M purchased
Pumps/Motors	\$ 3.09 M purchased
VSA (3 stage)	\$ 16.51 M purchased vendor quote
VSA Screw Compressors (3 stage)	\$ 5.84 M purchased
Hydrogen compression components	\$ 25.00 M installed from compressor

2025 Case

Single Tube Siliconized Graphite Reactors; 85% conversion; single stage VSA; 2nd step at pressure; \$90/m² heliostats

First Step

Heliostats (\$90/m ² installed);	\$ 211.4 M installed
Receiver Costs (14 receivers)	
Reactor Tubes	\$ 17.79 M purchased
- Secondary concentrators	\$ 4.03 M purchased
Towers/Piping (9)	\$ 202.3 M installed
Preheater/Recovery Heater	\$ 5.0 M purchased
Bag Filter/Tanks	\$ 0.69 M purchased
Structures/Improvements (\$3/m ² from Sargent and Lundy)	\$ 7.05 M
Zinc oxide (45.7 kg ZnO/kg H ₂ ; assuming Need for 13 hr inventory; inventory is 2.48 x 10 ⁶ kg ZnO); cost of Zn metal is \$1,650/mt, assuming ZnO similar (80% Zn), then (cost is \$1.33/kg)	\$ 3.30 M installed

Second Step

Steam Generation	\$ 2.09 M purchased
Zn/H ₂ O Reactor (2 X for 300 psig)	\$ 1.20 M purchased
Pumps/Motors	\$ 0.54 M purchased
Power Recovery Turbine:	\$ 1.56 M purchased
VSA (1 stage)	\$ 5.53 M purchased vendor quote
VSA Screw Compressors (1 stage)	\$ 1.96 M purchased

Electricity Usage

VSA needs 2.33 kW-h/kg H₂/stage
 So, for 2015 case, needs 7.0 kW-h/kg H₂
 For 2025 case, needs 2.33 kW-hr/kg H₂

Some minimal additional electricity, say total electricity for 2015 case is 7.5 kW-h/kg H₂ and for 2025 case is 2.5 kW-h/kg H₂.

This electricity can be obtained from the Turbine Power Recovery, described below. By those calculations, we recover 2.77 kW-hr/kg H₂ of electricity; thus, in the 2015 case, 4.73 kW-hr/kg H₂ electricity are required to be provided at solar rates. In the 2025 case, 0.27 kW-hr/kg H₂ of electricity can be sold back to the grid.

Turbine Power Recovery

First Step Heat Recovery

Heat recovered in the first step is used to preheat the ZnO and Ar feed streams, as described above.

Second Step Heat Recovery

For the second step, we take 100,000 kg/day H₂ which is 5.00×10^7 mol/day. The heat of reaction is -105 kJ/mol, so this gives an output of 5.25×10^{12} J/day, or based on a 24 hour day for the second step, 60.7 MW.

We will now determine the amount of energy needed to produce the steam from water to determine if the process is autothermal and if any additional steam can be produced. To produce 100,000 kg/day of H₂ requires 5×10^7 moles/day of water. To produce steam at 400 K requires 40.657 kJ/mol to vaporize and 5.67 kJ/mol to heat to the vaporization point (starting at 25 °C). This is 46.33 kJ/mol. Hence, in order to produce the necessary steam for the reaction, we need [5.67×10^7 mol water/day] (46,330 J/mol) = 2.63×10^{12} J/day. So, we can generate all of the steam we need from water for the second reaction using the heat of reaction. It is autothermal.

We have 5.25×10^{12} J – 2.63×10^{12} J = 2.62×10^{12} J/day remaining for electricity generation. For an 38% efficient power recovery turbine, (.38) (2.62×10^{12} J/day) (2.778×10^{-7} kW-h/J/day) = 2.72940×10^5 kW-hr/day. Relative to H₂, this is 2.77 kW-hr/kg H₂, for the second step in the process. In terms of cost of power recovery turbines, we need

$$(9.83 \times 10^{11} \text{ J/day})(1 \text{ day}/24 \text{ hr})(1 \text{ hr}/3600 \text{ s})(1.342 \times 10^{-3} \text{ hp/J/s}) = 15,262 \text{ hp.}$$

$$\text{Cost is } (15,262/5,000)^{.6} (\$416,308) = \$813,204$$

2nd step: \$813,204 million for a power recovery turbine to recover 2.77 kW-hr/kg H₂.

Efficiency

At the LHV of 120,000 kJ/kg H₂, 100,000 kg H₂/day will produce:

$$120,000 \text{ (kJ/kg)}(100,000 \text{ kg/day}) = 1.2 \times 10^{13} \text{ J/day}$$

At the HHV of 141,600 kJ/kg H₂, 100,000 kg H₂/day will produce:

$$141,600 \text{ (kJ/kg)}(100,000 \text{ kg/day}) = 1.416 \times 10^{13} \text{ J/day}$$

In the second reaction step, 2.62×10^{12} J/day is recovered for electricity generation at 80%, leaving 2.096×10^{12} J/day recovered energy as electricity

For the 2015 case, 7.5 kW-h/kg H₂ is required for separation and various plant electricity usage. This is 2.7×10^{12} J/day of energy; this will be taken from the generated electricity. For the 2025 case, 9.00×10^{11} J/day of energy are required for these costs.

