

Solar-thermal Water Splitting Using the Sodium Manganese Oxide Process & Preliminary H2A Analysis

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Abstract

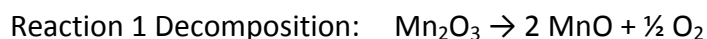
There are three primary reactions in the sodium manganese oxide high temperature water splitting cycle. In the first reaction, Mn_2O_3 is decomposed to MnO at $1,500^\circ C$ and 50 psig. This reaction occurs in a high temperature solar reactor and has a heat of reaction of 173,212 J/mol. Hydrogen is produced in the next step of this cycle. This step occurs at $700^\circ C$ and 1 atm in the presence of sodium hydroxide. Finally, water is added in the hydrolysis step, which removes NaOH and regenerates the original reactant, Mn_2O_3 .

The high temperature solar-driven step for decomposing Mn_2O_3 to MnO can be carried out to high conversion without major complication in an inert environment. The second step to produce H_2 in the presence of sodium hydroxide is also straightforward and can be completed. The third step, the low temperature step to recover the sodium hydroxide is the most difficult. The amount of energy required to essentially distill water to recover sodium hydroxide is prohibitive and too costly. Methods must be found for lower cost recovery.

This report provides information on the use of ZnO as an additive to improve the recovery of sodium hydroxide. All other work resulting from project support has been published in peer-reviewed research journals as cited in the report and that information is not repeated here. Readers are referred to that disseminated information.

I. Introduction

The manganese oxide high temperature water splitting cycle has three reactions. In the first reaction, Mn₂O₃ is decomposed to MnO at 1,500°C and 50 psig. This reaction occurs in a high temperature solar reactor and has a heat of reaction of 173,212 J/mol. Hydrogen is produced in the next step of this cycle. This step occurs at 700°C and 1 atm in the presence of sodium hydroxide. Finally, water is added in the hydrolysis step, which removes NaOH and regenerates the original reactant, Mn₂O₃. The reactions are shown below.



Previous experimental work is summarized in a number of publications. The published papers are summarized below with the reprinted abstracts:

Francis, T.M., C.J. Gump and A.W. Weimer, "Spinning wheel powder feeding device — fundamentals and applications," Powder Technology, **170**, 36-40 (2006).

Abstract - A spinning wheel powder feeding system has been developed as a conveying mechanism to feed fine particle aggregates on a laboratory scale. An example of a use of this conveying mechanism is with a transport tube reactor, since the reactor only provides a few seconds residence time to react the powder. Methods to shear the powder mechanically, as opposed to using a high gas velocity, are developed as to not reduce the available residence time in the reactor. The objective is to feed a powder at the smallest particle aggregate size possible rather than a large particle aggregate size generated by an upstream feeding device, and to achieve such dispersion using minimized gas flow. Statistical results show that the spinning wheel alone is able to reduce the mean aggregate size of the Particle Size Distribution (PSD) and when a minimal amount of gas is added to the system the PSD is reduced further. In addition, a fundamental model employing a discrete particle aggregate breakage equation combined with a Monte Carlo method has shown that the spinning wheel feeding system is able to consistently reduce particle aggregate size.

Francis, T.M., P.R. Lichty, and A.W. Weimer, "Manganese oxide dissociation kinetics for the Mn₂O₃ thermochemical water-splitting cycle. Part1:Experimental," Chemical Engineering Science, **65**, 3709 (2010).

Abstract - It is shown that the dissociation of Mn₂O₃ to MnO in a short residence time aerosol flow reactor can achieve high conversions approaching 75% when the concentration of oxygen is kept below 0.25%. Significant recombination reaction occurs when the oxygen content exceeds 0.25% by volume. Actual reaction mechanism for Mn₂O₃ dissociation was found. High levels of dissociation are achievable when the reaction is carried out in an inert gas environment using a reactor configuration that limits the reverse reaction.

Francis, T.M., C. Perkins and A.W. Weimer, "Manganese oxide dissociation kinetics for the Mn₂O₃ thermochemical water-splitting cycle. Part2: CFD model," Chemical Engineering Science, **65**, 4397-4410 (2010).

