“An R&D project designed to identify economically feasible concepts for the production of hydrogen from water using solar energy”

Funded by the U.S. Department of Energy
Solar Technologies Program

Contract DE-FG36-03GO13062

Award Recipient:

UNLV RESEARCH FOUNDATION
8311 W. Sunset Road, Suite 200
Las Vegas, NV 89113
702-895-2833
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Project Objective</td>
<td>1</td>
</tr>
<tr>
<td>Technical Project Organization</td>
<td>2</td>
</tr>
<tr>
<td>Executive Summary: Solar Thermo-Chemical Hydrogen Production (STCH)</td>
<td>2</td>
</tr>
<tr>
<td>Executive Summary: Solar Photo-Electrochemical Hydrogen Production (PEC)</td>
<td>3</td>
</tr>
<tr>
<td>Final Report Organization</td>
<td>4</td>
</tr>
<tr>
<td>Technical Approach – Solar Thermo-Chemical Hydrogen Production</td>
<td>4</td>
</tr>
<tr>
<td>Accomplishments - STCH</td>
<td>4</td>
</tr>
<tr>
<td>Thermo-Chemical Cycle Screening and Selection</td>
<td>4</td>
</tr>
<tr>
<td>Economic Consideration</td>
<td>5</td>
</tr>
<tr>
<td>Solar Collector/Receiver Consideration</td>
<td>6</td>
</tr>
<tr>
<td>Previous Level of Effort for Candidate Cycle</td>
<td>7</td>
</tr>
<tr>
<td>Safety and Environmental Consideration</td>
<td>7</td>
</tr>
<tr>
<td>Laboratory Feasibility Studies</td>
<td>9</td>
</tr>
<tr>
<td>Sulfate Cycles</td>
<td>9</td>
</tr>
<tr>
<td>Cadmium Oxide</td>
<td>10</td>
</tr>
<tr>
<td>Decomposition and Back-reaction</td>
<td>10</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>11</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>11</td>
</tr>
<tr>
<td>Hybrid Copper Chloride</td>
<td>13</td>
</tr>
<tr>
<td>Collector/Receiver/Reactor Studies</td>
<td>14</td>
</tr>
<tr>
<td>Advanced Heliostat Study</td>
<td>14</td>
</tr>
<tr>
<td>Solid Particle Receiver</td>
<td>14</td>
</tr>
<tr>
<td>Cavity Receiver/Reactor Development</td>
<td>16</td>
</tr>
<tr>
<td>Performance Analysis</td>
<td>17</td>
</tr>
<tr>
<td>Metal Sulfate</td>
<td>17</td>
</tr>
<tr>
<td>Cadmium Oxide</td>
<td>17</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>18</td>
</tr>
<tr>
<td>Hybrid Copper Chloride</td>
<td>18</td>
</tr>
<tr>
<td>Patents, Special Recognition, Awards</td>
<td>19</td>
</tr>
<tr>
<td>Publications</td>
<td>20</td>
</tr>
<tr>
<td>Presentations</td>
<td>21</td>
</tr>
<tr>
<td>Section</td>
<td>Page No.</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>Technical Approach - Solar Photo-Electrochemical Hydrogen Production</td>
<td>24</td>
</tr>
<tr>
<td>Tungsten Oxide Materials</td>
<td>24</td>
</tr>
<tr>
<td>Copper Chalcopyrite</td>
<td>25</td>
</tr>
<tr>
<td>Silicon Carbide Materials</td>
<td>26</td>
</tr>
<tr>
<td>Iron Oxide Materials</td>
<td>26</td>
</tr>
<tr>
<td>Zinc Oxide Materials</td>
<td>28</td>
</tr>
<tr>
<td>PEC Materials Characterization</td>
<td>29</td>
</tr>
<tr>
<td>Instrumentation</td>
<td>29</td>
</tr>
<tr>
<td>WO₃ Based Thin Films</td>
<td>30</td>
</tr>
<tr>
<td>ZnO Based Thin Films</td>
<td>30</td>
</tr>
<tr>
<td>SiC Based Thin Films</td>
<td>32</td>
</tr>
<tr>
<td>Fe₂O₃ Based Thin Films</td>
<td>32</td>
</tr>
<tr>
<td>In-Situ Studies</td>
<td>32</td>
</tr>
<tr>
<td>Publications</td>
<td>35</td>
</tr>
<tr>
<td>Presentations</td>
<td>37</td>
</tr>
</tbody>
</table>
ATTACHMENTS

A. University of Nevada, Las Vegas, “Optimization of Interfaces and Surfaces for Photoelectrochemical Hydrogen Production” (59 pgs)

B. University of California, Santa Barbara, “High Efficiency Generation of Hydrogen Fuels Using Solar Thermochemical Splitting of Water” (24 pgs)

C. University of Hawaii, “Photoelectrochemical Hydrogen Production” (13 pgs)

D. University of Nevada, Las Vegas, “High Temperature Rotary Drum” (33 pgs)

E. Argonne National Laboratory, “Status of the R&D Program for the Cu-Cl Thermochemical Cycle for Hydrogen Production” (50 pgs)

F. University of Colorado, “Development of a Solar Thermal ZnO/Zn Water Splitting Thermochemical Cycle” (19 pgs)


H. Sandia National Laboratory, “Development of a Solid Particle Receiver for High Temperature Thermochemical Processes” (26 pgs)
ACRONYMS

AECL – Atomic Energy of Canada, Limited
AFM - Atomic Force Microscopy
ALS - Advanced Light Source
ANL – Argonne National Laboratory
a-SiC – Amorphous Silicon Carbide
CBM – Conduction Band Minimum
CEA – Centre d’Etude Atomique
CRTF – Central Receiver Test Facility
CU – University of Colorado
DFT – Density Functional Theory
DOE – Department of Energy
DOE/EERE – DOE Office of Energy Efficiency and Renewable Energy
DOE/HQ – DOE Headquarters
DOE-GO – DOE Golden Field Office
GA – General Atomics Corporation
HFCIT – Hydrogen Fuel Cells and Infrastructure Technology
HNEI - Hawaii Natural Energy Institute
HX – Heat Exchanger
IDLH – Immediate Danger to Life and Health
ILS – Integrated Lab Scale
Intematix – Intematix Corporation
IPES - Inverse Photoemission Spectroscopy
LHV – Lower Heating Value
MT – Metric Ton
MVSystems – MVSystems Corporation
NETL – National Energy Technology Laboratory
NFPA – National Fire Protection Association
NIOSH – National Institute of Occupational Safety and Health
NREL – National Renewable Energy Laboratory
OER – Oxygen Evolution Reaction
PEC – Photo-Electrochemical Hydrogen Production
PID – Process Identification Number
PV - Photovoltaic
REL – Recommended Exposure Limit
RF – Radio Frequency
SALSA - Solid and Liquid Spectroscopic Analysis
SET – Solar Energy Technology Program
SHGR – Solar Hydrogen Generation Research
SNL – Sandia National Laboratories
SPR – Solid Particle Receiver
STCH – Solar Thermo-Chemical Hydrogen
STH – Solar-to-Hydrogen
TIAx – TIAx, LLC
UCSB – University of California, Santa Barbara
UH – University of Hawaii
UNLV – University of Nevada, Las Vegas
UHV - ultra-high vacuum
UPS - Ultraviolet Photoelectron Spectroscopy
VBM – Valence Band Maximum
XAS - X-ray Absorption Spectroscopy
XES - X-ray Emission Spectroscopy
XPS - X-ray Photoelectron Spectroscopy
Final Technical Accomplishment Report

**Project Title:** High Efficiency Generation of Hydrogen Fuels from Solar Power (Solar Hydrogen Generation Research)

**Project Period:** June 25, 2003 to June 30, 2011

**Date of Report:** September 2011

**Recipient:** UNLV Research Foundation

**Award Number:** DE-FG36-03GO13062

**Working Partners:**

**Thermo-Chemical Hydrogen Production (STCH) – Task 1**
University of Nevada Las Vegas (UNLV)
General Atomics Corporation (GA)
University of Colorado (CU)
Sandia National Laboratories (SNL)
Argonne National Laboratory (ANL)
National Renewable Energy Laboratory (NREL)
TIAX, LLC (TIAX)

**Cost-Sharing Partners:**
UNLV
GA
CU

**DOE Managers:** Richard Farmer, DOE-HQ Technology Manager
Paul Bakke, DOE-GO Project Manager

**Photo-Electrochemical Production of Hydrogen (PEC) – Task 2**
University of California-Santa Barbara (UCSB)
University of Hawaii (UH)
University of Nevada, Las Vegas (UNLV)
National Renewable Energy Laboratory (NREL)

**Cost-Sharing Partners:**
MV Systems, Inc. (MVSystems)
Intematix Corporation (Intematix)
UNLV
UCSB
UH

**DOE Managers:** Roxanne Garland, DOE-HQ Technology Manager
David Peterson, DOE Golden Field Office Project Manager

**Technical Contact:** Dr. Robert F.D. Perret
(702) 630-1542, ntsllc@rperret.com
PROJECT OBJECTIVE

The objective of this work is to identify economically feasible concepts for the production of hydrogen from water using solar energy. The ultimate project objective was to select one or more competitive concepts for pilot-scale demonstration using concentrated solar energy. Results of pilot scale plant performance would be used as foundation for seeking public and private resources for full-scale plant development and testing.

Economical success in this venture would afford the public with a renewable and limitless source of energy carrier for use in electric power load-leveling and as a carbon-free transportation fuel. The Solar Hydrogen Generation Research (SHGR) project embraces technologies relevant to hydrogen research under the Office of Hydrogen Fuel Cells and Infrastructure Technology (HFCIT) as well as concentrated solar power under the Office of Solar Energy Technologies (SET). Although the photoelectrochemical work is aligned with HFCIT, some of the technologies in this effort are also consistent with the skills and technologies found in concentrated solar power and photovoltaic technology under the Office of Solar Energy Technologies (SET).

Hydrogen production by thermo-chemical water-splitting is a chemical process that accomplishes the decomposition of water into hydrogen and oxygen using only heat or a combination of heat and electrolysis instead of pure electrolysis and meets the goals for hydrogen production using only water and renewable solar energy as feed-stocks.

Photoelectrochemical hydrogen production also meets these goals by implementing photo-electrolysis at the surface of a semiconductor in contact with an electrolyte with bias provided by a photovoltaic source. Here, water splitting is a photo-electrolytic process in which hydrogen is produced using only solar photons and water as feed-stocks.

The thermochemical hydrogen task engendered formal collaborations among two universities, three national laboratories and two private sector entities. The photoelectrochemical hydrogen task included formal collaborations with three universities and one national laboratory. The formal participants in these two tasks are listed above. Informal collaborations in both projects included one additional university (the University of Nevada, Reno) and two additional national laboratories (Lawrence Livermore National Laboratory and Lawrence Berkeley National Laboratory).
TECHNICAL PROJECT ORGANIZATION

The project consisted of two primary tasks:

- **Task 1:** Solar Thermo-chemical Hydrogen Production Research and Development
- **Task 2:** Solar Photoelectrochemical Production of Hydrogen Research and Development

EXECUTIVE SUMMARY: SOLAR THERMO-CHEMICAL HYDROGEN PRODUCTION

Thermo-chemical cycles were identified through literature search and contributions from cycle originators within and outside the project. Chemical reactions analysis provided theoretical chemical feasibility of individual cycle steps. An objective scoring process was developed and implemented in Phase 1 of the selection process to select the best, most cost-effective, cycles for further study. Flow sheets were developed in Phase 2 of the selection process to provide quantitative estimates of cycle efficiency, the primary metric for selection of cycles that would move into feasibility testing and economic evaluation. The inventory of thermochemical cycles and results of the analysis and selection processes were documented and are attached to this report.

Fourteen potentially competitive thermo-chemical cycles grouped in about four chemical reaction classes were identified and reaction thermodynamics and kinetics were documented using literature reports and laboratory scale experiments. Detailed chemical engineering analysis of attractive cycles using literature and laboratory data was applied to system design for testing and evaluation. Solar thermal concepts were developed in accord with cycle thermal energy requirements and integrated with the chemical plant design. Integrated plant-scale designs were developed and Aspen Plus™ was used to establish thermal efficiency metrics for each cycle under common annual production requirements with common annual average insolation values for operating conditions of both levelized and capacity production constraints. H2A analysis was applied to estimate hydrogen cost at the plant gate at 300 psi pressure. The ultimate project objective was to select one or more competitive concepts for pilot-scale demonstration using concentrated solar energy. This ultimate objective transitioned to the Department of Energy upon assumption of project management responsibility by the HFCIT Office in the Hydrogen Research Program.

For hybrid cycles, electro-chemical cell designs were reviewed and modeled for ideal reactions, equilibrium reactions and for reactions incorporating process kinetics. Various electrolyte solutions are explored in the laboratory to optimize the electro-chemical process.

Chemical engineering system modeling software was applied to quantify thermal efficiency of conceptual flowcharting of the most competitive thermo-chemical cycles, and plant design software was applied to provide capital cost estimates for the engineered thermo-chemical
concept design. These systems studies provided the process thermal efficiency for later use in determining system efficiency as well as early estimates of cycle-specific hydrogen costs.

Solar thermal energy for high temperature processes (T<1100°C) was studied using a solid particle receiver (SPR) concept that accumulates directed solar energy from a field of heliostats. Solar thermal energy for ultra-high temperature processes (T>1100°C) was studied using cavity receiver concepts equipped with a secondary concentrator design. An engineering assessment of current heliostat cost and performance defined the benefits and research and development options to reduce significantly the costs of heliostat fields and associated towers that represent the primary cost drivers for a solar thermal energy processing system.

Capital and operating cost estimates developed from study products were used to identify the most attractive several thermo-chemical cycles for test and evaluation in integrated closed-loop, bench-scale tests. Subsequent to successful integrated bench scale, closed-loop demonstrations, earlier capital and operating costs were planned to be refined and a “go/no-go” decision, based on economic potential, was to be made whether or not to proceed to pilot plant design. These final actions transitioned to the DOE/EERE STCH Project under HFCIT.

EXECUTIVE SUMMARY: SOLAR PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

The objective of this collaborative work is to accelerate development and demonstration of stable and efficient PEC hydrogen production systems. The project focus is on discovering and characterizing appropriate band-gap materials with adequate conductivity for higher solar-to-hydrogen (STH) conversion efficiencies. Initial studies expanded on earlier multijunction electrode concepts as well as analytic consideration of externally connected two-electrode concepts. Initial photoactive materials and redox reaction catalytic materials proved unsatisfactory in materials durability and/or solar-to-hydrogen (STH) production efficiency. The general approach of trial performance characterization and analysis of differently alloyed material interfaces was modified to incorporate numerical prediction of integrated band gap level relative to redox potentials, band gap alignment at interfaces and conduction band levels for selected alloys. Some analysis of corrosion potential accompanied the numerical studies. The modified approach, meant to accelerate the search for adequately performing materials, resulted in a feedback loop between theoretical prediction, material synthesis, experimental validation of theoretical results and laboratory characterization of performance metrics for semi-integrated design concepts.

The feedback loop approach and the PEC work reported here have continued under cooperative management by the UNLV Research Foundation and the DOE Hydrogen Research Program. This cooperative research effort is coordinated through the PEC Working Group that is directed by the DOE Hydrogen Research Program. System engineering and cost effectiveness assessments of system design concepts became an integral part of the DOE PEC research effort after the establishment of the jointly managed endeavor.
Final Report Organization
Task 1 and Task 2 differ significantly in technology base and differ generally in necessary skill sets and technology maturity. Each task will be reported separately under Technical Approach, Accomplishments, Special Recognitions, Awards and Patents and related Presentations and Publications.

TECHNICAL APPROACH – SOLAR THERMOCHEMICAL HYDROGEN PRODUCTION (STCH)

A screening process was developed and applied to all published and otherwise identified thermochemical water splitting cycles with potential for closed cycle operation requiring only the addition of water and thermal energy. The screening process was used to reduce the number of candidate cycles selected for more detailed study and analysis. The apparently most competitive cycles were subjected to laboratory study to establish thermochemical feasibility and performance metrics for use in further analytic comparative performance to select a few cycles that would be integrated for lab-scale (ILS) performance testing. Simultaneous effort was conducted to establish system concepts for integration of solar thermal power sources with thermochemical reactor designs. The results of laboratory thermochemical studies were used with these system design concepts to forecast plant capital and operating costs to produce 100 MT H2/day. Go/no-go decisions to advance to the next phase of research and development for each cycle were based on the assessed potential for the cycle to meet DOE targets for hydrogen gate costs and plant operating efficiencies using combined analysis tools of Aspen Plus™ and H2A.

More than 350 thermochemical cycles were considered, resulting in an enormous amount of information that had never before been compiled so a database was developed and a website established to provide open access to work that otherwise might have to be repeated.

Accomplishments – STCH
Accomplishments will be reported below in the broad categories described above:
1. Thermochemical Cycle Screening and Selection
2. Laboratory Feasibility Studies
3. Collector/Receiver/Reactor Studies
4. Performance Analysis

Thermochemical Cycle Screening and Selection
Since many hydrogen producing thermochemical cycles have been proposed over the last 40 years, a literature search was performed to identify all published cycles. These were added to an existing database that had been compiled to identify cycles suitable for nuclear hydrogen production. Additional cycles were contributed by other researchers, particularly Claude Royèr (private communication). A smaller scale survey was carried out by the scientists at CEA. More than 350 distinct cycles were identified and new ones were added as appropriate. Each cycle was assigned an identification number (PID) in and a process name for use in the database. Cycles were also categorized based on elements and chemicals to assist in database queries. The initial screening process was designed to restrict the number of cycles that qualified for detailed
evaluation. The purpose was not to select the best process but to eliminate from consideration those processes that likely would not be worth the effort of a detailed evaluation. The approach established screening criteria to discriminate against unlikely processes. The methodology used a set of objective criteria and for each criterion, defined a metric to generate a numerical comparative score in the range of 0 to 10. This along with a weighted average of the scores of the individual criterion would generate a composite score for the cycle.

Sixteen measurable criteria were devised for use in measuring the practicability of a cycle. For each criterion, a metric was defined and a score of between 0 and 10 was given for each thermochemical cycle. Every attempt was made to make the criteria objective, which was possible in most cases. For example, toxicity rankings were taken from EPA and NIOSH publications. When a chemical is not listed in these compilations, a ranking for the chemical was assigned by an experienced chemist. This ranking was then used for the chemical for any cycle in which it is present. Whenever there was not a published ranking for a criterion, one was established based on the experience and expertise of the contributing members. For example, the corrosiveness ranking stems from the rate of chemical attack on common engineering materials used in chemical plant construction.

The criteria used to screen the practicability of a thermochemical cycle can be broken down into four different general categories: i) economic considerations, ii) applicability to solar power system, iii) level of previous effort and iv) environmental and safety issues. The following sections provide a more detailed description of the criterion in each of these categories.

**Economic Consideration**

**Criterion 1. Number of chemical reactions**

A two-step cycle would in general be less complex than a five-step cycle: fewer movements of materials, fewer separations and fewer chemicals

**Criterion 2. Number of separation steps**

A much-abbreviated flow diagram was constructed for each cycle in order to determine the number of “difficult” separations needed. It is based solely on the fundamental reaction equations of each cycle. The following types of separations were classified as difficult:

- solid-solid separations, where the products are two solids
- solid-liquid separations, where a filtration or other means would be needed
- liquid-liquid separations, where two liquids (miscible or immiscible) were found.
- gas-gas separations, such as separating O₂ from HCl.
- aqueous/non-aqueous, such as dehydrating aqueous H₂SO₄ to make anhydrous H₂SO₄

Gas-liquid and gas-solid separations were considered “easy” and were not included in the tally for the total separation step within each cycle.

Two other assumptions were made in this evaluation. First, the details of the separation such as the actual operation were not considered. However, provisions were made to include certain simple procedures that could be implemented to reduce the number of separation steps. For example, if by cooling the products 100°C, a difficult gas-gas separation could become an easy
gas-liquid separation, the processing step would be included in the flow diagram. The second assumption concerns the recycling of chemicals. Since many reactions are at equilibrium and do not proceed to completion, recycle of all liquid and gas reactants from the product stream is required. A significant number of the difficult separations stemmed from recycle of gas or liquid reactants. On the other hand, it was assumed that reactions involving solids will proceed to completion turning all reactants into products and no recycling would be required.

**Criterion 3. Number of chemical elements**
The number of chemicals in a cycle indirectly reflects the complexity of the process as a greater number of species are involved. This normally results in a more complex process.

**Criterion 4. Abundance of chemical elements**
Favorable cycles are those that employ common chemicals and elements since these would usually be less expensive and readily available in large quantities. This criterion gauges abundance of the scarcest element in the cycle, and assigns points based on that limiting abundance.

**Criterion 5. Corrosiveness of chemicals**
Corrosive chemicals require the use of more expensive durable materials of construction. Chemicals were classified from least to most corrosive, based on their corrosiveness on common metallic materials of construction.

**Criterion 6. Solids transport**
This criterion determines the extent to which solid movement and batch processing are required. The movement of solids within a process is often difficult and costly whereas liquids and gases transport is common in plant designs. Thermochemical cycles with only continuous flow are deemed easy whereas batch processes are deemed difficult. Points were assigned to each cycle based on the most difficult handling step, which have been categorized as follow: (1) continuous flow of gases and liquid, (2) batch flow of gases and liquid through fixed beds of solids, (3) continuous flow of solids, and (4) batch flow of solids. A cycle requiring multiple handling steps was ranked based on its least desirable chemical transportation step.

