II.F.1 Solar Cadmium Hydrogen Production Cycle

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Objectives

To demonstrate the technical feasibility and determine the economics of a solar cadmium hydrogen cycle. This includes:

- Validate the key reaction steps within the cadmium hydrogen cycle with experiments.
- Establish design concepts for process equipment based on experimental data.
- Integrate design concepts and solar plant and create a solar hydrogen plant flowsheet to calculate the process thermal efficiency and hydrogen cost.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

(U) High-Temperature Thermochemical Technology
(V) High-Temperature Robust Materials
(X) Coupling Concentrated Solar Energy and Thermochemical Cycles

Technical Targets

This project is directed at demonstrating the feasibility of large-scale hydrogen production using a solar cadmium cycle. If successful, the project will address the following DOE cost and efficiency targets as outlined in the HFCIT Multi-Year RD&D Plan:

DOE Cost and Efficiency Targets for Hydrogen Production

Metric	Unit	2008	2012	2017
H_2 cost	\$/kg H_2	10.00	6.00	3.00
Efficiency (LHV)	%	25	30	>35

LHV-Lower heating value

Accomplishments

Experimental, design and modeling work has been carried out to determine the technical feasibility and financial viability of the cadmium solar hydrogen cycle with the following accomplishments:

- Established the effect of carrier gas and process parameters on cadmium oxide decomposition kinetics.
- Demonstrated sub 1,150°C cadmium oxide decomposition.
- Measured the cadmium-oxygen reaction rate with respect to temperatures and O_2 concentrations.
- Demonstrated means to use either molten or solid cadmium to generate H_2.
- Completed the process flowsheet and solar field design.
- Calculated H_2 cost using H2A.

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Introduction

Preliminary flowsheet evaluation of the cadmium solar thermochemical hydrogen cycle has shown thermal efficiencies of nearly 70% (59% LHV). This process has the potential to supply low-cost hydrogen produced with a renewable energy source. In this cycle cadmium oxide is decomposed using concentrated solar heat at elevated temperatures. The decomposed cadmium vapor is then rapidly quenched to form molten cadmium in order to minimize the back reaction with oxygen. Hydrogen is generated in the third step of the cycle via either solid or molten cadmium hydrolysis.

$$CdO(s) \rightarrow Cd(g) + \tfrac{1}{2} O_2(g) \qquad (1{,}450^\circ C) \qquad (i)$$

$Cd(g) \rightarrow Cd(l)$ (1,450–700°C) (ii)

$Cd(l,s) + H_2O \rightarrow CdO(s) + H_2(g)$ (25-450°C) (iii)

This project's first goal is to carry out feasibility demonstrations of the three process steps in the laboratory. The resulting experimental data was used to generate design concepts for large-scale production process equipment. These concepts were then incorporated into a process flowsheet with a solar plant so that the thermal efficiency and cost of hydrogen can be derived. This provides an assessment whether a solar cadmium cycle can meet DOE's cost and efficiency targets.

Approach

Cadmium oxide decomposition was studied using thermogravimetric analysis (TGA). The effect of carrier gas on the decomposition temperature and rate were determined. In addition, the heating rate and experiment set up geometry were varied in order to understand the interplay between kinetics and process parameters [1].

To determine the feasibility of quenching decomposed cadmium vapor into molten cadmium, one needs to establish the required quench rate which in turn is controlled by the back reaction rate between cadmium vapor and oxygen. To measure this reaction rate, cadmium vapor was generated through molten cadmium evaporation. The vapor was then mixed with Ar gas containing oxygen at various concentrations. The gases flowed through a constant temperature zone at temperatures between 700°C and 1,400°C and were quenched upon exiting the furnace. The cadmium-oxygen reaction rate was then calculated based on the cadmium evaporation rate, reduction in oxygen concentration and the time of flight.

Cadmium hydrolysis can be carried out using either solid or molten cadmium. Both options had been investigated and it was found that molten cadmium hydrolysis has faster kinetics. Experiments were conducted to explore means to increase steam-cadmium contact. The goal is to provide inputs to equipment designs for maximum hydrogen generation. Data from all experiments were used to establish design concepts for large-scale process equipment. A flowsheet was then developed to determine the thermal efficiency and the hydrogen cost was calculated using H2A.