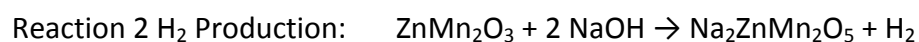
Abstract - A detailed CFD model was developed to better understand the kinetics and transport characteristics of Mn₂O₃ dissociation in an aerosol flow reactor (AFR). Radiation was the dominant mode of heat transfer and a relation for radiation from the walls and attenuating volume to any volume element in the reactor was developed. Results compared favorably to what was observed experimentally and showed that solid feed concentration into a high temperature AFR has a significant effect on conversion. If the concentration becomes too high, simply increasing the temperature of the reactor wall will not provide enough energy to drive the reaction to a high conversion. Additionally, the model showed that the bulk gas rate does not have that much effect on conversion in the AFR. This is important as a higher gas flowrate provides a faster quench, limiting the possibility of a recombination reaction. Finally, a case study for the diameter of the reactor tube showed that a higher conversion could be achieved by decreasing the size of the reactor tube. Multiple reaction tubes of smaller diameter are likely needed for scale-up.

Kreider, P.B., H.H. Funke, K. Cuche, M. Schmidt, A. Steinfeld, and A.W. Weimer, "Manganese oxide based thermochemical hydrogen production cycle," International Journal of Hydrogen Energy, **36**, 7028-7037 (2011).

Abstract - A MnO/NaOH based three-step thermochemical water splitting cycle was modified to improve the hydrolysis of α -NaMnO₂ (sodium manganate) and to recover Mn(III) oxides for the high-temperature reduction step. Sodium manganate forms in the reaction of NaOH with MnO that releases hydrogen. The hydrolysis of α -NaMnO₂ to manganese oxides and NaOH is incomplete even with a large excess of water and more than 10% sodium cannot be removed prior to the high-temperature reduction step. When mixed oxides of manganese with iron were used in the cycle, the NaOH recovery in the hydrolysis step improved from about 10% to 35% at NaOH concentrations above 1M. Only 60% sodium was removed at 0.5M from the mixed oxides whereas more than 80% can be recovered at the same NaOH concentration when only manganese oxides are used. 10:1 Mn/Fe sample was cycled through all steps three times to confirm that multiple cycles are possible. The high-temperature reduction was carried out for 5h at 1773 K under vacuum and the conversion was about

65% after the 3rd cycle. Since sodium carryover into the high-temperature reduction cannot be avoided, even with the energy intensive hydrolysis step, a modified two-step cycle without low temperature sodium recovery is proposed where α - NaMnO_2 is reduced directly to MnO at 1773 K under vacuum. On a laboratory scale, about 60% of the sodium that volatilized at the high temperatures was trapped with a water-cooled cold finger and conversions were stable at about 35% after three completed cycles.

There is difficulty separating sodium hydroxide from manganese in the hydrolysis step of this cycle. Therefore, zinc oxide, ZnO , has been investigated as an additive to manganese to help increase the conversion of reaction 3.



A. Capital Equipment Design & Costing

Screw conveyors are used to transport the ZnMn_2O_4 from the chemical plant up to the solar reactor. The conveyors have a maximum length of 37 meters while the 6 towers are 239 meters tall. A total of 36 conveyors are need for this plant for a total capital investment of \$2MM.

The conveyors feed hoppers at the top of the solar towers. There is one hopper per tower with a holding time of 90 minutes and a total cost of \$172k.

Star valve rotary feeders move the ZnMn_2O_4 from the hopper into the solar reactor and are also used to move the reduction products out of the solar reactors. Two valves per reactor or twelve valves total cost \$129k.

ZnMn_2O_4 is preheated in a titanium flat plate heat exchanger by the reduction product sensible heat. Each heat exchanger has a surface area of 711 m^2 and the total cost is \$3MM.

The solar reactors have a residence time of 30 seconds. They are 20 foot vertical vessels with four 12 inch silicon carbide reaction tubes. The total capital cost of 6 solar reactors is \$2.5MM.

Argon is used to fluidize the ZnMn_2O_4 feed. Oxygen produced in the decomposition reaction is mixed with the argon feed in the decomposition reaction. An oxygen transport membrane is used to separate O_2 from Ar downstream from the solar reactor. The membranes are 26.5 meters tall with a diameter of 8.8 meters and cost \$7MM.

Large volume field erected stainless steel storage tanks are used to store ZnMn_2O_3 at the base of each tower. The tanks have a holding capacity of 33.5 hours and will cost \$4.8MM.

Sodium hydroxide is mixed with water in a stainless steel agitated mixed tank. The total capital investment for 6 mixing tanks is \$262k.

The sodium hydroxide mixture is fed to the second reactor along with the ZnMn_2O_3 from the storage tank. The second reactor is a jacketed, stirred tank, 316 stainless steel, vertical vessel operating at 700°C and 1 atm. The reactors cost \$27.5MM.