**Solar Collector/Receiver Consideration**
**Criterion 7. Use of radiant heat transfer to solids**
The transfer of heat to and from solids is increased for higher temperatures, so cycles with very high temperature solids are favored. This criterion uses variable scale for temperature ranges from below 900°C to above 1800°C.

**Criterion 8. Temperature of high temperature endothermic step**
The highest temperature of a cycle was compared to the optimal temperature range for a solar thermal system. If the highest cycle temperature was near the optimal temperature then a high point score was assigned to the cycle when paired with this device. The further away the temperature was from the optimal temperature, the lower the point score. Our screening analysis considered the applicability of four solar collectors:
1. Trough – optimal temperature 375°C
2. Standard tower – optimal temperature 525°C
3. Advanced tower – optimal temperature 875°C
4. Dish – optimal temperature 1125°C

Cycles that were not well matched to a solar device received 0 points on this particular criterion and were excluded from further assessment even though they had high scores from the other criteria.

Criterion 9. Compatible with thermal transients and/or diurnal storage

**Previous Level of Effort for Candidate Cycle**

Criterion 10. Number of literature papers
A higher number of papers published on a cycle indicates higher maturity of understanding than for cycles that have not been studied, suggesting that problems associated with it might have already been addressed.

Criterion 11. Scale of testing
Favorable cycles that have attracted support for larger scale testing like integrated lab scale, demonstration testing and pilot plant testing are likely to have improved chance of commercial success.

**Safety and Environmental Consideration**

Criterion 12. Energy efficiency and Cost
Evidence of cost and efficiency studies is indicative of greater levels of effort and maturity of development.

Criterion 13. Acute toxicity to humans
Chemicals used in a production plant should not be an immediate hazard for injury and death. This criterion considered “the most dangerous chemical” in a cycle, as determined for acute human exposure. Points were assigned to the IDLH (Immediate Danger to Life and Health) values found in the NIOSH (National Institute of Occupational Safety and Health) Pocket Guide to Chemical Hazards.

Criterion 14. Long-term toxicity to humans
A chemical may be safe for short-term human exposure but can be dangerous over long term at low exposure level. This criterion considered “the most dangerous chemical” in a cycle, as determined by chronic long term human exposure. Points were assigned based on the REL (Recommended Exposure Limits) values taken from the NIOSH Pocket Guide to Chemical Hazards.

Criterion 15. Environmental toxicity
A chemical may be safe for human exposure but can be deemed damaging to the environment. This criterion examined “the most dangerous chemical” in a cycle, as determined for environmental exposure, from EPA categories of reportable quantities discharged to the
environment. These values were found in 40 CFR1, table 302.4 and Appendix A of part 355, and points were assigned accordingly.

Criterion 16. Reactivity with air or water
A chemical may be inert in an enclosed setting but may become very hazardous with an accidental exposure to air or water. This criterion took the sum of the NFPA (National Fire Protection Association) hazard ratings for flammability and reactivity with air & water, for each chemical in a cycle, and assigned points based on the highest sum.

The scoring scheme of each criterion, other than those derived from published ranking, was established after careful deliberation among the group members based on their technical expertise and practical experience. All the identified cycles received a base score for all criteria. However, depending on the solar thermal design, the importance of the individual criterion to the selection process will vary. For example, a trough will not be able to support a reaction that has an endothermic step above 1000°C and a tower is more adaptable to solid flow than a dish. Hence, a weighting factor is used when scoring the applicability of various solar thermal designs to each cycle.

This weighting factor was derived in two steps using a six-sigma methodology. First, the relative importance of each of the 16 criteria to the operation of a solar hydrogen production system was determined. Team members identified 5 factors which were essential in the development and operation of a solar thermal hydrogen production plant and they are i) capital cost, ii) operation and management, iii) development risk, iv) diurnal cycle and v) environmental risk. A multiplication factor (mp) between 1-5 was assigned to each of them based on their importance to the overall selection process. Next, the relevance of each criterion with respect to the 5 operational factors was determined. A relevance value of 0, 1, 3 or 9 was assigned to each criterion according to its significance to the factor. A preliminary set of raw weighting factors for each criterion was obtained by totaling the sum of products of the multiplication factor and the relevance value.

The next step was to arrive at a set of weighting factors that are specific to the individual solar devices. Based on the raw weighting factors and the expertise of the team members, weighting factors between 1-10 were generated and assigned to each criterion per solar device.

The scoring of each cycle was completed by multiplying criteria score with the weighting factor for each individual solar device and then normalized by a score multiplier to make the maximum score 100 points. Based on this method, 360 cycles were evaluated and 67 thermochemical cycles with the highest scores were selected for more detailed studies.

One question that must be addressed was how well this type of process eliminates from the study those cycles with a low probability of success. Stepwise regression and rank correlation methods were applied by Sandia National Laboratories to answer this question. The results of this study showed that (1) the selected cycles were not highly dependent on criteria weights, (2) the screening process was robust and (3) it was generally accurate in determining the most promising cycles for further analysis.
The 67 cycles with highest scores moved to the next phase of selection. HSC Chemistry Database assessments of

Details of the criteria, weighting factors, examples of their application and the full tabulation of the screening application can be found in the General Atomics Final Report, Attachment G. The following tabulation of results shows the set of thermochemical cycles that appeared competitive and would match well with existing solar collector concepts:

<table>
<thead>
<tr>
<th>Sulfuric Acid Cycles</th>
<th>Max Temperature C</th>
<th>Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid Sulfur</td>
<td>900</td>
<td>51</td>
</tr>
<tr>
<td>Sulfur Iodine</td>
<td>900</td>
<td>45</td>
</tr>
<tr>
<td>Multivalent Sulfur</td>
<td>1570</td>
<td>42</td>
</tr>
<tr>
<td><strong>Metal Sulfate Cycles (STCH)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium Sulfate</td>
<td>1200</td>
<td>55</td>
</tr>
<tr>
<td>Barium Sulfate</td>
<td>1200</td>
<td>47</td>
</tr>
<tr>
<td>Manganese Sulfate</td>
<td>1200</td>
<td>42</td>
</tr>
<tr>
<td><strong>Volatile Metal Oxide Cycles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc Oxide (STCH)</td>
<td>2200</td>
<td>53</td>
</tr>
<tr>
<td>Hybrid Cadmium</td>
<td>1600</td>
<td>53</td>
</tr>
<tr>
<td>Cadmium Carbonate (STCH)</td>
<td>1600</td>
<td>52</td>
</tr>
<tr>
<td><strong>Non-volatile Metal Oxides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>2200</td>
<td>50</td>
</tr>
<tr>
<td>Sodium Manganese</td>
<td>1560</td>
<td>59</td>
</tr>
<tr>
<td>Nickel Manganese Ferrite</td>
<td>1800</td>
<td>52</td>
</tr>
<tr>
<td>Zinc Manganese Ferrite</td>
<td>1800</td>
<td>52</td>
</tr>
<tr>
<td><strong>Other</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hybrid Copper Chloride (STCH)</td>
<td>550</td>
<td>49</td>
</tr>
</tbody>
</table>

The Sulfuric Acid group was already under study by the Nuclear Hydrogen Initiative and no work was funded under the STCH project reported here, although a watching brief was maintained to assure that STCH remained informed of progress and competitive posture relative to STCH cycles under study. The Hybrid Copper Chloride cycle received earlier support as an alternative cycle under the Nuclear Hydrogen Initiative, but soon became a primary cycle of interest within STCH. Hybrid cadmium was not studied under STCH due to its high temperature step and the Cadmium Carbonate cycle transitioned into a volatile Cadmium Oxide cycle. The Ferrite cycles were studied under internal support at Sandia National Laboratories. Finally, the Sodium Manganese cycle was pursued under a separate funding award through EERE.

**Laboratory Feasibility Studies**

**Sulfate Cycles**
Laboratory studies showed that the sulfate cycles could not generate any hydrogen in the low temperature hydrolysis step with a thermochemical approach. It was concluded that the sulfate group would likely require electrolysis to generate hydrogen. Since electrolysis would reduce thermal efficiency and since there is still required a high temperature step, the metal sulfate cycles were abandoned. Details of the work can be found in the General Atomics final report, Attachment G.
Cadmium Oxide

Further study after the selection process showed that a cadmium oxide cycle would be simpler than the cadmium carbonate cycle and more efficient besides:

\[
\text{Cadmium Carbonate Cycle} \\
\text{CdO(s)} \rightarrow \text{Cd(g)} + \frac{1}{2} \text{O}_2(g) \quad (1450\,^\circ C) \quad (1) \\
\text{Cd(s)} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CdCO}_3(s) + \text{H}_2(g) \quad (25\,^\circ C) \quad (2) \\
\text{CdCO}_3(s) \rightarrow \text{CdO} + \text{CO}_2(g) \quad (300\,^\circ C) \quad (3)
\]

\[
\text{Cadmium Oxide Cycle} \\
\text{CdO(s)} \rightarrow \text{Cd(g)} + \frac{1}{2} \text{O}_2(g) \quad (1450\,^\circ C) \quad (1) \\
\text{Cd(l,s)} + \text{H}_2\text{O} \rightarrow \text{CdO(s)} + \text{H}_2(g) \quad (25-450\,^\circ C) \quad (2)
\]

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Max Temperature °C</th>
<th>Efficiency (LHV) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium Carbonate</td>
<td>1450</td>
<td>52</td>
</tr>
<tr>
<td>Cadmium Oxide</td>
<td>1450</td>
<td>59</td>
</tr>
</tbody>
</table>

Feasibility studies for the cadmium oxide cycle were divided into three areas: \textit{i}) cadmium oxide decomposition, \textit{ii}) cadmium-oxygen decomposition back reaction and \textit{iii}) cadmium hydrolysis. It was found that cadmium oxide decomposition kinetics is very sensitive to the diffusion of oxygen gas away from the solid-gas interface. The diffusivity could be enhanced by either the use of an inert carrier gas or by highlighting geometric factors that could increase gas diffusivity. It was found that decomposition could be complete at temperature as low as 1150°C depending on measures taken to enhance oxygen transport from the decomposition interface. A design concept utilizing a fluidized bed decomposer inside the solar cavity was developed based on the study findings.

Decomposition and Back-reaction

Reaction rates between cadmium and oxygen vapors were measured at elevated temperatures and showed that 2% of the cadmium vapor reacted per second. Further measurements are required in order to determine the effect of temperature, flow rate and oxygen concentrations. This, along with future quench modeling studies, will provide inputs to design a quench process that inhibits back reaction efficiency losses.

Based on the results from cadmium oxide decomposition kinetics studies, a design concept for a decomposer was developed. This proposed design uses a fluidized bed in which the reactor cavity is heated directly by concentrated solar radiation. Windows are used to contain cadmium material and a gas sweep over the inside of the windows is used to prevent condensation of cadmium on the windows. The use of similar reactor has been demonstrated for other high temperature thermochemical hydrogen system. The skin of the reactor design is constructed from carbon steel and the inside wall is lined with high temperature bricks. Cadmium oxide particles are fed into the decomposer cavity and are then fluidized by a carrier gas, which can be either air or an inert like helium. Experiments showed that cadmium oxide particles formed by molten cadmium hydrolysis ranged between 1 to 10 µm in size, a size range that can be readily fluidized.
Hydrolysis
Experimental results showed that carbon dioxide and shear deformation were essential to high hydrogen generation rate using solid cadmium. The straightforward hydrolysis process converts Cd metal into Cd(OH)₂ and H₂ (g). The use of carbon dioxide converts an impervious cadmium hydroxide surface layer into granular cadmium carbonate. This, along with mechanical deformation, provides fresh cadmium surfaces for continued hydrolysis. Laboratories studies also successfully demonstrated the use of molten cadmium in hydrolysis. The optimal temperature for fast hydrogen generation was determined to be between 460°C – 480°C. Consequently, the 3-step cadmium carbonate cycle could be replaced by a more efficient 2-step cadmium oxide cycle by operating the hydrolysis step at much higher temperature. It was shown that increasing the surface contact between cadmium and steam could enhance hydrogen evolution. A rotary kiln loaded with inert pellets was used to demonstrate this. Based on the demonstration results, a scalable concept design for a high-pressure rotary hydrolysis kiln was developed.

The CdO cycle study continued under subcontract through Sandia National Laboratories to the DOE Hydrogen Research Program. Details of the CdO feasibility studies and resulting design concepts developed under this project can be found in the General Atomics final report, Attachment G.

Zinc Oxide
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 “steamed” 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.

\[
\begin{align*}
\text{ZnO} &\rightarrow \text{Zn} + \frac{1}{2}\text{O}_2 & 1800^\circ\text{C} – 2000^\circ\text{C} \\
\text{Zn} + \text{H}_2\text{O} &\rightarrow \text{ZnO} + \text{H}_2 & 450^\circ\text{C}
\end{align*}
\]  

Moreover, 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 night. As a result, startup and shutdown of the solar portion of the plant would not severely affect the hydrolysis portion of the plant. Nonetheless, the “ultra-high” temperature of the reduction step entails severe thermal stresses due to solar intermittency and so materials durability adds cost to plant construction.
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 commonly used in vitamins and sunscreens.

Challenges and Weaknesses
1. The back-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 ~7,000 “suns”. 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 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 provide useful results in on-sun experiments.

Reaction (1) is carried out using a high temperature transport tube reactor to dissociate zinc oxide. The forward zinc oxide dissociation reaction was shown to be fast, but overall conversion is limited by the back-reaction of oxygen with zinc vapor near the exit portion of the reactor. Reaction (2) of the process to react zinc powder with steam to produce hydrogen was carried out in both a thermogravimetric analyzer and a transport tube reactor. It was found that this step can be driven to completion with increased residence time (minutes instead of 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 back-reaction during the first step while maintaining high efficiency.

ZnO studies continued under subcontract through Sandia National Laboratories to the DOE Hydrogen Research Program. The research results and accomplishments under this reported project are summarized in detail in eight papers published in peer-reviewed research journals as well as in the University of Colorado final report, Attachment F.

**Hybrid Copper Chloride**

The Hybrid Copper Chloride cycle is a three-step thermochemical cycle that, while requiring an electrolysis step, nevertheless operates at temperatures much lower than those associated with pure thermochemical cycles.

- **Hydrolysis**
  \[ 2\text{CuCl}_2(s) + \text{H}_2\text{O}(g) \rightarrow \text{Cu}_2\text{OCl}_2(s) + 2\text{HCl}(g) \quad 340^\circ\text{C}-400^\circ\text{C} \quad (1) \]

- **Decomposition**
  \[ \text{Cu}_2\text{OCl}_2(s) \rightarrow \frac{1}{2}\text{O}_2(g) + 2\text{CuCl}(s) \quad 450^\circ\text{C}-530^\circ\text{C} \quad (2) \]

- **Electrolysis**
  \[ \text{CuCl}(s) + \text{HCl}(g) \rightarrow \text{CuCl}_2(a) + \frac{1}{2}\text{H}_2(g) \quad 100^\circ\text{C} \quad (3) \]

The cycle feasibility work under STCH focused on optimizing the hydrolysis reaction (Reaction 1) and development of the decomposition reactor (Reaction 2) to obtain 100% yields of the desired products. Other work, some conducted by Atomic Energy of Canada, Ltd (AECL) and some under the Nuclear Hydrogen Initiative and the Nuclear Energy Research Initiative addressed electrolyzer development (reaction 3).

Hydrolysis development effort led to a reactor design for which CuCl₂ is transferred in the form of a slurry at 22 bar to the hydrolysis reactor where it is sprayed into a superheated (400°C) steam environment at 1 bar. The CuCl₂ forms a free jet that expands and aspirates superheated steam into the jet resulting in high mass and heat transfer between the CuCl₂ in the jet and the steam. The CuCl₂ is converted to Cu₂OCl₂ and HCl. The HCl and unreacted steam exit the hydrolysis reactor to be cooled and are fed to the cathode of the electrolyzer. Sensitivity studies showed that high yield required either very low HCl concentration in the feed solution or very high steam to CuCl₂ ratio. Both result in diminished performance of the cycle. However, promising results were obtained with a nebulizer reactor in which very small droplets of CuCl₂ are formed. Upon contact with superheated steam, these droplets form very small particles accompanied by high heat and mass transfer resulting in high yield in Reaction (1).

For the decomposition section (Reaction 2), dry, free flowing copper oxychloride accumulates at the bottom of the hydrolysis reactor and is transferred to a decomposition reactor at 550°C to decompose into molten CuCl and oxygen. Heat is recovered from the molten CuCl in a direct heat exchanger where the CuCl is granulated while raising steam. This step is similar in design to the Batemen Slag Granulation (www.batemanengineering.com/) system. The solidified CuCl is then transferred to the anode feed tank where it is dissolved in an HCl-CuCl₂ solution.

The electrolyzer is based on PEM-type fuel cell technology. An anion exchange membrane will separate the anode and cathode and will allow the transfer of chloride ion from the cathode to the anode. The current process design specifies that the electrolyzer will be run at 80-100°C and at 24 bar. At the cathode, hydrogen is produced at 24 bar from HCl solution. The effluent from the cathode, also at 24 bar, is flashed to produce a vapor stream consisting of steam and <1 mole%
HCl and a liquid stream containing 87 mole % of HCl. The flashed acid-rich liquid stream is recycled back to a cathode feed tank. The flashed acid-poor steam stream is used for the feed for the hydrolysis reactor. At the anode, CuCl is oxidized to CuCl₂. The electrolyzer is being developed by the Atomic Energy of Canada Limited and proof-of-concept experiments have been completed.

Other details of the Hybrid CuCl feasibility study can be found in the Argonne National Laboratory (ANL) CuCl Cycle report, Attachment E, and in ANL reports submitted to the Nuclear Hydrogen Initiative as well as to the DOE Office of Energy Efficiency and Renewable Energy. Hybrid CuCl studies are continuing at Argonne National Laboratory under sponsorship of the DOE Hydrogen Research Program.

**Collector/Receiver/Reactor Studies**

**Advanced Heliostat Study**
Heliostats are the most important cost element of a solar thermal power tower plant. Heliostats contribute ~50% to the capital cost of the plant, so heliostat cost reduction is a prime driver of solar thermal hydrogen costs. Sandia National Laboratories was commissioned to assess the potential for heliostat cost reduction through research and development investments. The study concluded that a 2006 price-year goal of less than $100/m² would be consistent with levelized cost of electricity (<6 cents/kWh) or hydrogen (<$3/kg) from power towers. Such costs could be competitive on the open market, especially if carbon-offset trading becomes the norm. The analysis concluded that heliostat cost of ~$90/m² might be achieved through additional research and development combined with fabrication and installation cost reductions that accompany a several-year period of deployment. The full study and additional conclusions can be found in the Sandia National Laboratories report, SAND2007-3293, available through the link: [http://infoserve.sandia.gov/sand_doc/2007/073293.pdf](http://infoserve.sandia.gov/sand_doc/2007/073293.pdf).

**Solid Particle Receiver**
The solid particle receiver (SPR) is a direct absorption central receiver that can provide a solar interface with thermal storage for thermochemical hydrogen production processes requiring heat input at temperatures up to 1000°C, which is beyond the capability of traditional heat transfer fluids. In operation, a curtain consisting of ceramic particles ranging in size from 100 μm-1,000 μm is dropped within the receiver cavity and directly illuminated by concentrated solar energy. The heated particles exit the receiver and may either be stored in silos or sent through a heat exchanger to provide process heat input. Because the energy is directly absorbed on the particles the receiver is capable of operating at high flux levels relative to other receiver concepts where the heat transfer media is confined to tubes. The performance of the SPR is dependent on several factors including the characteristics of the particle flow velocity (residence time) and opacity (optical density), the geometry of the receiver, and the operating temperature. In addition, because this type of receiver has an open aperture it is possible that convective losses to the environment can be significant.
SPR development began in the early 1980s. The STCH interest developed when the solid particle receiver was identified as a possible solar interface for the Sulfur Iodine and Hybrid Sulfur cycles. From there the project proceeded in the following stages:

- Initial modeling using previously developed codes. These include PSI-Cell, which was used in the 1980s by Sandia National Laboratories to do performance modeling of the SPR. Collaboration was also begun with the National Energy Technology Lab (NETL) to use their multi-phase code MFIX to perform some comparative analysis. The purpose of this work was to estimate the level of performance that might be expected of a prototype device tested at Sandia’s Central Receiver Test Facility (CRTF).

- Receiver design: The design process for the prototype was initiated in 2005 and concluded in June of 2006.

- Off-sun studies: a small off-sun test fixture was built to investigate the optical properties of the falling particle curtain and provide some additional data for the modeling efforts. This work was begun in 2005 and included collaborators from UNLV working onsite at Sandia. The work concluded in early 2007.

- Prototype construction: The construction of the on-sun test prototype began in 2005 and was completed in December of 2007.

- On-sun testing: Testing at Sandia’s CRTF was conducted from December 2007 through February 2008.

- Computational modeling continued throughout the development and testing effort and included collaboration with researchers at UNLV and DLR (Germany). We began validating models developed at Sandia and DLR in early 2008 using experimental data from on-sun testing.
A computational model of particle flow through a solid particle receiver was developed. Two-phase particle/air flow models of the particle stream inside the SPR were coupled with external wind profiles through the aperture to address convective heat and particle exchanges across the aperture. Model results were compared with scaled laboratory experiments and showed reasonable agreement, permitting design modifications of particle stream introduction and SPR configurations to inhibit aperture convective heat and particle losses due to external winds. Solar irradiation, re-radiation and emission from the cavity walls, convection, wall conduction, and two-phase particle/air flow were also simulated in the developing model. Simulated results were compared to measured temperatures of the particles and walls during nine on-sun tests of the scaled SPR test device at the Sandia Central Solar Test Facility. Results were also compared to particle velocities and concentrations measured during unheated tests with good matches to the data. Results show that the model accurately predicts the salient distributions and trends in particle temperatures and efficiencies as a function of input power and particle mass flow rate. Based on the good agreement of model results with scaled test measurements, SPR development is prepared to move to scaled-up design, construction and test. Preliminary testing was done on particle attrition in a facility developed for this purpose. Additional funding would be necessary to carry this effort to useful conclusion.