Results

TGA experiments were carried out to identify processing parameters that can reduce the cadmium oxide decomposition temperature. This is because the solar plant makes up approximately two-thirds of the cost of hydrogen. Experimental results showed that an inert carrier gas, in particular helium, helps to reduce the decomposition temperature which stems from an increase in decomposition kinetics. Furthermore, by increasing the residence time of the CdO particle in the heated zone, the decomposition temperature can be reduced. Finally, enhanced oxygen diffusion kinetics also leads to a reduction in decomposition temperature. Figure 1 shows the cadmium oxide decomposition rate with respect to temperature under various carrier gases. The faster decomposition kinetics in helium, compared to an inert gas such as argon or CO_2, has to do with the higher diffusion rate of oxygen away from the decomposition interface in helium. The presence of oxygen leads to an increase in the decomposition temperature as expected, which is a result of the back reaction between cadmium and oxygen. Hence, an inert or reduced atmosphere environment will help to lower the decomposition temperature. The lowest decomposition completion temperature using the TGA was 1,140°C and it was accomplished using a low furnace heating rate. Based on the collected data, a cadmium oxide decomposer design concept was established. It is based on a fluidized bed which will enhance the heat and mass diffusion and increase particle residence time when compared to a flow through reactor. A schematic of this design concept is shown in Figure 2. This concept can be adapted to either a beam-down or beam-up tower.

The cadmium-oxygen reaction experiment results showed that the reaction rate was between 1%-6% of cadmium reacted per second for temperatures between 800-1,450°C. The oxygen concentration was between 1% to 20%. Most of the measured rates fall between 2%-3%. Modeling of the measurement results showed that the reaction rate has no dependence on oxygen concentration and is only slightly dependent on cadmium concentration. From the reaction rate data, the quenching of cadmium vapor into molten form

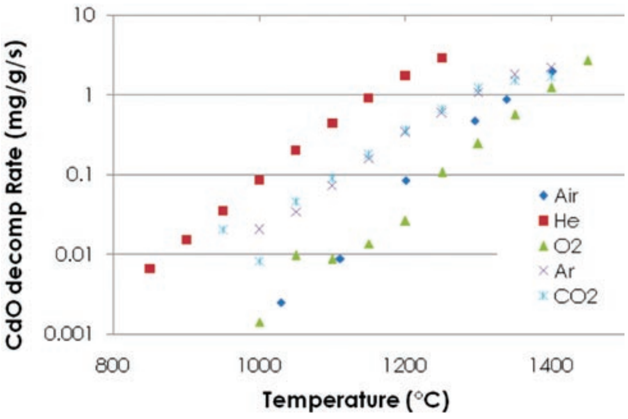

FIGURE 1. Decomposition rate of cadmium oxide as a function of temperature under various carrier gases. There are three regimes: i) helium, ii) argon and carbon dioxide and iii) air and pure oxygen.

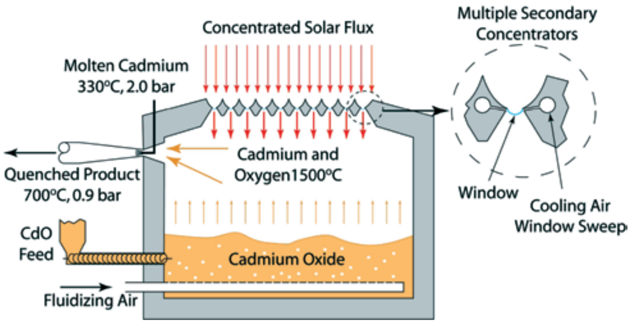

FIGURE 2. Design concept of a windowed cadmium oxide decomposer integrated with molten cadmium quenching of decomposed cadmium vapor. This design works with a reflector-down tower. Secondary concentrators are located at the entrance to the decomposer.

will need to be completed in the order of one second so the majority of molten cadmium can be retained for hydrolysis to generate hydrogen. The baseline concept is to use fine molten droplets as the quench medium. With this approach, cadmium vapor can condense on the droplets instead of homogeneously nucleating from the super cooled gas. This will minimize the total cadmium surface area available for reaction with oxygen. Single droplet modeling of the molten cadmium quenching process is ongoing. This will provide an indication as to whether quenching using molten cadmium will be practical. The baseline concept is to integrate vapor quenching at the exit of the cadmium oxide decomposer as shown in Figure 2.