Two heat exchangers follow the second reactor and are used to remove heat from the hydrogen production products by preheating the NaOH solution feed

into the second reactor. These heat exchangers are stainless steel floating head with 0.019 meter outside diameter tubes that have a 0.025 meter square pitch and a total heat exchange area of 209 m². The heat exchangers cost \$386k.

A carbon steel baghouse filter follows the NaOH heat exchanger. The filter will separate solids from the hydrogen/water product stream. The filters cost \$376k.

Hydrogen is produced at 14.7 psig in the second reactor and is then compressed to 318.4 psig before entering the pipeline. The system has a compression factor of 2.85 and has intercoolers with a pressure drop of 2 psig. The table below shows the resulting inlet and outlet pressures from each compression stage.

Stage #	Pin (psig)	Pout (psig)
1	14.7	41.9
2	39.9	113.7
3	111.7	318.4

The compression system cost was determined using the Department of Energy's H2A Delivery Components Model v2.0. There is one compression system per tower and 3 compressors will be installed while only 2 will be operating at any time. The total installed cost for the compressors is \$48MM.

After compressing the hydrogen and water vapor, a knockout drum is used to drop the gas temperature down to 50°C. Under the conditions the water is liquid, drops out the bottom, and the hydrogen has a composition of 99%. The knockout drums are \$3MM.

Reactor 3 is a stirred, glass lined, steel, vertical vessel with a volume of 54 m³ operating at 80°C and 1 atm with a total cost of \$2.4MM.

A hydroclone follows reactor 3 to separate ZnMn₂O₄ from the NaOH/water mixture. The hydroclones have a maximum flowrate of 1,200 gallons per minute. There will be three hydroclones per tower for a total of \$358k.

Water is removed from ZnMn₂O₄ using a rotary vacuum dryer with indirect flue gas and a drying time of 10 minutes. The dryers cost \$1.1MM.

After drying the ZnMn₂O₄ flows into small volume, field erected, 316 stainless steel, flat bottom, storage tanks. With a holding capacity of 36 hours the tanks have a total capital investment of \$2.2MM.

Finally, the NaOH/water mixture must be separated by a triple effect evaporator (TEE). The mixture is fed into the system using a 316 stainless steel centrifugal

pump costing \$22k. The feed moves from the pump into the 316 stainless steel, vertical, jacketed tank evaporators. The breakdown of evaporator heat transfer area to cost is shown in the table below.

HE Area (m ²)	T _{CI}
790	\$2.6MM
9	\$237k
0.55	\$52k

There is a heat exchanger following the TEE which is used to cool the vapor leaving evaporator 3. This is a carbon steel U-tube heat exchanger with 0.0254 meter square tube having a pitch 0.0254 m² and a heat transfer area of 420 m². These heat exchangers cost \$81k. A condensate tank collects the condensed water from the jacket of each evaporator has a diameter of 13 meters. The condensed water is recirculated through the cycle. The condensate tanks cost \$52k. The 6 complete TEE systems cost a total of \$7.5MM.

The following table shows the resulting total installed capital equipment cost.

Equipment	Installation Cost Factor	T _{CI}
Conveyors	1.61	\$ 3,228,291
Hoppers	2.3	\$ 396,154
Screw Feeders	2.3	\$ 295,972
Heat Exchangers	3.17	\$ 11,030,185
Solar Reactors	3.17	\$ 7,856,262
Oxygen Transport Membrane	2.32	\$ 16,179,494
Storage Tanks	1.86	\$ 12,968,237
Agitated Mixers	2.3	\$ 602,462
Reactor 2	4.16	\$ 114,474,538
Baghouse Filters	2.32	\$ 872,466
Compression Systems	2.15	\$ 102,909,486
Knockout Drums	4.16	\$ 12,562,546
Reactor 3	4.16	\$ 9,903,331
Hydroclones	1.73	\$ 619,988
Dryers	2.06	\$ 2,287,003
TEE	1	\$ 7,502,881
Argon	1	\$ 843,045
Mn2O3	1	\$ 15,498,560
ZnO	1	\$ 22,828,634
NaOH	1	\$ 230,278,976
Total		\$ 573,138,509

III. Solar Field Design

Solar heliostat and tower design in Daggett, CA with a production rate of 133,000 kg H₂ per 8 hour day.