Detailed reports on SPR modeling, construction and testing can be found in Attachment H.

Cavity Receiver/Reactor Development
A single tube insulating cavity and a multi-tubular reflective cavity solar reactor were designed, constructed and tested as part of this effort.

The single tube reactor was designed and built at the University of Colorado and then sent to ETH Zurich, Switzerland and tested for the rapid dissociation of ZnO. It was a lab-scale 5 kW reactor prototype and was subjected to high-flux solar radiation source in the range 448 – 2125 kW/m2. A heat transfer reactor model was formulated that encompassed the governing mass and energy conservation equations coupling radiation/convection/conduction heat transfer to the chemical kinetics, and their solution by Monte-Carlo ray-tracing and finite difference techniques. Validation of the reactor model was accomplished by comparing numerically computed and experimentally measured temperatures and reaction rates in the 1507°C – 1702°C range. The reactor model was further applied to simulate a continuous process, identify major sources of irreversibility, and predict solar-to-chemical energy conversion efficiencies. Details can be found in the peer-reviewed paper: Melchior, T., C. Perkins, A.W. Weimer, and A. Steinfeld, “A Cavity-receiver containing a tubular absorber for high-temperature thermochemical processing using concentrated solar energy,” International Journal of Thermal Sciences, 47, 1496-1503 (2008).

The multi-tubular reactor consisted of a cavity-receiver containing an array of tubular absorbers with considerations for carrying out ZnO dissociation. The continuity, momentum, and energy governing equations that couple the rate of heat transfer to the Arrhenius-type reaction kinetics were formulated for an absorbing-emitting-scattering particulate media and numerically solved using a computational fluid dynamics (CFD) code. Parametric simulations of reactor performance evaluated the influence of the solar flux concentration ratio (3000 - 6000 suns), number of tubes (1 – 10), ZnO mass flow rate (2-20 g/min per tube), and ZnO particle size
(0.06 - 1 μm). The forward reaction extent was calculated to reach completion within a residence time of 1 second at temperatures above 2273°C, yielding solar-to-chemical energy conversion efficiency up to 29%. Details can be found in the peer-reviewed paper: Hasussener, S., D. Hirsch, C. Perkins, A. Lewandowski, A. Steinfeld and A.W. Weimer, “Modeling of a multi-tube high-temperature solar thermochemical reactor or hydrogen production,” Journal of Solar Energy Engineering, 131, Article 024503 (2009).

Performance Analysis
All cycles under active development were subjected to performance analysis for plants scaled to produce ~100,000 kg H₂/day. The analyses incorporated laboratory experimental results and thermochemical reactions/products within a detailed flow sheet to quantify all mass and energy balances and included reasonable steps for heat recuperation. Equilibrium concentrations at each step were quantified using HSC Chemistry Software Database and flow sheet analysis used Aspen Plus™ modelling software. Parameters and processes were subjected to reasonable assumptions where hard data was unavailable and sensitivity studies of results were performed for these assumptions. Primary output for the analyses were overall plant efficiency and gate costs of hydrogen.

Metal Sulfate
The Metal Sulfate cycles would not generate hydrogen without the possible assistance of an electrolysis step. These cycles were abandoned and no performance analysis was performed.

Cadmium Oxide
A flow sheet was developed for a solar plant producing 100,000 kg H₂/day. The process was put together using the Aspen Plus™ software. The process used a direct solar cadmium oxide decomposer and the hydrolysis step was carried out with molten cadmium. Assuming constant thermal input, the thermal efficiency of the cadmium cycle was calculated to be 59%LHV. The electric power required to operate various equipment within the plant was taken from the grid. Since the heat within the process stream can be used to power an internal power generation circuit, a more advanced flow sheet was developed in which all the heat flow streams within the process were integrated. It incorporated the power generation circuit as part of the cycle and the electricity requirement was thus supplied internally. Excess electricity would be put back into the grid, reducing reliance on grid electric power.

A more advanced second generation flow sheet was developed to account for solar intermittency. In addition to integrating the various heat streams, it incorporated thermal heat storage using three different media: cadmium at 325°C, cadmium oxide at 325°C or cadmium at 700°C, permitting optimal 24 hour operation. The plant design performs cadmium decomposition only during the day and the decomposed cadmium vapor is quenched into liquid cadmium at 700°C. The heat from this molten cadmium was used to generate electricity and cooling the molten cadmium to between 350°C -450°C. The cooled cadmium was then used to drive the hydrolysis step around the clock. The hydrogen plant components were sized and costs were determined for a 100,000 kg/day. However, the decomposition reactor relies on an innovative “beam-down” collector/receiver. Following the conclusion of the project, work continued with the Weizmann Institute to design the solar field and the details of the receiver/reactor for a beam down tower design. No hydrogen gate costs were available at the conclusion of the project.
Details of the flow sheets and the beam-down decomposer receiver/reactor concept are available in the General Atomics Final Report, Attachment G.

**Zinc Oxide**
A detailed flow chart was developed, and Aspen Plus™ was used for heat and mass balance modeling. A vacuum swing adsorber was used to separate the inert gas (used to inhibit the decomposition back-reaction) and the hydrogen product was compressed to 300 psig to meet pipeline requirements at the plant gate. An economic evaluation of the process to produce 100,000 kg/day H₂ was done utilizing the DOE-developed H2A program. Two cases were considered:

1. **CY 2015 case** in which Reaction (1) was assumed to achieve 70% ZnO dissociation. A hydrogen compressor was required to supply pipeline hydrogen and where heliostats were $126.50/m²

2. **CY 2025 case** in which Reaction (1) was assumed to achieve 85% dissociation and Reaction (2) operated at 300 psig to eliminate the need for downstream compression 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, thermal efficiency 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).

Additional details of the performance analysis of the Zinc Oxide Cycle can be found in Attachment F.

**Hybrid Copper Chloride**
An Aspen Plus™ flow sheet was developed for a Hybrid CuCl plant. A production level of 125 MT H₂/day requires 210 MW of thermal energy and 87.8 MW of electrical energy and results in an efficiency of about 40%-42% (LHV). In conjunction with the Aspen results, pinch analysis developed an integrated heat exchange network to recover waste process heat. As with any conceptual process that is proposed with little experimental results and data, a number of key assumptions had to be made. These were:
1. Electrolysis reactor operates at:
   a. 0.5 volts
   b. 500 milliamps/cm²

   These conditions were assumed to be consistent with other hybrid processes that have electrochemical steps, for instance the hybrid sulfur process

2. The material of construction is porcelain coated carbon steel

3. The crystallizer operates with minimal water, HCl and CuCl entrainment

4. In the hydrolysis reactor, copper oxychloride forms rapidly in a zone of high heat and mass transfer in short residence time (5 sec)

5. Sublimation of CuCl in the oxy-decomposition reactor is negligible

6. CuCl₂ will flow from the crystallizer to the hydrolysis reactor given the large pressure drop (22 to 1 bar)

7. Ideal separators are used for the entire process

In completing the economic analysis the assumptions were:

1. The base year for the economic analysis was 2005 so the CEPCI = 468.

2. The plant design produces 125 MT H₂/day

3. The cost of the electrolysis cell (vessel and electrodes) was $2,500/m² of total active cell area.

4. Bulk HCl cost is $241/metric ton.

The preliminary efficiency and hydrogen production costs for 2015 were 39% and ~$4.53/kg H₂. For 2025, the hydrogen production costs are ~$3.48/kg H₂ and the efficiency is about 41%. The flow sheet is being optimized and further work is being done on process designs in the expectation that the performance metrics will improve.

Details of the performance analysis for the Hybrid Copper Chloride cycle can be found in the ANL CuCl Cycle report, Attachment E.
**Patents, Special Recognition, Awards**
Excellence in Research Award to the University of Colorado for ZnO Studies, EERE, May 2005.


**Publications**


Presentations


Francis, T. M; Carney, C. S; Lichty, P. R; Rennels, R.; Weimer, A. W. “The Rapid Dissociation of Manganese Oxide to Produce Hydrogen,” AIChE Annual Meeting, Salt Lake City, UT, 2007 #584b.


TECHNICAL APPROACH - SOLAR PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION (PEC)

The general approach of this collaborative effort between the UNLV-SHGR and the DOE PEC Working Group researchers integrated state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability and cost. From the application of density-functional theory to calculate band-structures and effects of co-incorporants on valence and conduction band positions; through the use of diverse synthesis techniques, including combinatorial methods, to create tailored materials; and by employment of microstructural, electron spectroscopic, and electrochemical characterization techniques, a comprehensive picture of the materials properties and resulting performance is being developed.

A combination of previous history, experience and theoretical investigation identified the following materials and material classes for in-depth study:

1. Tungsten oxide based
2. Copper chalcopyrite based
3. Silicon carbide based
4. Iron oxide based
5. Zinc oxide based

All of these materials have continued under study following the conclusion of the UNLV Research Foundation SHGR Project. Accordingly, this final report will address accomplishments and results, but should not be viewed as the “last word” on the performance of any of the reported materials. Research accomplishments under the SHGR Project are summarized below for the materials classes above and for the materials characterization efforts.

Tungsten Oxide Materials
With an optical band gap of approx. 2.6 eV, tungsten oxide was selected as a potential candidate for water splitting. For several years now, research at the University of Hawai‘i developed a low-cost deposition process to fabricate photoactive WO₃ films. Progress on deposition parameters, such as temperature and pressure, was made and a saturated photocurrent (measured under simulated AM1.5G illumination in 0.33M H₃PO₄ electrolyte) of about 3 mA/cm² was obtained. Mounted over a Si-based PV cell in a so-called mechanical stack (both PEC and PV devices shorted with WO₃ PEC electrode sitting over the PV cell), a solar-to-hydrogen efficiency of 3.1% was demonstrated. However, the DOE target of 12% STH efficiency cannot be achieved with pure WO₃ due to its relatively “high” band gap that limits the effective photoactive solar spectrum. Theoretical investigation was initiated to find co-incorporants that would expand the solar photoactive bandwidth by reducing the bandgap of the modified material. Moreover the conduction band minimum of WO₃ is lower than optimal for hydrogen production so additional theoretical study was used to model the effect of Mo incorporation in WO₃, incorporated experimentally for that purpose. Experimental details of WO₃ investigation can be found in the University of Hawaii Final Report, Attachment C.
Density functional theory (DFT) was applied to N incorporation in WO₃ to investigate the effect on bandgap. Substitutional N in the assumed monoclinic WO₃ causes spin polarization and introduces an impurity band above the valence band of WO₃. Interstitial N also introduces a partially occupied impurity band very close to the CBM of WO₃ while fully occupied impurity bands are formed just above the original WO₃ valence bands. The general theoretical result predicts that N incorporation in WO₃ should result in reduced bandgap leading to improved absorption in the visible portion of the solar spectrum.

The effect of Mo incorporation in WO₃ was studied theoretically by substitution of a Mo atom for a W atom. The CBM of WO₃ is primarily determined by W d states and partial density of state calculations for W and for substituted Mo result in nearly identical d states for both Mo and W. The general theoretical conclusion was that Mo incorporation in WO₃ is ineffective in modifying the CBM.

Validation of N incorporation predictions was sought experimentally. Despite a net band gap reduction of 0.5 eV after N incorporation, a drastic reduction of the maximum photocurrent to approx. 0.6 mA/cm² was observed, mainly due to lattice distortion and defects creation that trap photogenerated carriers. This indicated that a performance enhancement of tungsten-oxide-based PEC electrodes cannot be easily obtained by “impurity” incorporation solely focusing on reducing the band gap. Recent work has shown however than higher performance can be obtained with the use of bilayer PEC electrodes, where a bottom relatively thick film is used for light absorption and a thin top layer is added to modify the chemical and electronic surface properties. In the case of Mo-based bilayer WO₃ PEC electrodes, where Mo is incorporated only in the near-surface of WO₃, approx. 300 nm), a 20% increase of saturation photocurrent (I_{\text{photo, sat}}=3.6 \text{ mA/cm}²) was observed compared to pure WO₃-based champion devices (I_{\text{photo, sat}}=3 \text{ mA/cm}²). Future research will be focused on further understanding and improvement of bilayer devices, as well as RuO₂ nanoparticle deposition to enhance holes transfer in electrolyte. Details of the experimental study of N and Mo incorporation in WO₃ can be found on the University of Hawaii Final Report, Attachment C.

It should be noted that bilayer device fabrication is likely to increase system cost and it is still desirable to obtain photoactive materials that make use of as much of the solar spectrum as is available to generate current and still drive the redox process.

Transition metals in WO₃ were studied theoretically to see if transition metal incorporates, which have shallower d orbitals than W 5d would reduce the bandgap by coupling between the transition metal and the O 2p orbital. It was found the incorporation of Ta and Hf can lead to the up-shift of VBM of WO₃, but the effects on the CBM are small unless considerable Ta and Hf are incorporated.

**Copper Chalcopyrites**

Research on copper chalcopyrites (copper alloyed with combinations of indium, gallium and selenium) PEC electrodes benefits from decades of studies of photovoltaic devices. One main advantage of this material class is the possibility to tune the band gap by changing the film stochiometry (from 1.0 eV with CuInSe₂ to 2.43 eV with CuGaSe₂). This makes copper chalcopyrite an ideal candidate for solar-powered water splitting, where current research in PEC
aims to find a low-cost and corrosive resistant material with a 2.0 eV band gap. Recent improvements with CuGaSe₂ materials have been obtained by varying deposition parameters such as temperature. With deposition temperature decrease from 530°C to 480°C, a saturation photocurrent increase from 12 to 20 mA/cm² (measured under simulated AM1.5G illumination in 0.5M H₂SO₄ electrolyte) was observed. Research has been also addressed sulfur incorporation to increase the material band gap. In addition, it has been demonstrated that the inclusion of sulfur into copper-chalcopyrite material leads to a more favorable band edge alignment with respect to the water-splitting redox reactions. Preliminary tests were conducted on a CuInSeS thin-film electrode provided by the Hahn Meitner Institute in Berlin. This material showed a more favorable onset potential (validating the theoretical prediction that sulfur incorporation can provide better band edge alignment) but a lower saturation photocurrent and a poor “fill factor” (which correspond to the squareness of the J-V characteristic) when compared to CuInGaSe₂. Additional studies on process deposition will be required to optimize this material. Details of copper chalcopyrite experimental investigations can be found in the University of Hawaii Final Report, Attachment C.

Silicon Carbide Materials
Research on these materials was largely performed under a separate grant and managed by the DOE Hydrogen Research Program. Reports of activities and progress can be found through the Office of Energy Efficiency and Renewable Energy.

Under the SHGR Project, research on amorphous SiC (a-SiC) materials addressed concepts initiated by MV Systems. SHGR work on a-SiC films were mainly dedicated to surface modification. One example is the use of HF (24%) solution to etch the SiOₓ native oxide layer grown on top of the a-SiC films. The saturation photocurrent increases from -8.5 mA/cm² to -10mA/cm² after a 15 second HF etch (measured under simulated AM1.5G illumination in pH2 buffer solution). In addition, the fill factor is improved after HF treatment. More noticeable is the onset potential reduction (toward 0V vs. SCE) after this treatment, indicating that the “naturally” grown SiOx thin layer shifts the band-edges. This finding indicates again that great attention should be paid to surface chemistry and interface energy states to ensure high performance PEC electrode. Surface passivation is currently being investigated by MVSystmes to improve and stabilize PEC performance. Encouraging stability improvements have been realized. Current research includes the evaluation of palladium and nickel/ion nanoparticles deposition on a-SiC films to enhance surface catalytic activities. a-SiC study details can be found in the University of Hawaii Final Report, Attachment C.

Iron Oxide Materials
Hematite (α-Fe₂O₃) has many potential advantages as a photoelectrocatalysis for hydrogen production. It has a bandgap of 2-2.2 eV (absorbs approximately 40% of the solar spectrum), it is stable in electrolytes over a wide range of pH’s and is abundant, inexpensive and non toxic. Several fundamental properties have limited the use of this material as an efficient photocatalyst, including high electrical resistance and recombination rates of photogenerated electrons and a conduction band-edge that is lower than the redox level of H⁺/H₂. The undesirable electrical properties are partially due to the hopping mechanism of charge transfer via oxygen vacancies, grain boundaries, and surface traps, which results in relatively low quantum yields (low efficiency materials), while the low conduction band energy is due to the Fe 3d electrons.
Efforts have been devoted to reducing the resistivity of thin films by nanostructured crystal engineering. By growing crystalline hematite nanorods oriented in the (001) direction, this anisotropic electron transport can be exploited to improve photocatalytic rates. This last approach, combined with low level Si doping, has already shown some improvement over hematite. However, there is still much work to be done to increase the record IPCE (400nm) of 42%.

No theoretical effort to predict effects of quantum confinement or doping was reported. However, experimental efforts to improve hematite performance through controlled growth of nanorods from solution were not productive. Whereas nanorods could be selectively grown with diameters in the range of 12 nm to 35 nm, the distribution and orientation of nanorods gave inconsistent results relative to improved performance. The results showed that decreasing the rod size resulted in a decrease in the overall performance consistent with a higher rate of surface recombination as the surface to volume ratio increased. Finally, efforts to reduce nanorod diameter to ~5nm were unsuccessful. At this scale, quantum confinement effects might shift the conduction band to higher energies and permit spontaneous water splitting, but such effects were not observed because 5 nm rods could not be grown.

Effort to grow doped hematite rods from solution proved unsuccessful and work turned to indirect methods of doped nanorod production. Post-synthesis doping with Ti by physical vapor deposition produced nanorods with Ti dopant layers of controlled thickness from 5 nm to 20 nm. Ti was diffused into iron nanorods by annealing at 600°C to 700°C followed by calcination in air to produce doped Fe₂O₃ nanorods. The presence of Ti in the hematite was shown by X-ray spectroscopy. However, PEC performance was not improved.

Effort to improve PEC performance through reduction of the necessary over-potential for the oxygen evolution reaction (OER) showed important scientific results when expensive RuO₂ electrocatalyst is replaced with abundant and cheap NiFe electrocatalyst. It was found that the addition of RuO₂ or NiCo greatly decreased the over-potential required for oxygen evolution from 670 mV for the bare Fe₂O₃ to 505mV for the electrode with the electrocatalyst. An approximately 7-fold improvement in photocurrent was observed with the addition of NiFe electrocatalyst as compared to the reference sample. A functional relationship was apparent between the amount of electrocatalyst deposited and the performance of the sample, which depends on the absorption of light by the electrocatalyst as well as the size of the electrocatalyst on the surface of the hematite. Different synthesis methods of the NiFe electrocatalyst were tested by electrodepositing the electrocatalyst with different precursors. Very different properties were observed for the electrocatalyst deposited. It was found that the electrocatalyst deposited with Ni(II)Fe(II) had the highest OER activity which was very similar to those deposited with just Ni(II); however the photoelectrochemical performance of the electrocatalyst-photocatalyst system showed that the Ni(II)Fe(III) and the control sample had the highest performance and that the electrocatalyst with Ni(II)Fe(II) and Ni(II) showed diminished photocurrent.

The work on electrocatalytic enhanced PEC performance is continuing under a separate grant award. Details on hematite studies and other studies not summarized here can be found in the UCSB Final Report, Attachment B.
Zinc Oxide Materials

The effects of N incorporation into ZnO were investigated by first-principles density-functional theory that showed that N-incorporation in ZnO may lead to bandgap narrowing. This prediction was confirmed by synthesizing N-incorporated ZnO thin films using reactive RF magnetron sputtering in N$_2$/O$_2$ gas ambient. ZnO:N films with various bandgaps were achieved by varying N concentration, which was controlled successfully by varying the magnetron sputtering power. The microstructure of the ZnO:N films was characterized and the photoelectrochemical properties of these ZnO:N films were measured and compared with those of pure ZnO films. Measurements showed that ZnO:N films could provide considerable photoresponse in the long-wavelength region above 600 nm as well as 500 nm, whereas the ZnO films did not show any photoresponse. ZnO:N films could provide more useful photoresponse in the visible light regions than pure ZnO. However, the photocurrent is poor. One of the causes is the poor crystallinity. Use of transmission electron microscopy (TEM) showed that ZnO:N films exhibit intermediate ordering with very small ZnO:N grains that contain high N concentrations. DFT calculations showed that N incorporated in ZnO causes a lowering of the valence band maximum (VBM) while the conduction band minimum (CBM) remains unchanged, leading to bandgap reduction. Whereas photoactivity could be increased by N incorporation in ZnO, photocurrents remain inadequate.

Pure ZnO and ZnO:N films were synthesized at different temperatures. In addition to improved crystallinity, deposition in pure Ar ambient produces polycrystalline ZnO films, whereas deposition in mixed Ar and N$_2$ ambient formed single crystal ZnO nanorods aligned along the c-axis at temperatures above 300 °C. ZnO:N films with aligned nanorods grown at 500 °C exhibit significantly enhanced PEC response, compared to polycrystalline ZnO thin films deposited at the same temperature. These results suggest that the deposition ambient can be used to control the morphology of ZnO thin films and aligned single crystal nanorods can be potentially beneficial for PEC performance.