2015 case:

For this case, the heat input is:

$$3027 \text{ GWhr/yr} (1 \text{ yr}/365 \text{ days})(3600\text{s/hr})(10^9 \text{ W/GW})(1 \text{ J/W-s}) = 2.986 \times 10^{13} \text{ J/day}$$

In the LHV case: $(1.2 \times 10^{13} \text{ J/day} + 2.096 \times 10^{12} \text{ J/day} - 2.7 \times 10^{12} \text{ J/day})$ energy output / $(2.99 \times 10^{13} \text{ J/day})$ energy input = 38.2 % efficiency

In the HHV case: $(1.416 \times 10^{13} \text{ J/day} + 2.096 \times 10^{12} \text{ J/day} - 2.7 \times 10^{12} \text{ J/day})$ energy output / $(2.98 \times 10^{13} \text{ J/day})$ energy input = 45.4 % efficiency

2025 case:

For this case, the heat input is:

$$2904 \text{ GWhr/yr} = 2.865 \times 10^{13} \text{ J/day}$$

In the LHV case: $(1.2 \times 10^{13} \text{ J/day} + 2.096 \times 10^{12} \text{ J/day} - 9 \times 10^{11} \text{ J/day})$ energy output / $(2.865 \times 10^{13} \text{ J/day})$ energy input = 46.1 % efficiency

In the HHV case: $(1.416 \times 10^{13} \text{ J/day} + 2.096 \times 10^{12} \text{ J/day} - 9 \times 10^{11} \text{ J/day})$ energy output / $(2.865 \times 10^{13} \text{ J/day})$ energy input = 53.6 % efficiency

In summary, for the 2015 case, overall efficiency from sun to LHV H₂ production is $(0.449)(0.382) = 17.2\%$ efficient. For the 2025 case, overall efficiency from sun to LHV H₂ is $(0.449)(0.461) = 20.7\%$ efficient.

H2A Results Summary

The capital cost distribution for the H2A analysis for both 2015 and 2025 is shown in Figures 6 and 7. Total Direct Capital for the 2015 case is \$762M with a Total Depreciable Capital of \$1 T. For the 2015 case, 82% of the capital is solar related (heliostats, towers, reactors/receivers). For the 2025 case, Total Direct Capital is \$544 M with a Total Depreciable Capital of \$719M. For the 2025 case, 89% of the capital is solar related.

The base cost of H₂ for the 2015 case is \$5.58/kg H₂, while \$4.14/kg H₂ for the 2025 case. Tornado charts in Figures 8 and 9 show the sensitivity of selling price as a function of various cost inputs.

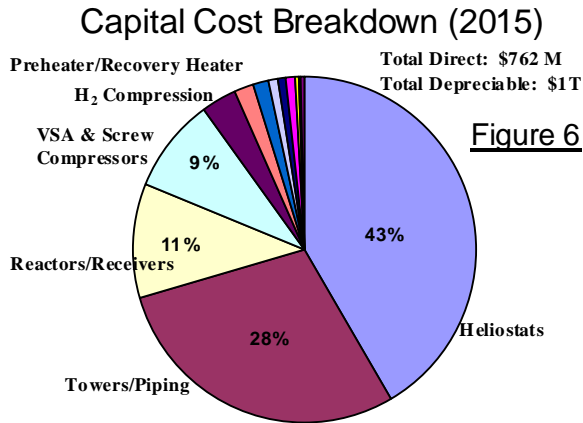


Figure 6

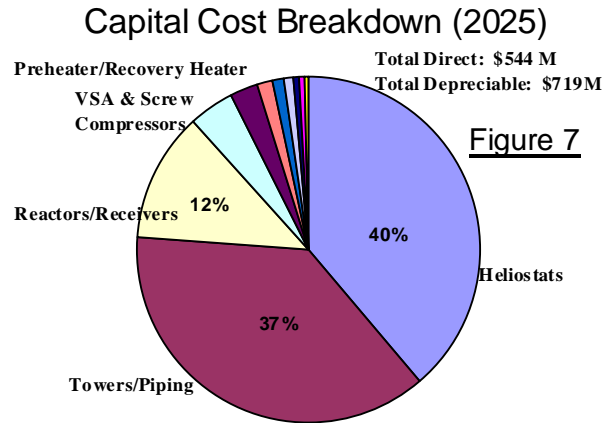
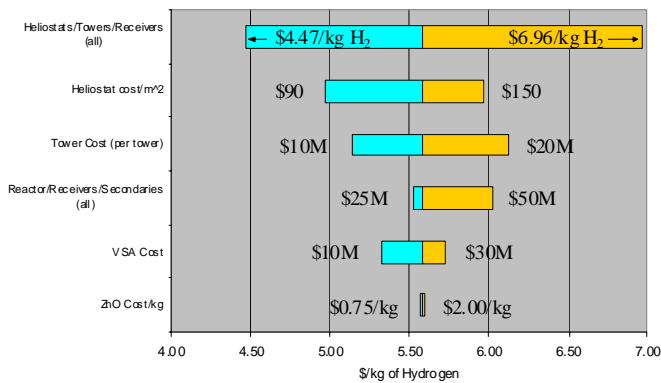