A. Solar Heat Input

Reduction heat of reaction required to produce 133,000 kg H₂/day:

$$\left(133,000 \frac{\text{kg H}_2}{\text{day}}\right) \left(\frac{\text{mol H}_2}{2.01588\text{g}}\right) \left(\frac{1 \text{ mol Mn}_2\text{O}_3}{1 \text{ mol H}_2}\right) \left(\frac{1,000\text{g}}{\text{kg}}\right) (80\% \text{ conversion}) \\ = 8.25\text{E}7 \frac{\text{mol Mn}_2\text{O}_3}{\text{day}}$$

$$\left(8.25\text{E}7 \frac{\text{mol ZnMn}_2\text{O}_4}{\text{day}}\right) \left(173,212 \frac{\text{J}}{\text{mol}}\right) = 1.43\text{E}12 \frac{\text{J}}{\text{day}}$$

$$\left(1.43\text{E}12 \frac{\text{J}}{\text{day}}\right) \left(\frac{\text{hr}}{3600\text{s}}\right) \left(\frac{\text{GW}}{10^9 * \frac{\text{J}}{\text{s}}}\right) = 3.97 \frac{\text{GWhr}}{\text{day}}$$

$$\left(3.97 \frac{\text{GWhr}}{\text{day}}\right) \left(365 \frac{\text{day}}{\text{yr}}\right) = \mathbf{1,449 \frac{\text{GWhr}}{\text{yr}}}$$

Sensible heat input required to heat Mn₂O₃, ZnO, and argon from the preheated temperature of 1,164K to the reaction temperature of 1,500K:

Mn₂O₃ sensible heat required:

$$\left(8.25\text{E}7 \frac{\text{mol Mn}_2\text{O}_3}{\text{day}}\right) \left(138.606 \frac{\text{J}}{\text{mol} * \text{K}}\right) (1,773 - 1,164)\text{K} = 6.96\text{E}12 \frac{\text{J}}{\text{day}}$$

$$\left(6.96\text{E}12 \frac{\text{J}}{\text{day}}\right) \left(\frac{\text{hr}}{3600\text{s}}\right) \left(\frac{\text{GW}}{10^9 * \frac{\text{J}}{\text{s}}}\right) = 1.93 \frac{\text{GWhr}}{\text{day}}$$

$$\left(1.93 \frac{\text{GWhr}}{\text{day}}\right) \left(365 \frac{\text{day}}{\text{yr}}\right) = \mathbf{706 \frac{\text{GWhr}}{\text{yr}}}$$

ZnO sensible heat required:

$$\left(8.25\text{E}7 \frac{\text{mol Mn}_2\text{O}_3}{\text{day}}\right) \left(\frac{1 \text{ mol ZnO}}{1 \text{ mol Mn}_2\text{O}_3}\right) \left(24.47 \frac{\text{J}}{\text{mol} * \text{K}}\right) (1,773 - 1,164)\text{K} \\ = 1.28\text{E}12 \frac{\text{J}}{\text{day}}$$

$$\left(1.28\text{E}12 \frac{\text{J}}{\text{day}}\right) \left(\frac{\text{hr}}{3600\text{s}}\right) \left(\frac{\text{GW}}{10^9 * \frac{\text{J}}{\text{s}}}\right) = 0.36 \frac{\text{GWhr}}{\text{day}}$$

$$\left(0.36 \frac{GWhr}{day}\right) \left(365 \frac{day}{yr}\right) = 130 \frac{GWhr}{yr}$$

Ar sensible heat required:

$$\left(8.25E7 \frac{mol Mn2O3}{day}\right) \left(\frac{3molAr}{1molMn2O3}\right) \left(20.786 \frac{J}{mol * K}\right) (1,773 - 1,164)K$$

$$= 3.13E12 \frac{J}{day}$$

$$\left(3.13E12 \frac{J}{day}\right) \left(\frac{hr}{3600s}\right) \left(\frac{GW}{10^9 * \frac{J}{s}}\right) = 0.87 \frac{GWhr}{day}$$

$$\left(0.87 \frac{GWhr}{day}\right) \left(365 \frac{day}{yr}\right) = 317 \frac{GWhr}{yr}$$

Total Solar Heat Input

$$(1,449 + 706 + 130 + 317) \frac{GWhr}{yr} = 2,602 \frac{GWhr}{yr}$$

The solar field design is determined using Allan Lewandowski's Soltrace program.

B. Heliostat Field and Towers

(6) 239 meter tall towers are required to produce 2,602 GWhr/yr.

Each receiver has 3 heliostat fields with 74.5 acres of land per field and an efficiency of 65.8%. Each field requires (934) 143 m² heliostats for a total area of 133,378 m²/field, which will supply 87.423 MW/field.

The entire plant will require 2.4E6 m² of heliostats with a total land area of 1,342 acres.