ZnO:Cu films were synthesized on conducting substrates by using reactive RF magnetron sputtering with different number of Cu chips on the Zn metal target followed by post-annealing process. Post-deposition annealing at 600 °C caused the formation of CuO phase in the ZnO:Cu films, whereas 500 °C-annealed films did not. XPS and optical absorption indicated that some of the Cu in as-grown ZnO:Cu films is metallic. The metallic Cu can be converted into Cu$^{+1}$ acceptor states by post-annealing at 500 °C in air. Mott-Schottky plots and optical absorption measurements revealed that both p-type and reduced bandgap ZnO thin films were synthesized successfully by heavy Cu-doping. However, the ZnO:Cu samples were not very stable in aqueous solutions.

Ga and N co-doping was applied in a different approach to enhance the incorporation of N into ZnO films. The Coulomb attraction between Ga and N is expected to result in reduced formation energies and thus increased N concentration. In addition, co-doping will effectively introduce charge compensation and thus suppress harmful recombination. Thin ZnO:(Ga, N) films were synthesized by dispersing Ga$_2$O$_3$ powders in Zn targets. ZnO:(Ga, N) thin films with reduced band gap and increased crystallinity have been successfully synthesized. These films exhibited greatly enhanced photocurrent comparing to all ZnO thin film synthesized to date. This co-doping method should be applicable to other wide gap metal oxides for band gap reduction.
PEC MATERIALS CHARACTERIZATION

The goal was to utilize a world-wide unique combination of surface and interface spectroscopies and microscopies to aid in the development of thin films for efficient hydrogen-producing photoelectrochemical (PEC) devices. This project investigated the chemical and electronic characteristics of materials for photoelectrochemical hydrogen production (PEC). The experimental plan included UNLV-lab-based techniques such as X-ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS), Inverse Photoemission Spectroscopy (IPES), and Atomic Force Microscopy (AFM). Synchrotron-based experiments were conducted at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory, and include X-ray Absorption Spectroscopy (XAS) and X-ray Emission Spectroscopy (XES). The combination of these techniques provides detailed information about the surface and near-surface electronic band gap, the surface band edge positions, work function, surface chemical composition, and surface morphology.

As highlights, novel instrumentation was installed to allow an unprecedented view of the electronic and chemical structure with a world-wide unique tool chest of experimental techniques. With this approach, the first all-experimental depiction of the electronic surface structure of WO3- (Section 2), ZnO- (Section 3), a-SiC- (Section 4), and Fe2O3-based (Section 5) thin film surfaces was painted. Furthermore, the chemical origins of unexpected PEC performance in a variety of samples, generally tracing over- or under-performance back to chemical impurities were elucidated. Surface treatment procedures have been studied and optimized, and exposure to PEC-relevant media and the associated surface modifications were elucidated. Finally, first steps towards in-situ spectroscopy of PEC materials were undertaken.

Instrumentation

Funding from this project allowed the implementation of several upgrades to the existing multichamber ultra-high vacuum (UHV) system. In particular, the electron analyzer was successfully replaced, now featuring a state-of-the-art 9-channeltron Specs PHOIBOS 150MCD spectrometer. This instrument is uniquely suited for experiments that need high spectral transmission (e.g., the detection of very small peaks on large backgrounds). Furthermore, funds could be contributed to the purchase of a second photoelectron spectroscopy system (VG Scienta). This system is uniquely designed for high-resolution photoemission experiments and thus presents a complementary approach to the photoemission system described above.

WO3-Based Thin Films

Numerous spectroscopic studies were undertaken to understand and optimize the electronic and chemical properties of WO3-based thin films prepared at the Hawaii Natural Energy Institute (HNEI). XPS survey spectra give a vast amount of information about the chemical composition at the surface. For example, the expected W and O lines are found, and only a relatively small amount of C surface contaminants. The absence of a Si line at approximately 100 eV indicates a successful removal of a previously detected Si contamination from the production process. Based on the pre-characterization at UNLV, several WO3 samples from HNEI at Beamline 8.0 at the ALS using XES and XAS were investigated. Based on initial experiments, which showed that WO3 is very sensitive to the photons and electrons used as excitations in photoemission and
inverse photoemission, the pristine spectra of a fresh WO₃ surface, as well as the beam damage occurring after longer exposure times, were measured.

The pristine spectra of the valence band (with UPS) and the conduction band (with IPES) were measured, giving the surface band gap and the position of the Fermi level. Such information is of central importance for understanding and optimizing the final PEC device. Note that the UV radiation used for UPS does not induce a beam damage effect, but, in contrast, the high-flux electron irradiation necessary for IPES does. Again, it is possible to collect spectra in a very short time frame (2 minutes in this case), which gives a good representation of a minimally affected spectrum, and furthermore allows us to monitor the impact of beam damage on the spectral characteristics.

ZnO-Based Thin Films

ZnO:N samples that are intended to exhibit improved band gap characteristics compared to pure ZnO without N-doping were studied. The NREL group has developed a deposition process in which the sputter power is used to control the N doping level (higher sputter powers correspond to nominally higher N contents). First results showed inconsistencies, namely unexpectedly low N concentrations for samples with nominally high N doping concentration. Together with additional observations by the NREL group, we tentatively interpreted it as instability of the ZnO samples with high N doping concentration. Thus, a new ZnO:N sample series was prepared and investigated. In a joint effort with the NREL group, great care was taken to minimize the time between sample preparation and measurement and avoid any exposure to ambient air.

The findings point to the partial conversion of the ZnN component in the samples into ZnO during air exposure. Note that the samples with the initially lowest N content are more stable, i.e., the relative decrease of the ZnN content is not as pronounced. In fact, they even show a higher ZnN content compared to the samples with higher initial N concentration. A speculative explanation could be that the ZnN in low N concentration samples is embedded in a ZnO matrix, which hinders its ‘oxidation’, whereas, for the high N concentration samples, more of the ZnN is accessible to be replaced by ZnO. Note that our measurements also show that the samples contained a certain amount of Ni and Cu.

In the following, the focus was placed on the quantification of the qualitative observation that the Cu content increases with increasing number of Cu pieces derived from the XES spectra. In general, the emission intensity I of an XES spectrum can be expressed as:

\[ I = \int_0^\infty c \cdot \sigma_{\text{eff}} \cdot I_{\text{in}}(z) \cdot e^{-\frac{z}{\lambda_{\text{out}}}} dz \]

where \( c \) is the concentration of the considered element, \( z \) is the penetration depth, \( \lambda_{\text{out}} \) is the attenuation length for the energy of the emission, \( \sigma_{\text{eff}} \) is the effective emission cross section (matrix element), and \( I_{\text{in}} \) is the (depth-dependent) excitation intensity, with

\[ I_{\text{in}}(z) = \frac{I_0}{\lambda_{\text{in}}} \cdot e^{-\frac{z}{\lambda_{\text{in}}}} \]
and $\lambda_{in}$, the attenuation length for the excitation energy, and $I_0$, the excitation intensity for $z = 0$. Combined, this results in the following equation:

$$I = \int_0^\infty c \cdot \sigma_{eff} \cdot I_0 \cdot e^{-\frac{1}{\lambda_{in}}} \cdot e^{-\left(\frac{1}{\lambda_{out}}\right)} dz = c \cdot \sigma_{eff} \cdot I_0 \cdot \frac{\lambda_{out}}{\lambda_{in} + \lambda_{out}}$$

Under the assumption that all Cu and Zn atoms are incorporated in a pure ZnO matrix ("Cu\_ZnO", "Zn\_ZnO"), the Cu/Zn concentration ratio can now be expressed as follows:

$$\frac{c_{Cu\_ZnO}}{c_{Zn\_ZnO}} = \frac{I_{Cu\_ZnO}^*}{I_{Zn\_ZnO}^*} \cdot \frac{\lambda_{Zn\_ZnO}^{out}}{\lambda_{in}} \cdot \frac{\lambda_{Zn\_ZnO}^{out}}{\lambda_{Cu\_ZnO}^{out} + \lambda_{Cu\_ZnO}^{out}} \cdot \frac{\sigma_{eff\_Zn\_ZnO}}{\sigma_{eff\_Cu\_CuO}}$$

where $c_{Cu\_ZnO}$, $c_{Zn\_ZnO}$ are the Cu and Zn concentrations; $I_{Cu\_ZnO}^*$, $I_{Zn\_ZnO}^*$ are the intensities of the respective spectral features (in our case Cu L$_3$ and Zn L$_3$ emission) normalized to $I_0$; $\lambda_{in/out}$ are the attenuation lengths of the excitation and emission in the ZnO matrix; and $\sigma_{Cu\_ZnO}^{eff}$, $\sigma_{Zn\_ZnO}^{eff}$ are the effective emission cross sections (matrix elements) of Cu and Zn in the ZnO matrix. The only parameters missing for the determination of the Cu/Zn ratio from the XES spectra are the effective emission cross sections. However, since we know the Cu and Zn concentration in the respective metal foils ($c_{Cu\_Cu} = c_{Zn\_Zn} = 1$), we can use the reference spectra to determine the ratio $\frac{\sigma_{Cu\_Cu}^{eff}}{\sigma_{Zn\_Zn}^{eff}} = 0.504$. This ratio is approximately equated with the ratio of the effective emission cross sections in a ZnO matrix $\frac{\sigma_{eff\_Zn\_ZnO}}{\sigma_{eff\_Cu\_CuO}}$ (see equation below).

$$\frac{c_{Cu\_ZnO}}{c_{Zn\_ZnO}} \approx \frac{I_{Cu\_ZnO}^*}{I_{Zn\_ZnO}^*} \cdot \frac{\lambda_{Zn\_ZnO}^{out}}{\lambda_{Zn\_ZnO}^{out}} \cdot \frac{\sigma_{Zn\_ZnO}}{\sigma_{Cu\_CuO}}$$

$$\approx \frac{I_{Cu\_ZnO}^*}{I_{Zn\_ZnO}^*} \cdot 0.804 \cdot 0.770 \cdot 0.504 = \frac{I_{Cu\_ZnO}^*}{I_{Zn\_ZnO}^*} \cdot 0.526$$

According to this equation the determined Cu/Zn ratios are 1.2% (0.9%), 2.6% (2.2%), and 6.1% (5.4%) for the as-deposited (post-annealed) ZnO:Cu samples, respectively.

SiC-Based Thin Films

In collaboration with our project partners at MVSystems, we focused on a study of amorphous SiC layers for PEC. We studied amorphous SiC (a-SiC) layers (nominal 100 Å [batch LCT-4744 & 4746] or 1000 Å [batch LCT-4743 & 4745] thick) deposited on SnO$_2$ covered glass. To avoid air contamination, the samples were packed under inert atmosphere using a glovebag and immediately shipped to UNLV. At UNLV, the sample packages were transferred into an N$_2$ filled glovebox (where the samples were also mounted) that is attached to our UHV surface characterization system. The samples were characterized by XPS and X-ray excited Auger electron (XAES) spectroscopy at UNLV and by XES at the ALS.
**Fe₃O₃-Based Thin Films**

This section reports on the analysis of Fe₂O₃ thin film samples. Initial results showed that the originally employed extraction method under nitrogen flow was not sufficient to diminish the carbon contamination of the surface significantly (compared to fully air-exposed samples).

Packing Procedure: In order to prevent air exposure of the samples after deposition of the thin films, the entire preparation chamber was connected to a glove bag, which was repeatedly evacuated and filled with dry nitrogen for purging. The chamber was also vented with dry nitrogen before the sample extraction.

Effect of packing procedure: The samples packed in the way described above showed significantly lower carbon signals. In order to shed light on the origin of these signals, further studies of the calcination process were performed, in particular on “bare” Pt films deposited on the Ti-coated substrate.

Effect of Calcination on the Pt Surface: Ti and Pt signals are found in spectra of calcined samples. The only obvious source for a Ti signal is the Ti layer underneath the comparably thick Pt film. In order to determine at which temperature the Ti atoms become mobile enough to penetrate the Pt film, two samples without additional Fe layer were stepwise annealed in UHV.

Combining the band edge positions (with respect to the Fermi energy) with the work function of the sample, the band edge positions can be given with respect to the vacuum level. Furthermore, by applying an IUPAC recommendation [S. Trasatti, Pure Appl. Chem. 58, 955 (1986)] and as done earlier for the case of WO₃, the vacuum level scale can be related to the Normal Hydrogen Electrode (NHE) scale:

\[-E(\text{NHE}) - 4.44 \text{ eV}^* = E_{\text{vacuum}} = E_F + \Phi.\]

**In-Situ Studies**

To prepare for future funding opportunities that would allow PEC in-situ studies, an optimization of the conditions/parameters for liquid contact mode atomic force microscopy (AFM) studies to investigate PEC materials (such as WO₃ prepared at the University of Hawaii) in-situ was the focus. One of the main challenges of PEC is the (photo) degradation of surfaces in aqueous solutions, specifically at extreme pH. This could adversely impact hydrogen conversion efficiency, as the interface deteriorates in the harsh electrolytic conditions of the PEC cell. The long term goal of our PEC activities is thus to investigate the electronic and chemical surface structure as well as the morphology of such materials in a functioning PEC cell. As a first step, the liquid electrochemical mode of our AFM (with a 3 electrode system in a small reservoir that holds up about 0.5-1cm³ of the electrolyte) was used. For initial optimization, a plain gold substrate was used as a reference material. As a first step, the electronics and software mode of the AFM were changed to the liquid mode.

As a next step towards real in-situ conditions, a buffer solution (pH = 0, 1M HClO₄) on the surface of the gold substrate was used. These initial experimental results are promising first steps towards the utilization of liquid contact AFM as an effective tool for in-situ investigation of electrode surfaces.
Next, a WO$_3$ sample series produced by our project partners at HNEI. WO$_3$ is generally considered to be stable under operating conditions of the PEC cell (pH~0.5) was the focus. Also, it has been noted that the stability decreases as the pH increases - especially for pH values above 7, disintegration of WO$_3$ films has been observed.

To shed further light on these processes, AFM imaging of WO$_3$ film surfaces under differently buffered conditions of pH=0.5, 4, 7, and 8 was conducted. The same thin film was then immersed in pH=7 buffer in the liquid cell of our AFM and imaging was continued after a wait time of about 30 minutes in the liquid cell. Comparing the images before and after submersion in the pH=7 buffer, gash-like features are observed, which might suggest some degree of deterioration even at neutral pH. Next, in-liquid imaging of WO$_3$ films at pH=8 was initiated, but the scanning could not be completed due to quick deterioration of the surface, leading to the disengagement of the AFM cantilever. Future projects will need to continue this work.

To also allow spectroscopic investigations of PEC candidate materials in in-situ cells in the future, the development of a liquid-solid in-situ cell for our SALSA end station was initiated. As a test case, the solid/liquid interface of a Mo reference sample (metal foil) under water in the group-operated SALSA ("Solid And Liquid Spectroscopic Analysis") end station at Beamline 8.0.1 of the ALS was investigated.

To measure the Mo/H$_2$O interface, a Mo sample plate was mounted on the micrometer caliper of the in-situ cell setup. Water was flowed through the cell at a constant flow rate and the solid/liquid system was separated from the vacuum by a thin carbon membrane (manufactured by J. Andersson, Uppsala University, Sweden). The strongest Mo signal was detected with a 10 µm layer of water between the membrane and the Mo sample. The system was excited by the synchrotron beam with an energy of 275 eV and the emitted photons were detected using a high-resolution, high-transmission x-ray spectrometer consisting of a spherical mirror, a variable-line-space (VLS) grating, and a CCD detector.

The spectrum shows a strong Mo 4p → 3d transition at ~192 eV and a weaker signal from the Mo 4s → 3d transition at ~168 eV. Although the excitation is done below the O K absorption onset, a dominant O K emission line is visible in the spectrum due to excitation by higher beamline orders. Additionally, since 275 eV is in the resonant region of the C K emission, the small carbon contribution of the window membrane is also present in the spectrum.

In summary, important first steps have been made towards a detailed characterization of materials in in-situ environments, both to study the morphology as well as the electronic and chemical properties at the electrode-electrolyte interface. Future projects will be proposed to develop these capabilities towards a routinely applied characterization for candidate materials for solar water splitting.
Publications


Presentations


C. Heske, “Investigating the electronic and chemical properties of surfaces, interfaces, and other buried things with soft x-ray spectroscopy”, Chemical Engineering Department, University of California Santa Barbara, October 25, 2007 (invited oral).


E. L. Miller, “Photoelectrochemical Hydrogen Production”, presented at 2007 IMRC (Cancun, Mexico, August 2007).


C. Heske, “How soft x-rays can help to optimize solar cells (and other electronic devices)”, University of Oregon IGERT graduate student seminar, University of Oregon, Eugene, February 27, 2008 (invited oral).


C. Heske, "Using XES and RIXS to investigate the chemical and electronic structure of materials for energy conversion", RIXS 08 Workshop, Uppsala, Sweden, June 13-14, 2008 (invited oral).

C. Heske, “How soft x-ray spectroscopy can help the ‘Hydrogen Economy’ (hopefully)”, Seminar Experimentelle Physik II, University of Würzburg, Germany, July 8, 2008 (invited oral).

C. Heske, “So, when will there finally be a breakthrough for these solar thingies?“, Western Regional Meeting of the American Chemical Society, Education Program Keynote Address, Las Vegas, Sept. 27, 2008 (invited oral).


C. Heske, “How soft x-ray spectroscopy can shed light on the electronic and chemical properties of interfaces“, PIRE-ECCI (Partnership for International Research and Education) Seminar, Electron Chemistry and Catalysis at Interfaces, Department of Chemistry and Biochemistry, University of California, Santa Barbara, November 5, 2008 (invited oral).

MRS March 24-28th 2008 LL7.5. “Multi-Component Nanostructured Semiconductors for Photoelectrocatalysis - Progress Towards Efficient and Stable Solar-to-Chemical Energy Conversion”


C. Heske, “Using soft x-rays to look into (buried) interfaces of energy conversion devices”, Chemistry and Geochemistry Department at the Colorado School of Mines, Golden, CO, September 25, 2009 (invited oral).


C. Heske, “Using soft x-rays to look into interfaces of energy conversion devices”, Materials Science & Engineering Colloquium (co-sponsored by ECE and Physics), Boston University, December 4, 2009 (invited oral).

M. Blum, “SALSA - an endstation for the study of liquids, solids, and liquid/solid interfaces”, ALS Users Meeting 2009 (invited oral).

C. Heske, “How x-ray and electron spectroscopies can help to tackle the energy problem”, Physics Department, Free University Berlin, Germany, January 20, 2010 (invited oral).

C. Heske, “Using soft x-rays to look into (buried) interfaces of energy conversion devices”, Department of Physics, Technical University of Denmark, March 12, 2010 (invited oral).


C. Heske, “Using soft x-rays to study the electronic and chemical properties of thin film solar devices”, 15th International Conference on Solid Films and Surfaces (ICSFS-15), Beijing, China, Oct. 9, 2010 (invited oral).

C. Heske, “Using soft x-rays to optimize materials for energy conversion devices”, Department of Physics, Renmin University, Beijing, China, Oct. 10, 2010 (invited oral).


C. Heske, “Using soft x-rays to understand and optimize materials for energy conversion”, Department of Physics, Hanoi University of Technology, Hanoi, Vietnam, Nov. 1, 2010 (invited oral).

ATTACHMENT A

University of Nevada, Las Vegas

Optimization of Interfaces and Surfaces for Photoelectrochemical Hydrogen Production

(59 Pages)
Final Report

Project Title: Optimization of Interfaces and Surfaces for Photoelectrochemical Hydrogen Production

Project Period: June 2006 – December 2010
Date of Report: June 20, 2011

Working Partners: Marcus Bär, Lothar Weinhardt, Kyle George, Monika Blum, Timo Hofmann, Stefan Krause, Sujittra Pookpanratana, Yufeng Zhang, Ich Tran, and Clemens Heske, UNLV
Hawaii Natural Energy Institute (HNEI)
Stanford University
National Renewable Energy Laboratory (NREL)
University of California, Santa Barbara (UCSB)
MVSystems

Contact: Clemens Heske, Department of Chemistry, University of Nevada Las Vegas, 4505 Maryland Pkwy., Las Vegas, NV 89154. Phone: ++1-702-895-2694. E-mail: heske@unlv.nevada.edu.

Project Objective: The goal of this project was to utilize a world-wide unique combination of surface and interface spectroscopies and microscopies to aid in the development of thin films for efficient hydrogen-producing photoelectrochemical (PEC) devices.

Background:
The goal of this project was to investigate the chemical and electronic characteristics of materials for photoelectrochemical hydrogen production (PEC). The experimental plan included UNLV-lab-based techniques such as X-ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS), Inverse Photoemission Spectroscopy (IPES), and Atomic Force Microscopy (AFM). Synchrotron-based experiments were conducted at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory, and include X-ray Absorption Spectroscopy (XAS) and X-ray Emission Spectroscopy (XES). The combination of these techniques provides detailed information about the surface and near-surface electronic band gap, the surface band edge positions, work function, surface chemical composition, and surface morphology.
As highlights, we installed novel instrumentation (see Section 1) to allow an unprecedented view of the electronic and chemical structure with a world-wide unique tool chest of experimental techniques. With this approach, we have painted the first all-experimental depiction of the electronic surface structure of WO$_3$- (Section 2), ZnO- (Section 3), a-SiC- (Section 4), and Fe$_2$O$_3$-based (Section 5) thin film surfaces. Furthermore, we have elucidated the chemical origins of unexpected PEC performance in a variety of samples, generally tracing over- or under-performance back to chemical impurities. Surface treatment procedures have been studied and optimized, and exposure to PEC-relevant media and the associated surface modifications were elucidated. Finally, first steps towards in-situ spectroscopy of PEC materials were undertaken (Section 6).