For the hydrogen generation step, experimental work has shown that the optimal hydrolysis temperature is between 450°-480°C. Furthermore, the hydrogen production rate can be enhanced by increasing the contact between steam and molten cadmium. This was demonstrated in a rotary kiln reactor in which molten cadmium was being turned over to expose fresh surfaces for hydrolysis. It was also shown that by placing inert pellets inside the rotary kiln, one can increase the molten cadmium surface area, thus further increasing the hydrogen generation rate. A design concept for a large-scale rotary kiln has been made and is shown in Figure 3. The reaction is carried out at elevated pressure and hydrogen is separated from steam with the aid of a membrane. This eliminates the need to condense the steam for separation and waste the excess heat energy. These design concepts were incorporated into a flowsheet and the process thermal efficiency was determined to be 58% (LHV) which exceeds DOE's target. This baseline case uses air as the carrier gas. For the hydrogen cost calculation, a solar plant was designed. It is based on a reflector-down geometry so that the chemical operations are on the ground. A final hydrogen cost between \$3.74 and \$5.53 for the 2015 case was calculated using H2A. It has the potential to meet the DOE 2017 target of \$3.00/kg of hydrogen.

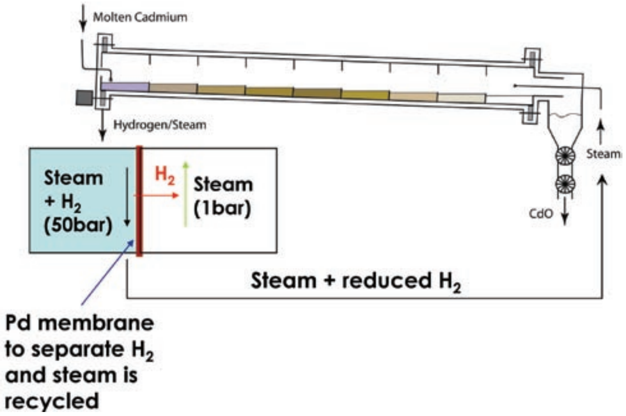

FIGURE 3. Design concept of a rotary kiln reactor for molten cadmium-steam reaction to produce hydrogen. Cadmium and steam flow in opposite direction. At the end of the reactor, solid cadmium oxide is expected, thus eliminating the need for solid-liquid separation.

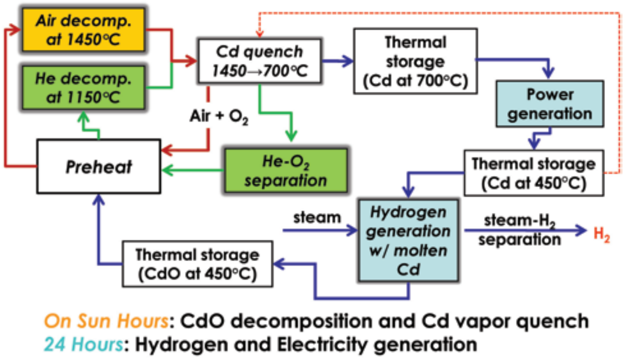

FIGURE 4. Block diagram of a solar-cadmium hydrogen plant. Cadmium oxide decomposition and decomposed vapor quenching take place during on sun hours. Hydrogen and electricity generation take place around the clock.

Figure 4 shows a simplified block diagram of the flowsheet for the hydrogen plant.

Conclusions and Future Directions

Key process steps of the cadmium solar hydrogen cycle have been demonstrated. Design concepts for a cadmium oxide decomposer and molten cadmium hydrolyzer have been established. The process efficiency and hydrogen cost meets the DOE 2012 target. In order to complete the feasibility study and to collect data for a future scale-up demonstration, the following work is recommended:

- Study the effect of quench rate on Cd-O_2 recombination.
- Measure the molten cadmium–oxygen reaction rate with a simulated bed quench set up.

- Conduct CdO decomposer prototype testing using a simulated solar source in order to better understand fluidization and materials handling issues.
- Conduct molten cadmium hydrolysis under pressure.
- Design a flowsheet based on a closed system using helium as carrier gas and calculate the hydrogen cost.

FY 2009 Publications/Presentations

1. "Solar Production of Hydrogen Using a Cadmium Based Thermochemical Cycle," AIChE Fall Meeting, Philadelphia, November 16–19, 2008.

2. "Solar Production of Hydrogen Using a Cadmium Based Thermochemical Cycle," NHA, March 29 through April 1, 2009.

3. DOE Annual Hydrogen Program Merit Review FY 2009, May 5–8, 2009.

References

1. Galwey, A.K., Brown, M.E., *Thermal Decomposition of Ionic Solids. Amsterdam*, Elsevier Science B.V. 1999.