The parasitic electrical requirement is 0.20 W/m² or

$$\left(0.20 \frac{W}{m^2}\right) (2.4E6 m^2) \left(\frac{MW}{10^6 W}\right) = 0.48 MW$$

$$(0.48 MW) \left(8 \frac{hr}{day}\right) = 3.84 \frac{MWhr}{day}$$

$$\left(3.84 \frac{MWhr}{day}\right) \left(\frac{GW}{1,000 MW}\right) \left(365 \frac{day}{yr}\right) = 1.40 \frac{GWhr}{yr}$$

Secondary Concentrators

Each CPC has a surface area of 169 m² with an efficiency of 91.5% and a concentration of 3,868 suns. There are 3 CPCs per receiver with a total area of 506.1 m².

Of the 87.423 MW delivered to the CPC from one field, 79.997 MW is delivered to the receiver from one field. 240 MW is supplied to each receiver by the 3 concentrators.

The overall annual efficiency is 40.2%.

IV. Reduction Product Heat Recovery

Sensible heat recovered from cooling the reduction products from 1,500°C to 900°C will be used to preheat the solar reactor feed from 727° to 890°C.

Mn₂O₃ sensible heat recovered:

$$\left(8.25E7 \frac{\text{mol Mn}_2\text{O}_3}{\text{day}}\right) \left(138.606 \frac{\text{J}}{\text{mol} * \text{K}}\right) (1,773 - 1,174)\text{K} (20\% \text{ unreacted})$$

$$= 1.37E12 \frac{\text{J}}{\text{day}}$$

$$\left(1.37E12 \frac{\text{J}}{\text{day}}\right) \left(\frac{\text{hr}}{3600\text{s}}\right) \left(\frac{\text{GW}}{10^9 * \frac{\text{J}}{\text{s}}}\right) = 0.38 \frac{\text{GWhr}}{\text{day}}$$

$$\left(0.38 \frac{\text{GWhr}}{\text{day}}\right) \left(365 \frac{\text{day}}{\text{yr}}\right) = \mathbf{139 \frac{\text{GWhr}}{\text{yr}}}$$

ZnO sensible heat recovered:

$$\left(8.25E7 \frac{\text{mol Mn}_2\text{O}_3}{\text{day}}\right) \left(\frac{1\text{mol ZnO}}{1\text{mol Mn}_2\text{O}_3}\right) \left(24.47 \frac{\text{J}}{\text{mol} * \text{K}}\right) (1,773 - 1,174)\text{K} (20\% \text{ unreacted})$$

$$= 5.03E10 \frac{\text{J}}{\text{day}}$$

$$\left(5.03E10 \frac{\text{J}}{\text{day}}\right) \left(\frac{\text{hr}}{3600\text{s}}\right) \left(\frac{\text{GW}}{10^9 * \frac{\text{J}}{\text{s}}}\right) = 0.014 \frac{\text{GWhr}}{\text{day}}$$

$$\left(0.014 \frac{\text{GWhr}}{\text{day}}\right) \left(365 \frac{\text{day}}{\text{yr}}\right) = \mathbf{5 \frac{\text{GWhr}}{\text{yr}}}$$

Ar sensible heat recovered:

$$\left(8.25E7 \frac{\text{mol Mn}_2\text{O}_3}{\text{day}}\right) \left(\frac{3\text{mol Ar}}{1\text{mol Mn}_2\text{O}_3}\right) \left(20.786 \frac{\text{J}}{\text{mol} * \text{K}}\right) (1,773 - 1,174)\text{K} = 6.16E11 \frac{\text{J}}{\text{day}}$$

$$\left(6.16E11 \frac{\text{J}}{\text{day}}\right) \left(\frac{\text{hr}}{3600\text{s}}\right) \left(\frac{\text{GW}}{10^9 * \frac{\text{J}}{\text{s}}}\right) = 0.17 \frac{\text{GWhr}}{\text{day}}$$

$$\left(0.17 \frac{\text{GWhr}}{\text{day}}\right) \left(365 \frac{\text{day}}{\text{yr}}\right) = \mathbf{62 \frac{\text{GWhr}}{\text{yr}}}$$