1. Instrumentation

Funding from this project allowed the implementation of several upgrades to the existing multichamber ultra-high vacuum (UHV) system shown in Fig. 1. In particular, the electron analyzer was successfully replaced, now featuring a state-of-the-art 9-channeltron Specs PHOIBOS 150MCD spectrometer (left hemisphere in Fig. 1). This instrument is uniquely suited for experiments that need high spectral transmission (e.g., the detection of very small peaks on large backgrounds). Furthermore, funds could be contributed to the purchase of a second photoelectron spectroscopy system (VG Scienta), shown in Fig. 1 on the right. This system is uniquely designed for high-resolution photoemission experiments and thus presents a complementary approach to the photoemission system described above.

For our experiments at the ALS, funds could also be contributed to the operation and further development of a unique endstation – SALSA (Solid And Liquid Spectroscopic Analysis, Fig. 2) – which was designed and built in close collaboration with the U of Würzburg and the Helmholtz-Zentrum Berlin, Germany. SALSA allows a variety of soft x-ray spectroscopic techniques on dry samples (in-vacuo) and liquid and gaseous systems under ambient conditions, and will form the platform for future in-situ PEC spectroscopy activities.
Fig. 1: Multichamber surface and interface spectroscopy system at UNLV.

SALSA: Solid And Liquid Spectroscopic Analysis at Beamline 8.0, Advanced Light Source, LBNL

Fig. 2: SALSA endstation at the Advanced Light Source, Lawrence Berkeley National Laboratory.
2. \textit{WO}_3-based thin films

Numerous spectroscopic studies were undertaken to understand and optimize the electronic and chemical properties of \textit{WO}_3–based thin films prepared at the Hawaii Natural Energy Institute (HNEI). Fig. 3 shows an XPS survey spectrum of such a film surface. XPS survey spectra give a vast amount of information about the chemical composition at the surface. For example, we find the expected W and O lines, and only a relatively small amount of C surface contaminants. The absence of a Si line at approx. 100 eV indicates a successful removal of a previously detected Si contamination (not shown) from the production process.

Based on the pre-characterization at UNLV, we were able to investigate several \textit{WO}_3 samples from HNEI at Beamline 8.0 at the ALS using XES and XAS. Fig. 4 shows, as an example, a series of O K edge XAS spectra of HNEI samples and reference compounds, clearly indicating that the local bonding environment of the majority of oxygen atoms is at or near the expected stoichiometry of \textit{WO}_3. Contributions from \textit{WO}_2 appear to be minimal.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{xps_spectrum.png}
\caption{XPS survey spectrum of a \textit{WO}_3 thin film surface supplied by HNEI.}
\end{figure}
Fig. 4: X-ray absorption (XAS or NEXAFS) spectra of the oxygen K edge of two HNEI WO\textsubscript{3} films as well as of several reference powders. Spectra were taken at the Advanced Light Source, Lawrence Berkeley National Laboratory.

Based on our initial experiments, which showed that WO\textsubscript{3} is very sensitive to the photons and electrons used as excitations in photoemission and inverse photoemission, we were able to measure pristine spectra of a fresh WO\textsubscript{3} surface, as well as monitor the beam damage occurring after longer exposure times. As an example, Fig. 5 shows the spectral changes occurring in the W 4f doublet during the exposure to Mg K\textsubscript{α} x-rays. The black spectrum corresponds to a minimally altered surface after (only!) 1 min exposure. It is apparent that all x-ray photoelectron spectra reported in the literature are affected by this beam-induced degradation, and that, due to the outstanding efficiency of our high-transmission electron spectrometer, none of the reported spectra reflect an as-pristine state as our spectra.

We were also able to measure pristine spectra of the valence band (with UPS) and the conduction band (with IPES), giving the surface band gap and the position of the Fermi level. Such information is of central importance for understanding and optimizing the final PEC device. Note that the UV radiation used for UPS does not induce a beam damage effect, but, in contrast, the high-flux electron irradiation necessary for IPES does. Again, it is possible to collect spectra in a very short time frame (2 min in our case), which gives a good representation of a minimally affected spectrum, and furthermore allows us to monitor the impact of beam damage on the spectral characteristics.
Fig. 5: W 4f x-ray photoemission spectra of a WO$_3$ surface after different exposure times to Mg K$_\alpha$ radiation. Parallel to a decrease of the pristine spectrum (black), as indicated by the arrows, an increase of intensity of additional components is observed, most easily seen in a filling of the “valley” between the two spin-orbit split peaks.

In order to modify the electronic band gap of WO$_3$, our project partners at HNEI performed a modification series using nitrogen co-doping. In Fig. 6 the XPS survey spectra of four samples sputtered under different N$_2$ partial pressures are shown. The samples were packed under nitrogen immediately after their preparation at HNEI and then transferred into vacuum without any air exposure, which results in a very low C contamination level. As expected, we find all pertinent O and W lines. Furthermore, a closer look at the survey spectrum reveals that also some N can be found at the sample surface.

In Fig. 7 the N 1s detailed spectra of the different WO$_3$ samples are shown. We can identify at least three different components. Since the line at a binding energy of around 400 eV can also be found on the nominally undoped sample, we attribute it to nitrogen adsorbates on the sample surface. In the right panel of Fig. 7 we have subtracted a maximal amount of this spectrum (blue) from each of the other spectra (black), resulting in the red spectrum now consisting of mainly two different nitrogen species.
Fig. 6: XPS survey spectra of WO$_3$ samples sputtered with different N$_2$ partial pressures (given on the right ordinate).

Fig. 7: N 1s XPS spectra of WO$_3$ samples sputtered with different N$_2$ partial pressures, as given on the right ordinate.
By taking the inelastic mean free path of the electrons, the cross sections of the corresponding line, and the transmission of the electron analyzer into account, we have calculated surface stoichiometries for the four different samples, which are shown in Table 1. We find N amounts of around 0.1% at the sample surface, with an increasing tendency as the partial sputter pressure of nitrogen increases (as expected).

Table 1: Relative N concentrations at the sample surface in %.

<table>
<thead>
<tr>
<th>p(N2) (mTorr)</th>
<th>Σ N</th>
<th>N (1)</th>
<th>N (2)</th>
<th>N (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.11</td>
<td>0</td>
<td>0</td>
<td>0.11</td>
</tr>
<tr>
<td>2</td>
<td>0.11</td>
<td>0</td>
<td>0.026</td>
<td>0.079</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>0.033</td>
<td>0.045</td>
<td>0.073</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>0.042</td>
<td>0.058</td>
<td>0.066</td>
</tr>
</tbody>
</table>

As part of our collaboration with the HNEI group, we continuously optimized the packing procedure of the samples for the shipment between Hawaii (sample preparation) and Las Vegas (sample characterization). We could reduce the observed C surface contamination significantly, which is of central importance for taking relevant data with the very surface sensitive techniques used by our group. Due to the bell-jar-type chamber used at HNEI, samples were previously shortly exposed to air (~ 1 min) prior to packing under nitrogen. XPS measurements clearly show significant C contaminations for the samples packed under dry nitrogen after short air exposure. To determine whether the C surface contamination stems from the sputtering process or is adsorbed during the short exposure to ambient air, we have jointly developed a simple packaging procedure which makes it possible to pack samples directly out of a bell-jar-type chamber without any air exposure. The procedure using a commercial glove-bag, together with plastic foil is shown in Fig. 8. The plastic foil and the glove-bag was connected to the base of the chamber and the bell-jar such that it expands when raising the bell-jar after venting with dry nitrogen, preventing any air from flowing into the chamber. The samples were removed from the bell-jar and sealed under nitrogen using a food safer. At UNLV, the samples were unpacked and mounted in the glove-box which is directly connected to the load-lock of the UHV characterization system (see Fig. 1).
Comparison of the survey spectra of a WO$_3$ sample packed with the old packing procedure with that of a sample packed with the new optimized procedure indeed shows that a reduction of the C 1s intensity can be observed. Nevertheless, some residual C is still observed, which is now attributed to the preparation process. It is interesting to note that no change was observed in the valence and conduction band spectra (UV and inverse photoemission, resp.) of the samples, which indicates that these spectra were not strongly affected by the C contamination level of the old packing procedure.

Note that an initially low surface contamination level is of critical importance since we find that a cleaning of the surface with Ar$^+$ ions (even with energies as low as 50 eV) leads to strong changes in our spectra. In general, we find (in accordance with literature) that the WO$_3$ surface is very sensitive to different kinds of irradiation, as mentioned above. We have carefully monitored the changes induced by the excitation sources used for our measurements and were able to measure spectra of an unaltered WO$_3$ surface by measuring suitably fast. Strong spectral changes were observed after irradiation with x-rays and low energy electrons, whereas no changes occur after irradiation with He I and He II UV irradiation used for the UPS experiments.

Fig. 8: Glove-bag attached to the HNEI bell-jar deposition chamber. The chamber is shown in the open position after venting with dry nitrogen.
Taking these findings into account, it was possible to measure the undisturbed electronic structure of the WO$_3$ surface. This was achieved by using a fresh film (prepared under the same conditions) for each of the experiments (XPS, UPS, and IPES) and keeping the total exposure (measuring) time short enough for the above described changes to be negligible.

Fig. 9 shows the result of these efforts, where the UPS and IPES spectra of the WO$_3$ surface are plotted on a common energy scale. We can derive the positions of the valence band maximum (VBM) and conduction band minimum (CBM) relative to the Fermi level ($E_F$) by a linear extrapolation of the leading edge in the spectra. We find the VBM at -2.89 ($\pm$ 0.1) eV and the CBM at 0.39 ($\pm$ 0.1) eV relative to $E_F$, showing that the surface of the investigated WO$_3$ films is n-type. Both numbers together give us a value of 3.28 ($\pm$ 0.15) eV for the band gap at the surface of the film. This value is significantly larger than the bulk value of about 2.7 eV found by optical measurements.

To convert the derived positions of VBM and CBM into useful information for the operation of a PEC device, we have to find their values relative to the vacuum level $E_{\text{Vacuum}}$, or, as commonly used, relative to the normal hydrogen electrode (NHE). Using the absolute potential of the normal hydrogen electrode of -4.44 eV, we can use the following expression:

$$-E(\text{NHE}) - 4.44 \text{ eV} = E_{\text{Vacuum}} = E_F + \phi,$$

where $\phi$ is the work function of the investigated material relative to $E_F$. $\phi$ can be derived by measuring the secondary electron cut-off in the UPS spectra, which is shown in Fig. 10. We derive a value of 4.49 ($\pm$ 0.05) eV. In literature, values between 4.3 eV (colorized films) and 4.9 eV were found for WO$_3$. By using the equation above, we can
now derive the positions of VBM and CBM relative to the NHE, as summarized in Table 2 and Fig. 11. For comparison, the relevant levels for the splitting of water are also included. Note that Fig. 11 constitutes the first-ever representation of the relevant energy levels entirely based on experiments (for any PEC material).

For a PEC-device to work efficiently, the following requirements have to be met. First, the VBM of the photo-anode (e.g., WO$_3$) has to be lower (on the vacuum energy scale) than the H$_2$O/O$_2$ oxidation potential to provide holes for the oxidation of H$_2$O to O$_2$ and H$^+$, which is clearly the case for WO$_3$, where the VBM lies 1.71 (± 0.11) eV below the H$_2$O/O$_2$ oxidation potential. Second, the Fermi level of the metal cathode has to be higher than the H$^+$/H$_2$ reduction potential to provide electrons for the reduction of H$^+$ to

<table>
<thead>
<tr>
<th>Energy Levels</th>
<th>E$_{rel.}$ EF (eV)</th>
<th>E$_{rel.}$ EVacuum (eV)</th>
<th>E$_{rel.}$ NHE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VBM</td>
<td>-2.89 (±0.10)</td>
<td>-7.38 (±0.11)</td>
<td>2.94 (±0.11)</td>
</tr>
<tr>
<td>CBM</td>
<td>0.39 (±0.10)</td>
<td>-4.10 (±0.11)</td>
<td>-0.34 (±0.11)</td>
</tr>
<tr>
<td>H$_2$O/O$_2$ oxidation potential</td>
<td></td>
<td>-5.67</td>
<td>1.23</td>
</tr>
<tr>
<td>H$^+$/H$_2$ reduction potential</td>
<td></td>
<td>-4.44</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2: Experimental energetic positions of VBM and CBM of WO$_3$ rel. to EF, EVacuum, and on an NHE energy scale. The positions of the H$_2$O/O$_2$ and H$^+$/H$_2$ redox potentials are given for comparison.

Fig. 10: Secondary electron cut-off measured by UPS. The work function [4.49 (±0.05) eV] can be derived by a linear extrapolation of the edge.

Fig. 11: Positions of VBM and CBM of WO$_3$ relative to EF, EVacuum and the NHE. For comparison, the H$_2$O/O$_2$ oxidation and the H$^+$/H$_2$ reduction potentials are also given. Grey bars for VBM and CBM indicate the error bars along the energy axis.
H₂. The latter can be achieved by a sufficient photo voltage of the photo-anode (i.e., a flat-band potential that is above the H⁺/H₂ reduction potential) or needs an additional bias. Therefore, assuming an ideal device, the CBM of the photo-anode surface has to be higher than the H⁺/H₂ reduction potential for the device to work without additional bias. Based on these considerations, the measured level positions in Fig. 11 indicate (at first sight) that a WO₃ device without addition bias might be possible. However, the CBM is only 0.34 (± 0.11) eV above the H⁺/H₂ reduction potential, giving neither room for non-idealities nor the possibility to draw a reasonable current from the device.

We have to note that the presented data corresponds to the levels at the WO₃ surface in vacuum. When immersing the anode in the PEC solution these levels are expected to shift by a certain amount. The vacuum values hereby can be assumed to be equal to those in solution with a pH where the surface charge of the sample is zero (isoelectric point). For oxides it was found that changing the pH value will shift the levels by about 60 mV/pH; to correct for this effect, we thus merely need to adjust the values in Table 2 by a few tenths of an eV when changing the pH of the solution.

We find the VBM to be low enough to initiate the oxidation of H₂O to O₂ and H⁺. In contrast, the CBM is only high enough for the reduction of H⁺ to H₂ at a backside metal cathode if assuming ideal conditions. Thus, the measurements indicate that an additional bias will be needed for an effective splitting of water using a WO₃ photoanode, for example, by an additional solar cell in a tandem configuration. In order to increase the CBM (i.e., to move it further away from the Fermi level), the HNEI group started to deliberately introduce Mo into their WO₃ thin films, which we then also investigated using XPS, UPS, and IPES.

As for the WO₃ samples, the WO₃:Mo samples were prepared by reactive sputtering from a metallic W target. Again, great care was taken to minimize surface contaminations due to air exposure. The samples were packed under nitrogen atmosphere immediately after film preparation at HNEI, then shipped to Las Vegas, unpacked in a glovebox under nitrogen atmosphere, and directly introduced into the ultra-high vacuum system used for the experiments. The samples were then investigated by XPS in order to shed light on their chemical surface structure. After initial characterization by XPS, we also investigated the WO₃:Mo samples by XES during our experimental run at the ALS in January 2008.

As exemplarily shown for Sample #341A in Fig. 12, the XPS survey spectra contain (as expected) all features ascribed to the components of the WO₃:Mo sample and further indicate a significant amount of C adsorbates at the WO₃:Mo surface.
We have again carefully monitored the changes induced by the excitation sources used for our measurements. Fig. 13 shows the most prominent XPS features of the WO$_3$:Mo samples (O 1s, left; Mo 3d, center; W 4f, right) and their change with measurement time (i.e., with exposure time to our Mg K$_{\alpha}$ X-ray source at a power of 300 W). In addition, similar spectral changes were also observed after irradiation with low-energy electrons.

![XPS survey spectrum of sample #341A of the WO$_3$:Mo samples series.](image1.jpg)

*Fig. 12: XPS survey spectrum of sample #341A of the WO$_3$:Mo samples series.*

![XPS detail spectra as a function of X-ray (Mg K$_{\alpha}$, 300 W) exposure.](image2.jpg)

*Fig. 13: O 1s (left), Mo 3d (center), and W 4f (right) XPS detail spectra as a function of X-ray (Mg K$_{\alpha}$, 300 W) exposure.*
(used for our IPES measurements) and low-energy Ar$^+$ ions (used for ion–stimulated desorption/surface cleaning), while no changes occur after irradiation with He I and He II UV irradiation (used for the UPS experiments).

In order to check the surface Mo/W ratio of the different WO$_3$:Mo samples (which were all prepared in one deposition run), we were particularly interested in the spectral window of the W 4d and Mo 3d lines (Fig. 14, left). Since these XPS features are energetically close together, one can directly use the peak intensities (corrected by the photoionization cross sections) to determine the concentration ratio (see Fig. 14, right) without considering the transmission function of the analyzer or the information depth (both are a function of the kinetic energy of the photoelectrons). As a result, we find that the investigated WO$_3$:Mo samples have a variation in surface Mo/W ratio, although they were all prepared in one deposition run.

In order to investigate whether the Mo/W ratio in the sample bulk also deviates from sample to sample we characterized the same set of samples by XES. The corresponding XES spectra of the WO$_3$:Mo thin films, together with selected reference materials, are shown in Fig. 15. The Mo 4s $\rightarrow$ Mo 3p transition is at 328 and 346 eV and the W 5s $\rightarrow$ W 4p$^{1/2}$ transition can be found at 345 eV. With the given low signal-to-noise (S/N) ratio, all spectra of #341 samples look similar, suggesting (in contrast to the more surface sensitive XPS measurements) similar Mo/W ratios.

![Fig. 14: XPS detail spectra of the W 4d and Mo 3d photoemission lines (left) for different WO$_3$:Mo samples and respective quantified Mo/W ratio (right).](image-url)
**Fig. 15:** Spectral window of the XES Mo and W feature shown for exemplary WO₃:Mo samples, together with related W and Mo references.

**Fig. 16:** XES O K spectra of one exemplary WO₃:Mo sample and related W and Mo oxide references.
In order to shed more light on how the Mo is incorporated into the WO₃ matrix, we additionally conducted XES O K measurements of one exemplary WO₃:Mo sample and related reference materials. Fig. 16 shows the O K emission spectrum of sample #341 B in comparison with Mo and W oxide references. At first sight, the spectra of #341 B look similar to that of a WO₃ powder reference. A closer comparison by means of a (weighted) difference spectrum, however, shows significant deviations. The comparison with the (shifted) MoO₃ powder reference spectrum reveals pronounced similarities. A contribution from the MoO₂ spectrum can, however, not be excluded.

We then studied HNEI WO₃ samples that were extracted from the vacuum system in which they were grown using a novel (and simpler) gas-flow technique, which will in the following be compared to results obtained with the previously used glovebag technique. The samples were extracted under a nitrogen stream and packed following the UNLV packing procedure. Instantly after their arrival at UNLV they were transferred into our glovebox and opened immediately before their insertion into the UHV system. In order to quantify the surface cleanliness of samples shipped with this technique, we compared the new set of samples to a previous series extracted with the glovebag.
technique and compared the amount of surface contaminants (carbon in particular). The following samples were compared for this purpose:

- Sample #WO327H: Pure WO₃ Sample (Dec. 08)
- Sample #WO332D: WO₃:Mo Sample (Dec. 08)
- Sample #W241: WO₃ (“Lothar” sample, used in our earlier JCP paper)
- Sample #W341A: WO₃:Mo Sample (Jan. 08, “Marcus” sample)

Fig. 17 shows the survey spectra for each of the samples. All peaks in the spectra are assigned to the corresponding element and energy level. The region between 200 and 320 eV binding energy is of particular interest, showing peaks of both the sample (W and Mo) as well as of the surface contaminants (C). This region was recorded in a detail scan shown in Fig. 18. Two main findings are observed. First, the Mo content is different for samples #341 and #332, i.e., when comparing the Jan. 08 and the Dec. 08 series. Second, the carbon peak is approximately twice as high for the gas-flow extraction procedure (both samples) as for the glovebag procedure, implying that the amount of surface contamination is significantly higher for the (simplified) gas-flow extraction procedure.

Fig. 18: Detail XPS scan of a region with sample (W and Mo) peaks as well as a contaminant peak (C).
3. ZnO-based thin films

In close collaboration with Yanfa Yan and Mowafak Al-Jassim at the National Renewable Energy Lab (NREL), we have studied ZnO:N samples that are intended to exhibit improved band gap characteristics compared to pure ZnO without N-doping. The NREL group has developed a deposition process in which the sputter power is used to control the N doping level (higher sputter powers correspond to nominally higher N contents). First results showed inconsistencies, namely unexpectedly low N concentrations for samples with nominally high N doping concentration. Together with additional observations by the NREL group, we tentatively interpreted it as an instability of the ZnO samples with high N doping concentration. Thus, a new ZnO:N sample series was prepared and investigated. In a joint effort with the NREL group, we took great care to minimize the time between sample preparation and measurement and avoid any exposure to ambient air. A graduate student was sent to Denver to take over freshly prepared and carefully (under nitrogen) packed samples, then traveled directly to Berkeley, where the samples were measured immediately (the time between sample preparation and first measurement was less than 8 hours).