Figure 7

Figure 8
Sensitivity study – 2015
(Base Cost: \$5.58/kg H₂)

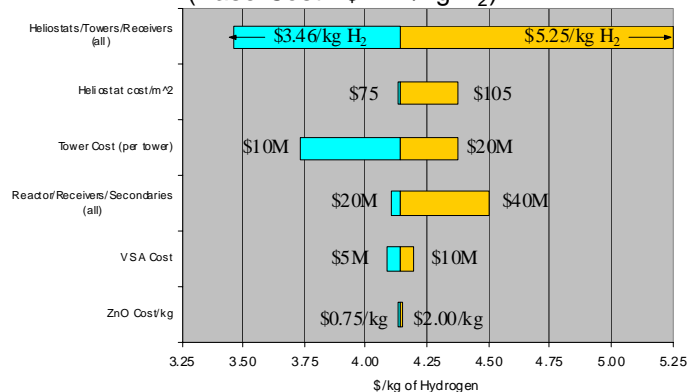


For the 2015 case, a decrease in installed heliostat cost from \$126.50/m² to \$90/m² decreases the selling price of H₂ to \$4.97/kg. Likewise, a decrease in the tower cost from \$14.45M/tower to \$10M/tower reduces the cost of H₂ to \$5.14/kg. If all of the solar cost reductions of heliostat, tower, and reactor/receiver costs could be achieved, the selling price of H₂ could be reduced to \$4.47/kg. Likewise, if costs all rose to \$150/m² heliostat, towers of \$20M/tower installed and \$50M

purchased for reactor/receivers, the selling price of H₂ would be increased to \$6.96/kg.

For the 2025 case, a decrease in installed heliostat cost from \$90/m² to \$75/m² decreases the selling price of H₂ to \$3.91/kg. Likewise, a decrease in the tower cost from \$14.45M/tower to \$10M/tower reduces the cost of H₂ to \$3.73/kg. If all of the solar cost reductions of heliostat, tower, and reactor/receiver costs could be achieved, the selling price of H₂ could be reduced to \$3.46/kg. Likewise, if costs all rose to \$125/m² heliostat, towers of \$20M/tower installed and \$40M purchased for reactor/receivers, the selling price of H₂ would be increased to \$5.25/kg.

Figure 9
Sensitivity study – 2025
(Base Cost: \$4.14/kg H₂)



Recommendation

It is believed that the ZnO/Zn cycle can be developed to work. Primary issues revolve around both (1) materials development for operation day in and day out at 1800°C in the presence of air and for rapid heating/cooling (i.e. thermal shock resistance) and (2) the development of heat recovery methods out of the solar reactor while at the same time preventing recombination.

However, even with installed heliostat costs of \$75/m² and 250 m tower costs of \$10M installed, the required selling price of 300 psig delivered H₂ for the 2025 case can only be reduced to \$3.46/kg which is above the \$3/kg targeted plant gate price. This assumes 85% conversion for Reaction (1) and 100% conversion for Reaction (2).

Significant reductions in solar field costs (especially towers and heliostats) will be required to reduce the required selling price to \$3/kg (for the 10% IRR). It is recommended that research focus on developing suitable reactor materials and an efficient reactor design that reduces the tendency for reverse reaction from occurring (without inefficient quenching). Progress in these areas have been reported by Steinfeld and co-workers:

Gstoehl D., Brambilla A., Schunk L., Steinfeld A., "A Quenching Apparatus for the Gaseous Products of the Solar Thermal Dissociation of ZnO", Journal of Material Sciences, 43, 4729-4736 (2008).

Schunk L., Haeberling P., Wepf S., Willemin D., Meier A., Steinfeld A., "A Solar Receiver-Reactor for the Thermal Dissociation of Zinc Oxide", ASME Journal of Solar Energy Engineering, 130, 021009 (2008).

An additional paper has been published from the research relative to the design of a solar reactor for carrying out ZnO dissociation:

Haussener, S., D. Hirsch, C. Perkins, A.W. Weimer, A. Lewandowski, A. Steinfeld, "Modeling a Multitube High-temperature Solar Thermochemical Reactor for Hydrogen Production," Journal of Solar Energy Engineering, 131, 024503 (2009).