MnO sensible heat recovered:

$$\left(8.25E7 \frac{\text{mol Mn}_2\text{O}_3}{\text{day}}\right) \left(\frac{2\text{mol MnO}}{1\text{mol Mn}_2\text{O}_3}\right) \left(58.496 \frac{\text{J}}{\text{mol} * \text{K}}\right) (1,773 - 1,174)\text{K} (80\% \text{ conversion}) = 9.25E11 \frac{\text{J}}{\text{day}}$$

$$\left(9.25E11 \frac{J}{day}\right) \left(\frac{hr}{3600s}\right) \left(\frac{GW}{10^9 * \frac{J}{s}}\right) = 0.26 \frac{GWhr}{day}$$

$$\left(0.26 \frac{GWhr}{day}\right) \left(365 \frac{day}{yr}\right) = 94 \frac{GWhr}{yr}$$

O2 sensible heat recovered:

$$\left(8.25E7 \frac{mol Mn2O3}{day}\right) \left(\frac{\frac{1}{2} mol O2}{1 mol Mn2O3}\right) \left(37.329 \frac{J}{mol * K}\right) (1,773 - 1,174)K (80\% conversion) = 1.48E11 \frac{J}{day}$$

$$\left(1.48E11 \frac{J}{day}\right) \left(\frac{hr}{3600s}\right) \left(\frac{GW}{10^9 * \frac{J}{s}}\right) = 0.041 \frac{GWhr}{day}$$

$$\left(0.041 \frac{GWhr}{day}\right) \left(365 \frac{day}{yr}\right) = 15 \frac{GWhr}{yr}$$

Total Sensible Heat Recovered

$$(139 + 5 + 62 + 94 + 15) \frac{GWhr}{yr} = 315 \frac{GWhr}{yr}$$

Sensible heat required for feed preheat:

Mn2O3 sensible heat required:

$$\left(8.25E7 \frac{mol Mn2O3}{day}\right) \left(138.606 \frac{J}{mol * K}\right) (1,164 - 1,000)K = 1.88E12 \frac{J}{day}$$

$$\left(1.88E12 \frac{J}{day}\right) \left(\frac{hr}{3600s}\right) \left(\frac{GW}{10^9 * \frac{J}{s}}\right) = 0.52 \frac{GWhr}{day}$$

$$\left(0.52 \frac{GWhr}{day}\right) \left(365 \frac{day}{yr}\right) = 190 \frac{GWhr}{yr}$$

ZnO sensible heat required:

$$\left(8.25E7 \frac{mol Mn2O3}{day}\right) \left(\frac{1 mol ZnO}{1 mol Mn2O3}\right) \left(24.47 \frac{J}{mol * K}\right) (1,164 - 1,000)K = 3.45E11 \frac{J}{day}$$

$$\left(3.45E11 \frac{J}{day}\right) \left(\frac{hr}{3600s}\right) \left(\frac{GW}{10^9 * \frac{J}{s}}\right) = 0.10 \frac{GWhr}{day}$$

$$\left(0.10 \frac{GWhr}{day}\right) \left(365 \frac{day}{yr}\right) = 35 \frac{GWhr}{yr}$$

Ar sensible heat required:

$$\begin{aligned} \left(8.25E7 \frac{mol Mn2O3}{day}\right) \left(\frac{3molAr}{1molMn2O3}\right) \left(20.786 \frac{J}{mol * K}\right) (1,164 - 1,000)K \\ = 8.45E11 \frac{J}{day} \end{aligned}$$

$$\left(8.45E11 \frac{J}{day}\right) \left(\frac{hr}{3600s}\right) \left(\frac{GW}{10^9 * \frac{J}{s}}\right) = 0.23 \frac{GWhr}{day}$$

$$\left(0.23 \frac{GWhr}{day}\right) \left(365 \frac{day}{yr}\right) = 86 \frac{GWhr}{yr}$$

Total Solar Heat Input

$$(190 + 35 + 86) \frac{GWhr}{yr} = 311 \frac{GWhr}{yr}$$

V. Efficiency

A. H₂ Energy Production

The lower heating value (LHV) of hydrogen is 120,000 kJ/kg. The solar plant produces 133,000 kg/day running 8 hours per day while the chemical plant runs 24 hours per day with an operating efficiency of 75%. Therefore, the total plant output is 99,750 kg/day hydrogen.

$$\left(99,750 \frac{\text{kg H}_2}{\text{day}}\right) \left(120,000 \frac{\text{kJ}}{\text{kg}}\right) \left(1,000 \frac{\text{J}}{\text{kJ}}\right) = 1.2E13 \frac{\text{J}}{\text{day}}$$

$$\left(1.2E13 \frac{\text{J}}{\text{day}}\right) \left(\frac{\text{hr}}{3600\text{s}}\right) \left(\frac{\text{GW}}{10^9 * \frac{\text{J}}{\text{s}}}\right) = 3.33 \frac{\text{GWhr}}{\text{day}}$$

$$\left(3.33 \frac{\text{GWhr}}{\text{day}}\right) \left(365 \frac{\text{day}}{\text{yr}}\right) = 1,214 \frac{\text{GWhr}}{\text{yr}}$$