In Fig. 19, the O K XES spectra taken of the fresh samples are shown in comparison with the spectrum of a ZnO reference powder. Three different features can be observed in the spectra:

![O K XES spectra](image)

**Fig. 19:** O K XES spectra of ZnO:N samples sputter-deposited with varying rf-power. For comparison, the spectrum of a ZnO powder is also shown.
1. The feature between 508-515 eV corresponds to transitions from valence states into the O 1s core hole. When increasing the sputter power, the low-energy shoulder of this feature increases in intensity and we observe the emergence of a tail on the high energy side of the line. This is in accordance with the expected shift of the VBM to lower binding energies when going from ZnO towards ZnN for higher sputter power.

2. The feature at 506.5 eV is due to transitions from Zn 3d levels into the O 1s core hole. This transition is a direct indicator for Zn-O bonds.

3. In addition to the O K emission, we also find Zn L emission in second order at 504.0 eV (note that this emission is excited by higher harmonics/orders of the undulator/monochromator of the beamline).

Features 2 and 3 can be used to derive the ratio between Zn atoms bound to O atoms and the overall number of Zn atoms. Fig. 19 shows that the intensity of the Zn L emission (feature 3) increases relative to the intensity of the Zn 3d → O 1s transition (feature 2) with increasing sputter power. Assuming that the samples only contain ZnO and ZnN as possible Zn compounds, the increasing intensity ratio can directly be related to an increasing ZnN:ZnO ratio. This finding is in agreement with the initial intention of increasing the ZnN content by increasing the sputter power. Only the

![Fig. 20: O K XES spectra of ZnO:N samples sputter-deposited with varying rf-power and stored in ambient air (black) or in ultra-high vacuum (UHV, red).](image-url)
sample with the nominally highest N-content (sputter power of 200 W) does not follow this trend. We explain this behavior by an extremely high instability of the ZnN rich samples as mentioned above.

To further investigate the stability of the ZnN films, we remeasured all samples after five days. For this experiment the samples were cut into two pieces. One sample set was stored in ambient air, while the other set was kept in ultra-high vacuum (UHV). The comparison of the emission spectra of the “aged” samples is shown in Fig. 20. While the O K emission spectra of the 'UHV-stored' samples (red curves) are similar to the initially recorded spectra, the spectra of the samples stored in ambient air show pronounced differences (black curves):

A. The low-energy shoulder of the feature related to nitrogen-induced valence states decreases in intensity (relative to the main line). In addition, also the tail on the high energy side of the valence band emission decreases.

B. While the intensity of the Zn L emission is substantially reduced, the feature directly indicative for Zn-O bonds does not significantly change in intensity upon air exposure (again with respect to the intensity of the main line).

The findings point to the partial conversion of the ZnN component in the samples into ZnO during air exposure. Note that the samples with the initially lowest N content are more stable, i.e., the relative decrease of the ZnN content is not as pronounced. In fact, they even show a higher ZnN content compared to the samples with higher initial N concentration. A speculative explanation could be that the ZnN in low N concentration samples is embedded in a ZnO matrix, which hinders its ‘oxidation’, whereas, for the high N concentration samples, more of the ZnN is accessible to be replaced by ZnO. Note that our measurements show also that the samples contained a certain amount of Ni and Cu.

Based on the findings on ZnO:N samples reported above, a third sample series was prepared in order to also investigate the electronic properties (band gap) and to shed more light on the air-exposure “instability” reported earlier.

In Fig. 21, the O K XES (left) and XAS (right) spectra taken of the fresh samples are shown in comparison with the spectrum of a ZnO reference powder. As already discussed above, three different features can be observed in the XES spectra:

1. The feature between 523-528 eV corresponds to transitions from valence states into the O 1s core hole. When increasing the sputter power, the low-energy shoulder of this feature increases in intensity and we observe the emergence of a tail on the high
energy side of the line. This is in accordance with the expected shift of the VBM to lower binding energies when going from ZnO towards Zn$_3$N$_2$ for higher sputter power.

2. The feature at 520 eV is due to transitions from Zn 3d levels into the O 1s core hole. This transition is a direct indicator for Zn-O bonds.

3. In addition to the O K emission, we also find Zn L emission in second order at 517.5 eV (note that this emission is excited by higher harmonics/orders of the undulator/monochromator of the beamline).

Features 2 and 3 can again be used to derive the ratio between Zn atoms bound to O atoms and the overall number of Zn atoms. Fig. 21 (left) shows that the intensity of the Zn L emission (feature 3) increases relative to the intensity of the Zn 3d $\rightarrow$ O 1s transition (feature 2) with increasing sputter power. Assuming that the samples only contain ZnO and Zn$_3$N$_2$ as possible Zn compounds, the increasing intensity ratio can directly be related to an increasing Zn$_3$N$_2$:ZnO ratio. As found before, this finding is in agreement with the initial intention of increasing the Zn$_3$N$_2$ content by increasing the sputter power.

![Fig. 21: O K XES (left) and XAS (right) spectra of ZnO:N samples, sputter-deposited with varying rf-power. For comparison, the spectrum of a ZnO powder is also shown.](image-url)
To further investigate the stability of the Zn$_3$N$_2$ films, we have remeasured the samples after 5 days and 196 days. For this experiment the samples were cut into two pieces. One sample set was stored in ambient air, while the other set was kept in ultra-high vacuum (UHV). The comparison of the emission spectra of the differently “aged” samples is shown for the samples stored in air in Fig. 22 (left) and for the samples stored in UHV in Fig. 22 (right). While the O K emission spectra of the ‘UHV-stored' samples (right) are similar to the initially recorded spectra, the spectra of the samples stored in ambient air (left) show pronounced differences:

A. The low-energy shoulder of the feature related to nitrogen-induced valence states decreases in intensity (relative to the main line). In addition, also the tail on the high energy side of the valence band emission decreases (see also discussion below).

B. While the intensity of the Zn L emission is substantially reduced, the feature directly indicative for Zn-O bonds does not significantly change in intensity upon air exposure.

These findings confirm our previous measurements and point to the partial conversion of the Zn$_3$N$_2$ component in the samples into ZnO during air exposure. According to the

\[ \text{Zn}^{3d} \rightarrow \text{O} \ 1s \]

\[ \text{Zn} \ L \ \beta \ 1 \]

\[ \text{O} \ K \ - \ XES \ \ h\nu = 560 \text{ eV} \]

**Fig. 22:** O K XES spectra of ZnO:N samples sputter-deposited with varying rf-power and stored in ambient air (left) or in UHV (right).
discussion of the spectral features of the O K – XES spectrum from above, the Zn$_3$N$_2$/ZnO+Zn$_3$N$_2$ ratios of the investigated samples was derived from the corresponding spectra shown in Figs. 21 and 22. Fig. 23 shows the results of this quantification. The sample with the initially lowest N content (the “100 W sample”) is most stable, i.e., the decrease of the Zn$_3$N$_2$/ZnO+Zn$_3$N$_2$ ratio is - compared to that of the other samples - not as pronounced.

Fig. 24 shows the onsets of the O K XES (left) and XAS spectra (right, from Fig. 21) of the investigated samples. They can be used to determine the band gap energy ($E_g$). (Note: The accordingly derived band gap is approximate and a lower limit due to potential core excitons in the XAS spectra.) While no significant shift in the XAS onset can be observed, the XES onset clearly shifts to higher emission energies, which is indicative for a decreasing band gap energy. Assuming a $E_g$ of 3.3 eV for the ZnO pwd. reference, band gap energies between 2.00 and 1.85 ($\pm$ 0.2) eV can be estimated for the ZnO:N samples (see Fig. 25). For comparison, the literature band gap energies for Zn$_3$N$_2$ vary between 1.23 eV and 1.52 eV. The estimated $E_g$ values for the ZnO:N samples are thus in good agreement with the determined Zn$_3$N$_2$ content.
During two additional experimental runs at the ALS we have investigated ZnO:Cu layers prepared by the NREL group (K.-S. Ahn, Y. Yan, and M. Al-Jassim). Using XES, we were able to confirm the incorporation of Cu into the ZnO layers. By additional measurements of reference materials (Cu and Zn foil) we were also able to quantify the Cu/Zn ratio.

Fig. 24: Onset of the O K XES spectra (left) and O K XAS spectra (right, from Figs. 1) of the investigated samples.

Fig. 25: Estimated band gap energies derived from the corresponding O K XES and O K XAS spectra. (see Figs. 21 and 24) of the investigated samples.

During two additional experimental runs at the ALS we have investigated ZnO:Cu layers prepared by the NREL group (K.-S. Ahn, Y. Yan, and M. Al-Jassim). Using XES, we were able to confirm the incorporation of Cu into the ZnO layers. By additional measurements of reference materials (Cu and Zn foil) we were also able to quantify the Cu/Zn ratio.
The ZnO:Cu thin films were prepared at NREL by reactive sputtering from a metallic Zn target. Due to the lack of co-sputtering capabilities, the preparation of ZnO:Cu layers was implemented by putting a different number of Cu "pieces" onto the Zn target before starting deposition (see Table 3 for a detailed list of investigated samples). After deposition, a part of the samples was additionally heat-treated in a quartz tube furnace for 2 h at 500°C in air. After sample preparation, the samples were packed under nitrogen, shipped to the ALS, unpacked in a glovebag under nitrogen atmosphere, and directly introduced into the ultra-high vacuum endstation used for the XES experiments.

Table 3: Detailed list of investigated samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th># of Cu pieces</th>
<th>As-deposited</th>
<th>Post annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/glass</td>
<td>0</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>ZnO:Cu [2]/glass</td>
<td>2</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>ZnO:Cu [6]/glass</td>
<td>6</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>ZnO:Cu [12]/glass</td>
<td>12</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Cu foil</td>
<td>N/A</td>
<td>✓</td>
<td>N/A</td>
</tr>
<tr>
<td>Zn foil</td>
<td>N/A</td>
<td>✓</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Fig. 26: XES spectra of the characterized reference materials Cu and Zn foil as well as an as-deposited ZnO layer on glass on linear (left) and logarithmic scale (right).
Fig. 27: XES spectra of the characterized set of ZnO:Cu samples together with a ZnO reference. The spectra are shown on linear (left) and logarithmic scale (right).

Fig. 26 shows the XES spectra (energetic window of the Cu L_{α,β} and Zn L_{α,β} emission) of the characterized reference materials (Cu and Zn foil, and a ZnO layer on glass). The most prominent spectral features are the Cu L_{α,β} (at approx. 928 and 947 eV) and the Zn L_{α,β} emissions (at approx. 1011 and 1034 eV), which can be observed in the spectra of the Cu foil and Zn-containing samples, respectively. The features at approx. 906 and 884 eV in the spectra of the Zn-containing samples can be attributed to Zn L_{l} (Zn 3d \rightarrow Zn 2p_{1/2} & 2p_{3/2}) emissions. The higher intensity of the Zn L_{l} emissions (at approx. 906 and 1034 eV) of the ZnO layer compared to that of the Zn foil can be explained by less pronounced self-absorption in the less Zn-dense ZnO. Close inspection of the spectra on a logarithmic scale (Fig. 26, right) shows additional features. The emission peak at approx. 1019 eV in the XES spectrum of the Cu foil can be attributed to Cu 3p \rightarrow Cu 2s transitions. The origin of the two small features at approx. 928 and 948 eV is not fully clear. At first sight one would interpret these features to be indicative for Cu (contamination) of the Zn-containing samples, since these features appear at the same position as the Cu L_{2,3} emission. However, these features are also present in the spectrum of a ZnO powder reference and other Zn-compounds (not shown), and we thus rather ascribe these features to the (nominally dipole-forbidden) Zn L_{2,3} M_{2,3} emission.

Fig. 27 shows the XES spectra (energetic window of the Cu L_{2,3} and Zn L_{2,3} emission) of the investigated ZnO:Cu samples before (black) as well as after (red) annealing in comparison to a ZnO reference. As can be observed in Fig. 27 (on linear (left) and on logarithmic scale (right)), the intensity of the Cu L_{2,3} emission increases with increasing number of Cu pieces on the metallic Zn sputter target, indicating that Cu is indeed incorporated into the ZnO film by this deposition set-up. The comparison of the as-
Deposited and post-annealed samples display no strong differences. Close inspection of the data, however, reveals a small but significant difference in the Cu L\textsubscript{2,3} emission intensity before and after annealing. After heat treatment, the intensity of the Cu L\textsubscript{2,3} emission is slightly decreased. As shown by the respective difference spectra (Fig. 28, left), the difference in Cu L\textsubscript{2,3} emission intensity before and after heat treatment increases with increasing Cu content.

In the following, we will focus on the quantification of the qualitative observation that the Cu content increases with increasing number of Cu pieces derived from the XES spectra shown in Fig. 27. In general, the emission intensity I of an XES spectrum can be expressed as:

\[
I = \int_0^\infty c \cdot \sigma_{\text{eff}} \cdot I_{\text{in}}(z) \cdot e^{\frac{-z}{\lambda_{\text{out}}}} dz
\]

where c is the concentration of the considered element, z is the penetration depth, \(\lambda_{\text{out}}\) is the attenuation length for the energy of the emission, \(\sigma_{\text{eff}}\) is the effective emission cross section (matrix element), and \(I_{\text{in}}\) is the (depth-dependent) excitation intensity, with

\[
I_{\text{in}}(z) = \frac{I_0}{\lambda_{\text{in}}} \cdot e^{\frac{-z}{\lambda_{\text{in}}}}
\]

and \(\lambda_{\text{in}}\), the attenuation length for the excitation energy, and \(I_0\), the excitation intensity for \(z = 0\). Combined, this results in the following equation:
Under the assumption that all Cu and Zn atoms are incorporated in a pure ZnO matrix ("Cu\_ZnO", "Zn\_ZnO"), the Cu/Zn concentration ratio can now be expressed as follows:

\[
I = \int_0^{\infty} c \cdot \sigma_{\text{eff}} \cdot I_0 \cdot e^{-\left(\frac{1}{\lambda_{\text{in}}} + \frac{1}{\lambda_{\text{out}}}\right)} \, dz = c \cdot \sigma_{\text{eff}} \cdot I_0 \cdot \frac{\lambda_{\text{out}}}{\lambda_{\text{in}} + \lambda_{\text{out}}}
\]

where \( c_{\text{Cu}\_ZnO} \), \( c_{\text{Zn}\_ZnO} \) are the Cu and Zn concentrations; \( I^*_{\text{Cu}\_ZnO} \), \( I^*_{\text{Zn}\_ZnO} \) are the intensities of the respective spectral features (in our case Cu L3 and Zn L3 emission, see Fig. 27) normalized to \( I_0 \); \( \lambda_{\text{in/out}}^* \), \( \lambda_{\text{in/out}}^{*\_\text{Zn\_ZnO}} \) are the attenuation lengths of the excitation and emission in the ZnO matrix (see Table 4); and \( \sigma_{\text{eff\_Cu\_ZnO}} \), \( \sigma_{\text{eff\_Zn\_ZnO}} \) are the effective emission cross sections (matrix elements) of Cu and Zn in the ZnO matrix. The only parameters missing for the determination of the Cu/Zn ratio from the XES spectra shown in Fig. 27 are the effective emission cross sections. However, since we know the Cu and Zn concentration in the respective metal foils (\( c_{\text{Cu\_Cu}} = c_{\text{Zn\_Zn}} = 1 \)), we can use the reference spectra (see Fig. 26) to determine the ratio \( \sigma_{\text{eff\_Cu}} / \sigma_{\text{eff\_Zn}} = 0.504 \). This ratio is approximately equated with the ratio of the effective emission cross sections in a ZnO matrix \( \sigma_{\text{eff\_Cu\_ZnO}} / \sigma_{\text{eff\_Zn\_ZnO}} \) (see equation below).

\[
\frac{c_{\text{Cu}\_ZnO}}{c_{\text{Zn}\_ZnO}} \approx \frac{I^*_{\text{Cu\_ZnO}}}{I^*_{\text{Zn\_ZnO}}} \cdot \frac{\lambda_{\text{out}}^{*\_\text{Zn\_ZnO}}}{\lambda_{\text{in}}^{*\_\text{Zn\_ZnO}}} \cdot \frac{\lambda_{\text{in}}^{*\_\text{Cu\_ZnO}}}{\lambda_{\text{out}}^{*\_\text{Cu\_ZnO}}} \cdot \frac{\sigma_{\text{eff\_Zn}}}{\sigma_{\text{eff\_Cu}}} \\
\approx \frac{I^*_{\text{Cu\_ZnO}}}{I^*_{\text{Zn\_ZnO}}} \cdot 0.804 \cdot \frac{1}{0.770} \cdot 0.504 = \frac{I^*_{\text{Cu\_ZnO}}}{I^*_{\text{Zn\_ZnO}}} \cdot 0.526
\]

According to this equation, we have derived the Cu/Zn ratio based on the XES spectra shown in Fig. 27. The determined Cu/Zn ratios are 1.2% (0.9%), 2.6% (2.2%), and 6.1% (5.4%) for the as-deposited (post-annealed) ZnO:Cu samples, respectively.

Table 4: Densities (used for the calculation of the attenuation lengths) and attenuation lengths used for the calculations described in the text.

<table>
<thead>
<tr>
<th></th>
<th>( \rho )</th>
<th>( \lambda_{\text{in}} ) (1090eV) [( \mu \text{m} )]</th>
<th>( \lambda_{\text{out}} ) (930eV) [( \mu \text{m} )]</th>
<th>( \lambda_{\text{out}} ) (1012eV) [( \mu \text{m} )]</th>
<th>( \frac{\lambda_{\text{out}}}{\lambda_{\text{in}} + \lambda_{\text{out}}} ) (930eV)</th>
<th>( \frac{\lambda_{\text{out}}}{\lambda_{\text{in}} + \lambda_{\text{out}}} ) (1012eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8.96</td>
<td>0.089</td>
<td>0.510</td>
<td>0.852</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>7.14</td>
<td>0.101</td>
<td>0.652</td>
<td>0.866</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>5.67</td>
<td>0.145</td>
<td>0.487</td>
<td>0.594</td>
<td>0.770</td>
<td>0.804</td>
</tr>
</tbody>
</table>
4. SiC-based thin films

In collaboration with our project partners at MVSystems, we focused on a study of amorphous SiC layers for PEC. We studied amorphous SiC (a-SiC) layers (nominally 100 Å [batch LCT-4744 & 4746] or 1000 Å [batch LCT-4743 & 4745] thick) deposited on SnO$_2$ covered glass. To avoid air contamination, the samples were packed under inert atmosphere using a glovebag and immediately shipped to UNLV. At UNLV, the sample packages were transferred into an N$_2$ filled glovebox (where the samples were also mounted) that is attached to our UHV surface characterization system. The samples were characterized by XPS and X-ray excited Auger electron (XAES) spectroscopy at UNLV and by XES at the ALS.

Fig. 29 shows the XPS survey spectra of the a-SiC/SnO$_2$/glass structure (sample LCT-4745 #1) recorded with Mg K$_\alpha$ (black spectrum) and Al K$_\alpha$ excitation (red spectrum). Both spectra are dominated by O, C, and Si XPS and XAES features, which points to an oxidized a-SiC surface. Furthermore, we find additional traces of Co, N, Cl, Ca, and Sn. Note that the latter may very well stem from the SnO$_2$/glass substrate. However, since the nominal a-SiC thickness of 1000 Å for this particular sample is far beyond the information depth of XPS/XAES (which is in the range of a few 10 Å), the observation of Sn can only be explained by an incomplete a-SiC coverage of the substrate or an incorporation/diffusion of Sn into the a-SiC layer during the a-SiC deposition.

![Fig. 29: XPS survey spectrum of the “as-received” a-SiC/SnO$_2$/glass sample (LCT-4745 #1) measured with Mg K$_\alpha$ (black spectrum) and Al K$_\alpha$ (red spectrum) excitation.](image)
To shed more light on the possible oxidation of the a-SiC, we have investigated the region of the Si 2p photoemission line in more detail (see Fig. 30). The left panel shows the Si 2p feature of the as-received a-SiC/SnO2/glass structure (sample LCT-4745 #1), again measured with Mg Kα (black spectrum) and Al Kα excitation (red spectrum). We find a main peak at around 100.3 eV and a very pronounced shoulder at around 103.9 eV. The first agrees well with the position of the Si 2p photoemission line for SiC (100.4 eV) and the latter agrees with the position of the Si 2p XPS line for SiO2 (103.1 – 104.1 eV). Note that the Si 2p feature would be expected at (101.7 -102.7) eV for SiO. Comparing the Si 2p spectra measured with Mg Kα (hν = 1253.56 eV) and Al Kα (hν = 1486.58 eV), respectively, we also observe that the feature ascribed to SiO2 is lower in intensity for the Al Kα spectrum. Since the kinetic energy of the Si 2p photoelectrons is higher when measured with Al Kα excitation (compared to Mg Kα) the information depth is larger relative to the Mg Kα measurement (as given by the “universal curve” of the electron inelastic mean free path). Hence, the Al Kα XPS measurements are more bulk-sensitive compared to those using Mg Kα excitation, and thus the SiO2 must indeed be predominantly located at the sample surface. In order to clean the sample surface, we have etched the samples in concentrated (48 %) HF-solution for 10, 30, and 60 s, as documented in the right panel of Fig. 30. We find that already after a 10 s etch, the SiO2 feature of the Si 2p spectrum is greatly decreased though still visible. It seems, however, that a 60 s etch step is sufficient to remove all of the surface oxide. Note that, in that case (60 s HF-dip), also the SnO2 of the substrate starts to dissolve in the etch

Fig. 30: Si 2p XPS detail spectra of the as-received a-SiC/SnO2/glass sample (left) and of a-SiC layers of the same batch after HF etching for different times (right).
solution, causing a partial peeling of the a-SiC as well. Furthermore, respective XPS survey spectra after HF etching (not shown) show distinct F and O XPS and XAES features, indicating that even after a thorough sample rinse some residue of the etch solution is adsorbed on the sample.