B. Electricity Consumption

Solar field consumes 4,271 kWhr per 8 hour day, the water pumps use 119,318 kWhr per 24 hour day, and the compression system consumes 194,688 kWhr per 24 hour day.

$$(4,271 + 119,318 + 194,688) \frac{\text{kWhr}}{\text{day}} \left(\frac{\text{GW}}{10^6 * \text{kW}}\right) \left(365 \frac{\text{day}}{\text{yr}}\right) = 116 \frac{\text{GWhr}}{\text{yr}}$$

C. Solar Field Efficiency

40.2% based on the Soltrace solar field design program by Allan Lewandowski.

D. Thermal Efficiency

$$\eta_{\text{Thermal}} = \frac{H_{2,\text{LHV}} + e_{\text{produced}}}{\text{Solar} + e_{\text{consumed}}} = \frac{1,214}{2,602 + 116} = 44.6\%$$

E. Process Efficiency

$$\eta_{\text{Process}} = \eta_{\text{Solar}} * \eta_{\text{Thermal}} = 0.402 * 0.446 = 17.9\%$$

F. STCH Efficiency

$$\eta_{\text{STCH}} = \frac{H_{2,\text{LHV}}}{\text{Solar} / \eta_{\text{Field}}} = \frac{1,214}{\frac{2,602}{0.402} + \frac{116}{0.400}} = 17.9\%$$

VI. Economic Analysis

A. DOE EERE Technical Targets

All cases are evaluated for the years 2015 and 2025 according to Sargent and Lundy's tower cost as well as the EERE heliostat costs and hydrogen selling price goals. All capital item costs are based on equipment pricing in 2007.

2015: Heliostats are \$126.50/m² installed and the secondary concentrators are \$1,265/m² installed. This is assuming that secondary concentrators cost 10X the price of a heliostat. Hydrogen will be delivered at 300 psig.

2025: Heliostats are \$90/m² installed and the secondary concentrators are \$900/m² installed. This is assuming that secondary concentrators cost 10X the price of a heliostat. Hydrogen will be delivered at 300 psig.

In all cases, the towers cost $(\$710,000 + 20.97 * h^{2.392}) * 1.12$ where h is the tower height in meters. (Inflation has been taken into account.) The site preparation cost is $\$8.5E6 * \frac{Field\ Area(m^2)}{2.67E6}$. The number of chemical plant staff required is equal to $(6.20 + 31.7 * p^2 + 0.23 * N)^{0.5}$ where P is the number of processing steps involving handling of particulate solids and N is the number of non-particulate processing steps generally the total pieces of equipment. 0.016 staff will be required for the solar field per 100 m² of the solar field.

B. H2A Operating Assumptions

Capital Costs	
Engineering & Design	17.7% T _{Cl,Solar}
Project Contingency	16.8% T _{Cl,Solar}
	18% T _{Cl,Chemical}
Up-Front Permitting Costs	3% T _{Cl}
Cost of land per acre	\$2,024

Variable Operating Costs	
Total Unplanned Replacement Capital Cost Factor per year	0.05% T _{Cl}

Financial Input Values	
Length of Construction Period	3 yrs
% of Capital Spent in 1st Year of Construction	10%
% of Capital Spent in 2nd Year of Construction	25%
% of Capital Spent in 3rd Year of Construction	65%
Start-up Time	0.5 yr
Plant life	40 yrs
Analysis period	40 yrs
Depreciation Schedule Length	20 yrs
Depreciation Type	MACRS
% Equity Financing	100%
% of Fixed Operating Costs During Start-up	100%
% of Revenues During Start-up	50%
% of Variable Operating Costs During Start-up	75%
Decommissioning costs	10%
Salvage value	10% T_{CI}
Inflation rate	1.9%
After-tax Real IRR	10%
State Taxes	6%
Federal Taxes	35%
Total Tax Rate	38.9%
Working Capital	15%

Fixed Operating Costs	
Total FTE Plant Staff	
Solar Operators at \$28/hr	
Plant Operators at \$50/hr	
G&A Rate	20%
Property Taxes and Insurance	1% $T_{CI,Solar}$ 2% $T_{CI,Chemical}$
Material costs for maintenance and repairs	0.5% $T_{CI,Solar}$ 6% $T_{CI,Chemical}$

C. 2007 Chemical Engineering Plant Cost Index

CE Index	525.4
Equipment	624.4
Heat Exchangers & Tanks	592.1
Process Machinery	598.3
Pipe, Valves, & Fittings	733.6
Process Instruments	425.2
Pumps & Compressors	831.2
Electrical Equipment	430.5
Structural Supports	662.6
Buildings	476.8

D. Solar Field Specifications & Capital Equipment

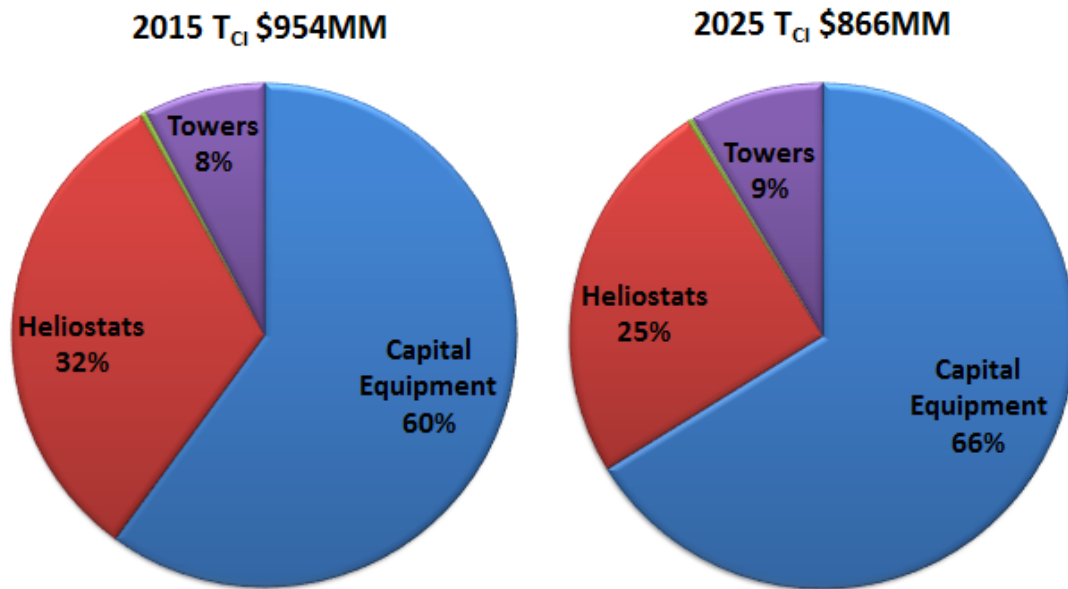
Solar Field Design			
		Chemical Plant Staff	56
		Solar Staff	38
		Site Preparation	\$ 7,642,982
	\$ 127	Heliostats	\$ 303,700,647
2015	\$ 1,265	Secondary Concentrators	\$ 3,840,976
		Towers	\$ 73,794,273
	\$ 90	Heliostats	\$ 216,071,607
2025	\$ 900	Secondary Concentrators	\$ 2,732,710
		Towers	\$ 73,794,273

E. H2A Results

	H2 selling Price (\$/kg)	DOE STCH Target
2015	\$6.48	\$6.00
2025	\$6.09	\$4.00

VII. Results & Conclusions

This cycle has uncovered several challenges. First, the allowable hydrogen selling price in 2015 is \$6.48/kg and \$6.09/kg in 2025. While the DOE selling price targets are \$6.00/kg in 2015 and \$4.00/kg in 2025. Hence, this cycle does not achieve either target in its present form. The pie charts below show that the cost of capital equipment required in this cycle accounts for 60-66% of the total capital investment.



The solarthermal reaction step appears feasible. However, there is an issue with this cycle relative to the recovery of sodium hydroxide from water. A lot of energy is required for this step. The process variation presented here by adding ZnO is still a challenge since it is still difficult to completely remove sodium hydroxide from manganese in the second reaction. Since sodium hydroxide is not completely removed in this step, approximately 10% is recycled with manganese to the solar reaction.

Finally, this analysis relies on the availability of an oxygen transport membrane (OTM) to separate oxygen from argon used in the solar reaction. This separation allows argon to be recycled, thus reducing the variable operating cost associated with argon use. OTMs are currently in the research phase and, therefore, not immediately available on the market.

A key issue is the ability to recover sodium hydroxide at low cost from an aqueous stream. The development of such a process will move the sodium manganese process closer to a viable process for producing renewable H₂.