Fig. 31 shows the Si L\textsubscript{2,3} XES spectra of an as-received and HF-etched (30 s) a-SiC/SnO\textsubscript{2}/glass sample in comparison to different reference materials (SiC [4HN] wafer, Si wafer, and fused silica [i.e., SiO\textsubscript{2}]). We find that the (in comparison to the XPS/XAES measurements) much more bulk sensitive XES spectra (information depth in the range of a few 100 Å) of the as-received and HF-etched a-SiC layer are very similar, which confirms that the oxidization of the Si is indeed limited to the very surface of the sample. Note that the very pronounced SiO\textsubscript{2} features in the Si L\textsubscript{2,3} XES spectrum at 89 and 95 eV (see respective spectrum of the fused silica) cannot be even observed in the as-received a-SiC/SnO\textsubscript{2}/glass sample. Furthermore, we can observe that the Si L\textsubscript{2,3} XES spectrum of the a-SiC layer also significantly deviates from that of the SiC wafer, which might be explained by the amorphous nature of the MVSystems samples. The comparison of the Si L\textsubscript{2,3} XES spectra of the different materials also shows that the Si L\textsubscript{2,3} emission is very sensitive to the chemical structure, which could be used in future experiments focusing on the interaction between electrolyte and a-SiC.

![Fig. 31: Si L\textsubscript{2,3} XES spectrum of an as-received and HF-etched (30 s) a-SiC/SnO\textsubscript{2}/glass sample in comparison to different reference materials (SiC [4HN] wafer, Si wafer, and fused silica [i.e., SiO\textsubscript{2}]).](image-url)
We now further discuss the characteristic differences between 100 Å [batch LCT-4744 & 4746] and 1000 Å [batch LCT-4743 & 4745] thick) deposited on SnO$_2$-covered glass. Both the Mg K$_\alpha$ and Al K$_\alpha$ XPS survey spectra (Fig. 32) of LCT-4744 (before acid exposure) show the presence of Si and C, but O and Sn features are also observed. The O signal is likely from SiO$_2$ and/or SnO$_2$. The Sn signal in the spectra is significant because it suggests the growth of SiC islands on the substrate, instead of the presence of a homogeneous, 100 Å-thick film.

![Fig. 32: XPS survey spectra of the a-SiC/SnO$_2$/glass structure (sample LCT-4744) recorded with Mg K$_\alpha$ (red spectrum) and Al K$_\alpha$ excitation (blue spectrum).](image)

![Fig. 33: XPS survey spectra of LCT-4744 (100Å) vs. LCT-4745 (1000 Å), normalized to the Si 2p peak.](image)
As seen in Figure 33, comparison of the 4745 sample and the 4744 sample shows that the latter exhibits a less-pronounced Cl signal and no N signal, indicating that the degree of surface contamination is smaller for the thinner sample.

![Si 2p XPS spectrum](image)

*Fig. 34: Al Kα and Mg Kα detailed spectra of the Si 2p peak.*

In order to shed more light on the possible oxidization of the a-SiC, we have investigated the region of the Si 2p photoemission line in more detail (see Fig. 34). The spectra shows the Si 2p feature of the as-received a-SiC/SnO$_2$/glass structure (sample LCT-4744), again measured with Mg K$_\alpha$ (red spectrum) and Al K$_\alpha$ excitation (blue spectrum). The spectra were normalized to the peak height of the dominant SiC peak. Consequently, the relative intensities of the two peaks at 100.4 eV and 104 eV, corresponding to SiC and SiO$_2$, respectively, can give indication about the location of the SiO$_2$. Since the area under the curve for SiO$_2$ is larger for the Mg K$_\alpha$ energy than for the Al K$_\alpha$ energy, it is apparent that the SiO$_2$ exists in larger proportion on the surface of the sample than in its bulk.

When the 4745 sample is compared to the 4744 sample (Fig. 35), the 4744 sample shows a smaller relative presence of SiO$_2$. This indicates that, for the thinner sample, a smaller fraction of the Si atoms is found in an oxidized environment. Future experiments will need to clarify whether this due to a difference in sample handling and storage or due to a fundamental difference in the preparation process of the thinner film (e.g., the presence of the SnO$_2$ substrate).
Fig. 35: Mg Kα XPS detailed spectra of the Si 2p peak of Samples 4744 and 4755.

We have also studied a second batch of MVSystems a-SiC samples (batch LCT-5701, which consist of a 6 nm a-SiC(p) layer and a 188 nm a-SiC(i) layer deposited on SnO₂.

Fig. 36: XPS survey spectra of the a-SiC/SnO₂/glass structure (sample LCT-4744) and a-SiC(i)/a-SiC(p)/SnO₂/glass structure (sample LCT-5701), recorded with Mg Kα and normalized to the Si 2p peak height.
covered glass), and compared the result with that from the former samples (batch LCT-4744, a 10 nm a-SiC layer on top of SnO\textsubscript{2} covered glass). Again, the samples were vacuum-sealed under inert atmosphere and sent to UNLV and ALS immediately, in order to minimize air contamination. At UNLV and ALS, the samples were mounted on sample holders and transferred into the UHV analysis system in an N\textsubscript{2} filled glovebox or glovebag, respectively. The samples were characterized by XPS, XES, and XAS.

XPS survey spectra were measured with Mg K\textsubscript{\alpha} excitation for both samples (4744 and 5701) at UNLV (Fig. 36). The results were normalized to the Si 2p peak height for easy comparison. Both spectra consist of not only Si and C signals, but also signals from other elements, such as O, N, and Sn. It was found that the Sn 3d signal from substrate (SnO\textsubscript{2}) is stronger for 4744 and weak for 5701. Meanwhile, the O 1s signal, likely from SiO\textsubscript{x} and SnO\textsubscript{2}, is larger for 4744 and smaller for 5701. This indicates that the thinner a-SiC might not be a continuous layer, so that Sn (and O) signals from the substrate can be observed. The finding of a N signal is surprising. To shed more light on the potential origin and impact, detail spectra of the N 1s region were recorded for both samples, as shown in Fig. 37. Sample 5701 has a main feature at around 400 eV, which is much stronger than that of 4744. This feature could be a result of surface N species, such as N-H or N-C, but not likely from N-Si, which would be expected around 397.5 eV. These species could be by-products during sample preparation, possibly from the walls of the PECVD chamber.

Fig. 37: N 1s spectra of sample 4744 and 5701, recorded with Mg K\textsubscript{\alpha}, normalized to the background at lower binding energy.
Fig. 38: Si 2p spectra of sample 4744 and 5701, recorded with Mg Kα, normalized to the background at lower binding energy.

To address the environment of Si atoms in the samples, Si 2p spectra from both samples were recorded with Mg Kα (Fig. 38). Both spectra consist of two main features. The feature at 100 eV is associated with Si atoms in Si-C bonds, and the feature at 103 eV is indicative of Si-O bonding. The energy position of the Si-O feature is different for 4744 and for 5701, which indicates that Si atoms in the sample 5701 have a slightly higher average oxidation state than for 4744. Meanwhile, the spectrum of 4744 shows a higher Si-O/Si-C ratio than that of 5701. Note that these spectra probe the local chemical environment at the Si atoms, and thus this finding cannot be caused by the fact that the substrate (SnO₂) signal is visible as well.

For sample 5701, a C K-edge XES spectrum, providing information about the occupied valence states, was measured at the ALS (Fig. 39). In order to minimize the impact of excitation energy on the measurement, the spectrum was recorded by above-threshold excitation. The corresponding C K-edge XAS spectrum, providing information about the unoccupied conduction band states, is also plotted in Fig. 39, normalized to same spectral height as the main feature in the XES spectrum for easy comparison. The two linear extrapolations are added in the plot to provide an estimation of VBM and CBM. The energy separation of the two band edges, about 3.3 eV, is a lower bound for the real band gap of the sample, because of the potential presence of a core exciton. This
value is close to that of HF-etched sample (LCT-4745). It also lies within the upper region of the range of reported optical band gap values for a-SiC.

Fig. 39: C K-edge XES and XAS spectra of sample 5701.

**Fe₂O₃-based thin films**

In this section, we report on the analysis of Fe₂O₃ thin film samples, prepared by our collaboration partners at UCSB (A. Kleiman, A. Forman, and E. McFarland). Fig. 40 shows the design of the layer structure used by the UCSB group. On a quartz wafer, a 50 nm thick Ti layer was grown first, followed by a 150 nm thick Pt layer. An Fe layer of variable thickness was then deposited on top of the Pt, and the entire sandwich structure was calcined in air for 4 hours.

Fig. 40: Layer structure of the UCSB Fe₂O₃ films before and after calcination in air.
The following set of UCSB samples was investigated at UNLV:

- Sample #1: 10 nm Fe (calcined in Stucky oven)
- Sample #2: 200 nm Fe (calcined in Stucky oven)
- Sample #3: 400 nm Fe (calcined in Stucky oven)
- Sample #4: 200 nm Fe (calcined in small McFarland oven)
- Sample #5: 0 nm Fe
- Sample #6: 10 nm Fe, not calcined

These samples offer a wide variety of investigative options. As a start, we concentrated on the effect of calcination on the thin (10 nm) Fe film. Fig. 41 shows the survey spectra of the two samples with the same nominal thickness of the iron layer, with (sample #1) and without (sample #6) the calcination step.

*Fig. 41.* Survey spectra of sample #1 (10 nm Fe, calcinated) and sample #6 (10 nm Fe, not calcinated).

In the spectrum of sample #6, one can only detect the elemental lines of Fe, C and O. After the calcination at 700°C for 4 hours, very strong Pt and Ti signals are visible. Two possible explanations for this behavior are viable:
- The high temperature during the calcination step increased the mobility of Pt and Ti atoms and led to a diffusion of these elements into the iron (oxide) film.
- A change in the surface morphology, including the formation of areas with incomplete iron (oxide) coverage.

To shed light on the latter explanation, we investigated the calcined sample with atomic force microscopy (AFM) in air. Fig. 42 shows a $50 \times 50 \, \mu m^2$ region of the sample #1 surface. Evidently, the surface is rough and grain-like, with isolated regions (islands) protruding from the surface plane.

![AFM image of a 50 x 50 mm² area of sample #1.](image)

Initial results showed that the originally employed extraction method under nitrogen flow was not sufficient to diminish the carbon contamination of the surface significantly (compared to fully air-exposed samples). In order to implement our optimized (standard) packing procedure at UCSB and to increase our understanding of the growth processes of the Fe₂O₃ samples, one of our group members (K. George) travelled to Santa Barbara and helped in both, the implementation of the packing procedure, as well as the actual growth of the Fe₂O₃ samples. The packing procedure and its impact on the carbon contamination will be shown first, followed by results that shed light on processes occurring during the calcination step.

**Packing Procedure:**
In order to prevent air exposure of the samples after deposition of the thin films, the entire preparation chamber was connected to a glove bag, which was repeatedly evacuated and filled with dry nitrogen for purging. The chamber was also vented with
dry nitrogen before the sample extraction. A picture of the preparation chamber and the attached glove bag can be found in Fig. 43. After the final preparation step, the samples were packed into an evacuated bag (utilizing a Foodsaver) and into a second evacuated bag with desiccant.

![UCSB preparation chamber with attached glove bag.](image)

**Fig. 43: UCSB preparation chamber with attached glove bag.**

**Effect of packing procedure:**
The samples packed in the way described above showed significantly lower carbon signals. Fig. 44 shows the survey spectra of two calcined 10 nm Fe samples which were shipped under different conditions.
Fig. 44: Comparison of the XPS survey spectra of two calcined 10 nm Fe films that were shipped in air (Dec. ’08) and under nitrogen atmosphere (May ’09).

It is clearly visible that the C1s peak of the May sample is reduced to about one third of the intensity of the December sample. The remaining carbon contamination probably originates from the growth process, which is conducted in the 10⁻⁶ mbar pressure range. Figure 44 also clearly shows the presence of Pt and Ti peaks, despite the fact that surface sensitive XPS should not detect these signals for Pt and Ti layers buried under a 20 nm-thick Fe₂O₃ film (note: the 10 nm Fe film is expected to form a 20 nm Fe₂O₃ film upon calcination). In order to shed light on the origin of these signals, further studies of the calcination process were performed, in particular on “bare” Pt films deposited on the Ti-coated substrate.

**Effect of calcination on the Pt surface:**
As mentioned, Ti and Pt signals are found in spectra of calcined samples such as those shown in Fig. 44. The only obvious source for a Ti signal is the Ti layer underneath the comparably thick Pt film. In order to determine at which temperature the Ti atoms become mobile enough to penetrate the Pt film, two samples without additional Fe layer were stepwise annealed in UHV.
Fig. 45: Detail XPS spectra of the Ti 2p region. Spectra (a) - (f) were taken from the same Pt thin film on top of a Ti layer, annealed in ultra-high vacuum at temperatures of (a) 300°C, (b) 400°C, (c) 500°C, (d) 600°C, (e) 700°C, and (f) 800°C. Spectrum (g) was recorded for a different sample of the same sample system after annealing directly to 770°C.

Fig. 45 shows the results of the temperature-dependent XPS series of the Ti 2p region. The spectra (a) to (d) correspond to annealing temperatures between 300 and 600°C and show no significant Ti signal. A first small change can be observed at 700°C in (e), which becomes obvious at 800°C in spectrum (f). This observation was repeatable by directly heating the sample to 770°C without intermediate steps (g).

The temperatures given were measured with a thermocouple underneath the sample, and were corroborated with a pyrometer reading to derive the actual surface temperatures: 630°C for spectrum (f) and 700°C for spectrum (g). Note that standard calcination steps at UCSB are performed at 700°C (and above), indicating that Ti atoms are available at the surface of the Pt/Ti bilayer at these temperatures. Thus, to avoid the presence of Ti at the surface of the Fe₂O₃ film upon calcination, the findings suggest that calcination at lower temperatures (e.g., 500°C) would be more suitable to prepare pristine Fe₂O₃ film surfaces (note that the presence of Ti at the surface appears to be favorable for PEC applications).
To further aid in the optimization of Fe$_2$O$_3$ thin films prepared by the UCSB group, we investigated the chemical origin of the following effect: It was observed that the PEC performance of Fe$_2$O$_3$ thin film samples with similar configuration (e.g., same Fe thickness before calcination) but treated at different locations (i.e., Stucky’s vs. McFarland’s furnace) were different. In order to understand the microscopic and elemental origin of the differences in sample performance, a detailed comparative XPS study was thus carried out.

Two samples with the same structure as shown in Fig. 40 (200 nm of Fe), were calcined at 700°C for 8 hours in air in Stucky’s and McFarland’s furnace, respectively. Fig. 46 shows XPS survey spectra of the two samples. Fe and O signals are observed, as expected. Furthermore, other elements, such as C and Ti, are observed as well. As discussed above, the here-observed presence of Ti on the Fe$_2$O$_3$ surface is ascribed to a thermally driven diffusion mechanism. The presence of a C signal is not surprising due to the intermittent exposure to air. The exact origin of the other contaminants, such as F and Cr, is unknown.

![XPS survey spectra of the two samples](image)

Fig. 46: XPS survey spectra of the two samples: “Stucky” and “McFarland” sample, which were annealed in Stucky’s and McFarland’s furnace, respectively. The spectra were normalized to the secondary electron background and offset vertically for easier comparison.
Fig. 47 shows a difference spectrum between the two survey spectra from the “Stucky” and “McFarland” samples. It is clear that the sample surface prepared in McFarland's furnace has a higher C content and less Fe, O, Cr, and F signals than the “Stucky” sample. This indicates a direct impact of the furnace used for the calcination process on the surface composition of the sample. This is possibly due to several factors, such as the temperature distribution inside the furnace, various concentrations of other elements in/on the walls of the quartz tube, and the detailed composition of the lab air. The presence of Cr might have an impact on the catalytic properties of the surface. Note, also, that the change of Ti spectral intensity between the two samples is relatively small. Apparently, the surface concentration of Ti after calcination is not directly influenced by the choice of the furnace.

Since Ti atoms only appear at the surface of samples that have been calcined, additional experiments investigating the effect of temperature on the samples were performed. The XPS spectrum of a 10 nm Fe calcined film (deposited on a Pt-covered Ti film) was compared to that of a 10 nm uncalcined film, as shown in Figure 48.

![Difference spectrum](image)

*Fig. 47: Difference spectrum of the “Stucky” and “McFarland” XPS survey spectra, as shown in Fig. 46.*
As seen with all calcined samples, the XPS spectrum of the calcined 10 nm film shows Ti 2p peaks; in addition, strong Pt peaks are also present. In contrast, neither Ti nor Pt peaks are visible for the non-calcined sample (a 10 nm-thick Fe overlayer is beyond the information depth for Pt (and Ti) detection with Mg Kα XPS), again pointing to a significant diffusion process at the surface.

To examine possible morphological differences between calcined and uncalcined films, samples were removed from vacuum for imaging after completion of all XPS experiments, and Atomic Force Microscope (AFM) images were taken. Figures 49 and 50 show the surface morphology of the 10 nm uncalcined Sample 6.
The AFM image in Fig. 49 is a (5 \( \mu \text{m} \))^2 view of Sample 6, and was taken in Contact Mode with a scan rate of 0.5 Hz. We find small islands, approximately 10 nm in height, and an otherwise generally rather closed and smooth surface morphology (note the difference in scale for the x/y- and z-axes). A (50 \( \mu \text{m} \))^2 view of the same region shows that this holds true even at the more macroscopic level, as is shown in Figure 50.

After calcination at 700 °C for 4 hours, distinct changes to the surface morphology of the film can be seen. Figure 51 [(5 \( \mu \text{m} \))^2] shows enhanced islands, with peaks approximately 30 nm in height (i.e., about three times as high as in the uncalcined case in Figure 49). The AFM image also shows more regions with “negative” negative depths. This may be due to several reasons – most likely, island formation is occurring for the Fe\(_2\)O\(_3\) layer and a dewetting of the previous Pt substrate occurs. This would explain the observation of Pt peaks in the XPS spectrum of the calcined 10 nm film, but does not account for the presence of a Ti signal. Alternatively, this island formation and its corresponding holes may be due to the diffusion of either Pt and/or Ti atoms into and through the Fe\(_2\)O\(_3\) layer.
Top-down SEM images of the 10 nm calcined films taken by the McFarland Group at UCSB show that for thin (10 nm) samples, the film coverage is incomplete, whereas 200 nm films show more fully formed grains. This explains the presence of a Pt signal in XPS spectra of thin films, but its absence in the spectra of thicker films. Cross-sectional SEM images from UCSB further reveal the growth of whisker-like structures in calcined samples. Large needle-like outcroppings with diameters less than 20 nm are visible on
the surface of the 200 nm film, and AFM analysis (Figure 52) shows that the observed islands reach up to 80 nm in height.

![AFM image of 200 nm Fe PEC film.](image)

Having elucidated the impact of calcination on the chemical surface properties of the UCSB thin films, we focused on the characterization of the electronic structure of a Fe$_2$O$_3$ sample that demonstrated particularly high solar water splitting performance.

The occupied and unoccupied electronic states were probed with UPS and IPES, respectively, as shown in Fig. 53a. The binding energies (abscissa) were adjusted relative to the Fermi Energy and plotted within the same graph. The leading edges of each spectrum were then extrapolated to the baseline. The positions of the intercepts with the baseline determine the positions of the valence band maximum (VBM, in the UPS spectrum, left) and conduction band minimum (CBM, in the IPES spectrum, right). The combination of both band edges allows a determination of the electronic surface band gap (1.9 ± 0.2 eV). The work function (4.23 ± 0.05 eV) was experimentally determined by measuring the secondary electron cut-off region of the sample under He I excitation (Fig. 53b) and by evaluating the intercept of the linear extrapolations of the baseline and the secondary electron cut-off.
Combining the band edge positions (with respect to the Fermi energy) with the work function of the sample, the band edge positions can be given with respect to the vacuum level. Furthermore, by applying an IUPAC recommendation [S. Trasatti, Pure Appl. Chem. 58, 955 (1986)] and as done earlier for the case of WO$_3$, the vacuum level scale can be related to the Normal Hydrogen Electrode (NHE) scale:

$$-E_{(NHE)} - 4.44 \text{ eV}^* = E_{\text{vacuum}} = E_F + \Phi.$$ 

By plotting the position of the VBM and CBM relative to the Fermi energy, vacuum level, and NHE on one plot, a comprehensive picture of the electronic picture can be painted, as shown in Figure 54.
Fig. 54: Band edges and positions of the Fe$_2$O$_3$ sample surface, relative to $E_F$, $E_{\text{Vacuum}}$, and NHE. 

Note that the plot in Fig. 54 is derived from vacuum-based measurements and thus includes a potential surface band bending at the solid/vacuum interface. It does not, however, include potential variations of this band bending upon formation of the liquid-solid interface in an electrolyte environment. As is well known, a Helmholtz layer is formed in this case, and experimental and theoretical approaches to assess the impact of this layer on the electronic structure will need to be performed in subsequent projects.

In the current state, the plot in Figure 54 shows that the Fe$_2$O$_3$ sample surface simultaneously satisfies two conditions necessary for solar water splitting: The CBM and VBM straddle the H$^+$/H$_2$ reduction and H$_2$O/O$_2$ oxidation potentials, and the surface band gap of 1.9 ± 0.2 eV lies in the optimal range for photoelectrochemical hydrogen production with a single-gap material.
5. In-situ studies

To prepare for future funding opportunities that would allow PEC in-situ studies, we focused on an optimization of the conditions/parameters for liquid contact mode atomic force microscopy (AFM) studies to investigate PEC materials (such as WO$_3$ prepared at the University of Hawaii) in-situ. One of the main challenges of PEC is the (photo)degradation of surfaces in aqueous solutions, specifically at extreme pH. This could adversely impact hydrogen conversion efficiency, as the interface deteriorates in the harsh electrolytic conditions of the PEC cell. The long term goal of our PEC activities is thus to investigate the electronic and chemical surface structure as well as the morphology of such materials in a functioning PEC cell. As a first step, we have used the liquid electrochemical mode of our AFM (with a 3 electrode system in a small reservoir that holds up about 0.5-1cm$^3$ of the electrolyte).

For our initial optimization, we use a plain gold substrate as a reference material. As a first step, the electronics and software mode of the AFM were changed to the liquid mode. Figure 55(a) illustrates the topography of the gold substrate in air. Then, a thin (3-4 mm) layer of water was added onto the gold surface. Figure 55(b) shows the AFM image of the same substrate immersed in water (pH ~7). It was found that hydration of the surface leads to a reduced apparent surface roughness on the substrate. This is possibly due to interactions between the water and the surface gold oxide layer, but other effects might be playing a role, too. In contrast to the bare gold surface, we do not observe any kinks “under water”, probably due to aggregation of water around the rough edges of the kinks.

(a)          (b)

Fig. 55: (a) Contact mode AFM image of a gold substrate in air, (b) after the addition of a thin layer of water on the surface. These images were taken using a Si$_3$N$_4$ cantilever specially designed for liquid phase imaging.
As a next step towards real in-situ conditions, we used a buffer solution (pH = 0, 1M HClO₄) on the surface of the gold substrate. Figure 56 shows the topography of the gold surface submerged in electrolyte under these conditions. These initial experimental results are promising first steps towards the utilization of liquid contact AFM as an effective tool for in-situ investigation of electrode surfaces.

Next, we focused on a WO₃ sample series produced by our project partners at HNEI. WO₃ is generally considered to be stable under operating conditions of the PEC cell (pH~0.5). Also, it has been noted that the stability decreases as the pH increases - especially for pH values above 7, disintegration of WO₃ films has been observed.

Fig. 56: AFM images in 1M HClO₄ obtained under liquid mode imaging.

Fig. 57: (a) and (b) contact mode AFM images of a WO₃ thin film surface in air. Scan sizes are 20x20 and 10x10 μm², respectively.
To shed further light on these processes, we conducted AFM imaging of WO$_3$ film surfaces under differently buffered conditions of pH=0.5, 4, 7, and 8. Figure 57 represents the topography of a WO$_3$ thin film surface in air, i.e., before immersion of the sample in liquid.

The same thin film was then immersed in pH = 7 buffer in the liquid cell of our AFM and imaging was continued after a wait time of about 30 minutes in the liquid cell (Fig. 58). Comparing the images before and after submersion in the pH = 7 buffer, gash-like features are observed, which might suggest some degree of deterioration even at neutral pH. Next, in-liquid imaging of WO$_3$ films at pH=8 was initiated, but the scanning could not be completed due to quick deterioration of the surface, leading to the disengagement of the AFM cantilever. Future projects will need to continue this work.

To also allow spectroscopic investigations of PEC candidate materials in in-situ cells in the future, we also initiated the development of a liquid-solid in-situ cell for our SALSA endstation. As a test case, we investigated the solid/liquid interface of a Mo reference sample (metal foil) under water in the group-operated SALSA ("Solid And Liquid Spectroscopic Analysis") endstation at Beamline 8.0.1 of the ALS.

A schematic drawing of the flow-through in-situ cell of the SALSA endstation is shown in Figure 59.

Fig. 58: (a) and (b), liquid mode AFM images of a WO$_3$ thin film surface. Scan sizes are 20x20 and 10x10 μm$^2$, respectively. Gash-like structures on the surface suggest some degree of deterioration already at pH=7 (i.e., neutral).
Fig. 59: Cutaway diagram of the SALSA liquid cell (M. Blum et al., Rev. Sci. Instrum. 80, 123102 (2009)).

Fig. 60: XES Spectrum of a Mo reference sample under 10 µm of water.
To measure the Mo/H$_2$O interface, a Mo sample plate was mounted on the micrometer caliper of the in-situ cell setup. Water was flowed through the cell at a constant flow rate and the solid/liquid system was separated from the vacuum by a thin carbon membrane (manufactured by J. Andersson, Uppsala University, Sweden). The strongest Mo signal was detected with a 10 µm layer of water between the membrane and the Mo sample. The system was excited by the synchrotron beam with an energy of 275 eV and the emitted photons were detected using a high-resolution, high-transmission x-ray spectrometer consisting of a spherical mirror, a variable-line-space (VLS) grating, and a CCD detector. The resulting X-ray Emission Spectroscopy (XES) spectrum is shown in Fig. 60.

The spectrum shows a strong Mo 4p → 3d transition at ~192 eV and a weaker signal from the Mo 4s → 3d transition at ~168 eV. Although the excitation is done below the O K absorption onset, a dominant O K emission line is visible in the spectrum due to excitation by higher beamline orders. Additionally, since 275 eV is in the resonant region of the C K emission, the small carbon contribution of the window membrane is also present in the spectrum.

In summary, thus, important first steps have been made towards a detailed characterization of materials in in-situ environments, both to study the morphology as well as the electronic and chemical properties at the electrode-electrolyte interface. Future projects will be proposed to develop these capabilities towards a routinely applied characterization for candidate materials for solar water splitting.

Publications:


Presentations:


3. C. Heske, “Investigating the electronic and chemical properties of surfaces, interfaces, and other buried things with soft x-ray spectroscopy”, Chemical Engineering Department, University of California Santa Barbara, October 25, 2007 (invited oral).


7. C. Heske, “How soft x-rays can help to optimize solar cells (and other electronic devices)”, University of Oregon IGERT graduate student seminar, University of Oregon, Eugene, February 27, 2008 (invited oral).


12. C. Heske, "How soft x-ray spectroscopy can help the 'Hydrogen Economy' (hopefully)", Seminar Experimentelle Physik II, University of Würzburg, Germany, July 8, 2008 (invited oral).

13. C. Heske, "So, when will there finally be a breakthrough for these solar thingies?“, Western Regional Meeting of the American Chemical Society, Education Program Keynote Address, Las Vegas, Sept. 27, 2008 (invited oral).


16. C. Heske, "How soft x-ray spectroscopy can shed light on the electronic and chemical properties of interfaces“, PIRE-ECCI (Partnership for International Research and Education) Seminar, Electron Chemistry and Catalysis at Interfaces, Department of Chemistry and Biochemistry, University of California, Santa Barbara, November 5, 2008 (invited oral).


27. C. Heske, “Using soft x-rays to look into (buried) interfaces of energy conversion devices”, Chemistry and Geochemistry Department at the Colorado School of Mines, Golden, CO, September 25, 2009 (invited oral).


29. C. Heske, “Using soft x-rays to look into interfaces of energy conversion devices”, Materials Science & Engineering Colloquium (co-sponsored by ECE and Physics), Boston University, December 4, 2009 (invited oral).


31. C. Heske, “How x-ray and electron spectroscopies can help to tackle the energy problem”, Physics Department, Free University Berlin, Germany, January 20, 2010 (invited oral).
32. C. Heske, “Using soft x-rays to look into (buried) interfaces of energy conversion devices”, Department of Physics, Technical University of Denmark, March 12, 2010 (invited oral).


37. C. Heske, “Using soft x-rays to optimize materials for energy conversion devices”, Department of Physics, Renmin University, Beijing, China, Oct. 10, 2010 (invited oral).


ATTACHMENT B

University of California, Santa Barbara (UCSB)

High Efficiency Generation of Hydrogen Fuels Using Solar Thermochemical Splitting of Water

(24 Pages)
SHGR-PEC Final Project Report

Project Title: High Efficiency Generation of Hydrogen Fuels Using Solar Thermo-Chemical Splitting of Water (SHGR)

Project Period: October 1, 2006 to December 31, 2007 NCE until: November 30, 2008

Recipient: University of California Santa Barbara through subcontract from The UNLV Research Foundation #RF-07-SHGR-011

Award Number: DE-FG36-03GO13062 subcontract #RF-07-SHGR-011

Working Partners: UNLV, NREL

Cost-Sharing Partners: University of California Santa Barbara

Contact: Eric W. McFarland
Dept. of Chemical Engineering
University of California
Santa Barbara, CA 93106-5080
Phone: 805-893-4343;
Fax: 805-893-4731
mcfar@engineering.ucsb.edu


This report does not contain any proprietary, confidential, or otherwise restricted information.

Executive Summary

The overall project objective is to discover and optimize efficient, practical, and economically sustainable materials for photoelectrochemical production of hydrogen. The goal is to provide a material system with the following characteristics: i) appropriate bandgap for solar absorption and production of sufficient electron/hole energetics to drive a reaction producing hydrogen (or a hydrogen carrier molecule), ii) band edge engineering for optimal water redox chemistry, iii) nanostructured morphologies for efficient bulk to surface site charge transfer, iv) inhibition of photodegradation/photocorrosion, and v) active electrocatalytic surfaces.

To date, no material system has been discovered for the photoelectrochemical production of hydrogen which is economically competitive to hydrogen production from reforming or grid powered electrolyzers. The highest efficiency systems developed are too expensive and unstable in electrolytes and the inexpensive systems are inefficient. Our goal is to employ abundant and non-toxic semiconducting materials, such as iron oxide, and improve upon the pure phase materials by engineering their electronic behavior and nanoscale structures.
Hematite ($\alpha$-Fe$_2$O$_3$) has many potential advantages as a photoelectrocatalysis for hydrogen production. It has a bandgap of 2-2.2 eV (absorbs approximately 40% of the solar spectrum), it is stable in electrolytes over a wide range of pH’s and is abundant, inexpensive and non toxic. Several fundamental properties have limited the use of this material as an efficient photocatalyst, including high electrical resistance and recombination rates of photogenerated electrons and a conduction band-edge that is lower than the redox level of H$^+$/H$_2$. The undesirable electrical properties are partially due to the hopping mechanism of charge transfer via oxygen vacancies, grain boundaries, and surface traps, which results in relatively low quantum yields (low efficiency materials), while the low conduction band energy is due to the Fe 3d electrons. Efforts have been devoted to reducing the resistivity of thin films by nanostructured crystal engineering. By growing crystalline hematite nanorods oriented in the (001) direction, this anisotropic electron transport can be exploited to improve photocatalytic rates. This last approach, combined with low level Si doping, has already shown some improvement over hematite however there is still much work to be done to increase the record IPCE (400nm) of 42%.

**Our hypothesis is that through a combination of deliberate doping of hematite with selected heteroatoms (guided by theory) and the control nanoscale morphology, the material can be made significantly better for PEC applications.** There is much diversity to explore in searching for the appropriate combination of dopant species to improve photocatalytic performance, as well as to understand and engineer the crystal structure, orientation and size of the crystalline domains of hematite. We have drawn on theory and our experience in high throughput experimentation to increase the efficiency of exploring these combinations. The next technical barriers must be overcome to achieve DOE targets for 2010 Y. Materials Efficiency, AA. PEC Device and System Auxiliary Material.

Fuel production must be economically competitive and history has shown that costs above $10/GJ are unacceptable. Engineering process modeling shows that at 10% solar-to-hydrogen costs the solar PEC system must be less than $50/m$^2$, installed. This immediately limits the potential materials and systems that might be considered for evaluation. The challenges of PEC are not fundamental physics (these issues were addressed in the 1980’s) it is the applied science necessary to make a cost-competitive system.

The focus of the work under the UNLV program has been on Iron Oxide (Fe$_2$O$_3$) because if a 8-10% efficient iron oxide based hydrogen producing PEC material was found which did not require an external bias, then a realistic, cost effective, system might be built around it. We wanted to push iron oxide to its limits to see if there was a means by which we could overcome its fundamental, pure phase, limits. We have learned a great deal in the course of this project and made significant improvements in the performance of iron oxide. However, the best performance we have achieved is not close to what is needed for a practical commercial system. The results of the work performed under this program has been shared with the scientific community through presentations and publications in peer reviewed journals (below), more papers are in preparation. Although there is no direct retribution to the taxpayers, indirectly the discoveries that have been made contribute to the collective scientific knowledge that might pave the way for an efficient photocatalyst system to be developed in the future.
Summary of task activities

The following 6 tasks were outlined for the subcontract #RF-07-SHGR-011 with UNLV: (1) Develop means for reducing the Fe₂O₃ nanorod diameter, (2) Synthesis of doped Fe₂O₃ nanorods, (3) Morphological and photo-electrochemical characterization, (4) Deposition of nanoparticle catalysts on Fe₂O₃ nanorods, (5) Efficiency of Hydrogen Production From Organic Substrate Oxidation and (6) Electrochemical deposition of Iron Oxide. A Summary of the task activities for the entire period of funding, including the original hypotheses, approaches used, problems encountered and departure from planned methodology, and an assessment of their impact on the task results is presented below.

Task 1: Reduce Fe₂O₃ Nanorod diameter

Work was performed to understand and control the diameter of iron oxide (Hematite) nanorods synthesized by solution growth techniques (Task 1.2.3). By modifying the growth conditions (temperature, pH, time, reagent, supporting electrolyte and structure directing agent concentration) the shape and orientation of the iron oxide nanorods can be modified; changes in the morphology of the samples should have an impact on the PEC performance of the samples. By changing the orientation of the rods higher electron conducting planes can be aligned perpendicular to the substrate to enhance electron transport to the back contact. Figure T1-1 shows the XRD pattern and table with intensities for different (hkl) peaks for two different samples. An increase in the (110) peak is observed in one of the samples, which could be indicative of a preferred orientation in this direction by changing the synthesis condition.

By changing the size of the nanorods, higher surface areas and roughness factors can be obtained which have obvious benefits for PEC systems. As shown in figure T1-2, the aspect ratio of the nanorods can be controlled by modifying the growth conditions of the α-FeOOH nanorods. In figure T1-3 Tem of selected nanorods are shown. The rod diameter can currently be tuned from 12 to 35 nm. The UV-Vis absorption for the different diameter nanorods is shown in figure T1-4. Variations in absorbance are primarily due to either cross-sectionally thin “fields” of nanorods or low densities of rods within the field. The latter is primarily observed with small diameter rods. Although we expected to further decrease the nanorods diameter to ~5nm, where quantum confinement effects will widen the bandgap; which in turn will shift the conduction band to higher energies, allowing for spontaneous photocatalytic water splitting, we were not able to achieve a widening of the bandgap or to further increase the photoelectrochemical performance by decreasing the size of the nanorods.

Our results showed that decreasing the rod size resulted in a decrease in the overall performance consistent with a higher rate of surface recombination as the surface to volume ratio was increased. We were not able to made rods of sizes necessary to observe quantum confinement and given the decreased performance downgraded the importance of further effort on this task. Further work on this task would be to attempt surface passivation (as we are doing in other PEC tasks) and we hope to return to the work with rods once an efficient means of passivating the surface is identified.
Task 2: Synthesis of doped Fe$_2$O$_3$ nanorods

Two methodologies have been developed for the synthesis of doped Fe$_2$O$_3$ nanorods. The first methodology consists on the growth of doped nanorods with the dopant species added to the growth solution while the second method consists on the doping of the nanostructures after the growth of the nanorod via gas phase doping or surface-to-bulk doping.

In spite of significant effort, we were not able to grow hematite nanorods containing dopants directly. The process of hydrothermal crystallization seems to exclude incorporation of energetically unfavorable heteroatoms. Experimental results have shown that it was not possible to grow nanorods when dopant species such as Ti (TiCl$_3$, TiCl$_4$, TiOCl$_2$, Ti-Acetyl-peroxo complex), Al (AlCl$_3$, Al(NO$_3$)$_3$), W (W-peroxo), Ni (NiCl$_3$, Ni(NO$_3$)$_3$) amongst other dopants where used. We believe that the hydrolysis reaction of the iron to the polycation Fe$_{24}$(OH)$_{17}$ which is stabilized by chloride ions in the inner cage, is destabilized by the different cations in solution and the B-FeOOH which is the precursor of the hematite nanorods, does not form.

We changed approaches and explored post synthesis doping by addition of gas phase reactants or surface diffusion of dopants.

The doping of nanorods by titanium is shown in figure T2-2. The synthesis methodology consisted of the growth of $\beta$-FeOOH nanorods followed by reduction at 350°C in 10% H$_2$/N$_2$. After the reduction process metallic iron nanorods were obtained. Onto the metallic iron titanium metal was added by physical vapor deposition (sputtered or E-beam evaporation) with different thicknesses of titanium metal (~5-20 nm thickness, which corresponds to about ~1 nm thick overlayer). Diffusion of the titanium into the iron was achieved by annealing at 600-700°C for 24 hours in an N$_2$ atmosphere followed by calcination in air to yield doped Fe$_2$O$_3$ nanorods (image not shown). We demonstrated the presence of Ti in the iron by X-ray spectroscopy. Having succeeded (finally) in doping the nanorods, the PEC performance was measured. Figure T2-2 shows that, unfortunately, there was no improvement in the doped rods. We succeeded in doping the nanorods with several of the cations shown in thin films to produce higher efficiency materials, unfortunately, in the nanorods no significant improvement was observed. We suspect the same surface recombination processes that decreased the performance of the smaller rods (Aim 1) are responsible for the negative results observed in the doped rods.

The optimization of the thickness of iron oxide films and nanostructures was also performed with the aims of finding the best growth conditions for nanorods to be used as is or be further processed to developed doped materials. The performance of select iron oxide nanorods is shown in Figure T2-1. From this figure we can see that the highest performance is achieved for the samples grown for 8 to 12 hr and this represent ~10 fold improvement from the samples grown for 23 hr. The zero bias and biased photocurrents show that the growth conditions necessary to achieve maximum performance are slightly different. Thicker films perform better at an applied potential, thinner films at lower applied potential. This is explained as follows; thicker films absorb more photons and generate more carriers. In an unbiased state, the carriers can’t make it to the back contact to be collected, in a biased state, more carriers are forced to the contact and are collected.

Unfortunately the results from this task were discouraging and emphasis was shifted towards the more promising results from the doped thin films (below).
Task 3: Morphological and photo-electrochemical characterization

The morphological and photo-electrochemical characterization of samples has been developed during the entirety of the program without any delay or major detour from the original plan. During this project improvements to our combinatorial screening system were made which increase the screening yield by 20% and simplified the overall characterization process. A combined DOE H2 program was developed to provide a collaboration on photoelectrochemical characterization techniques (May 2008) and generate a separate report in which best practices are outlined for the testing of photocatalyst for hydrogen production. The task force meets every week and a major report of this work will be published shortly (Q3-Q4 2009).

Task 4: Deposition of nanoparticle catalysts on Fe2O3 substrates

Critical to the efficiency of a PEC material system is the reduction in the overpotential for the Oxygen Evolution Reaction (OER). The OER hinders the photoelectrochemical performance of the Iron Oxide Nanorods and thin films. OER catalysts such as RuO2 have shown promise in increasing the performance for PEC, however the deposition methods typically used provide RuO2 particles that are not consistent with the nanorod or nanoparticle length scales. The methodology used to improve the kinetics of the OER on hematite has been divided into 3 different approaches which are shown below: 1) metal oxide (RuO2) nanoparticle catalysts are deposited onto hematite nanorods, 2) Pt and Au are deposited onto electrodeposited Fe2O3, and 3) a series of NiFe electrocatalysts and RuO2 are deposited on both FTO and Fe2O3 to compare the OER activities and separate electrocatalytic effects from photoelectrocatalytic effects. Independent of the method used for the deposition of the electrocatalyst and the type of electrocatalyst used the hypothesis of using noble metals or known OER electrocatalyst for the improvement of the photoelectrochemical performance by facilitating the oxygen evolution reaction kinetics and therefore increasing the reaction rate should decrease the electron-hole recombination rate and improve the overall performance.

Two methods were investigated to deposit RuO2. The first method consists on the electrodeposition of RuO2 particles, while the second method is based on the formation of RuO2 nanoparticles by decomposition of RuO4. Figure T4-1 shows the SEM of the Nanorods before and after electrochemical deposition of RuO2, in this case the deposition conditions need to be optimized such that a smaller coverage of RuO2 is obtained. Figure T4-2 shows the TEM image of α-Fe2O3 nanorods with RuO2 nanoparticles, in this case the loading of RuO2 is very low and further research will be conducted to increase the loading of RuO2 such that the PEC performance is improved.

Loading of noble metal electrocatalysts on the surface of doped iron oxides has also been used to improve the PEC performance at a lower applied bias of hematite. It is generally accepted that the kinetics of oxygen evolution are slow for iron oxide even though the band position of iron oxide is suitable for O2 evolution from water. To overcome this problem, electrocatalyst, which can decrease the overpotential for O2 evolution in aqueous solution, are
deposited on the iron oxide. Here Pt/Au nanoparticles were loaded on iron oxide films by the electrodeposition synthetic approach. Several parameters such as voltage, time, solution concentration, are being explored such that we can control the nanoparticles deposition on iron oxide thin films. In the case of Pt nanoparticles loading samples, uniform and well-dispersed nanoparticles with the size of about 10 nm can be achieved (see Figure T4-3c). For the Au nanoparticles loading samples, the smallest particle size of about 15 nm can be obtained (see Figure T4-4b). We tested the PEC performance of Pt-loaded Ti-doped iron oxide samples. The results are presented in Figures T4-5 and T4-6. It can be seen from IV curves (Figure T4-5) that the response photocurrent was improved about 2 times at low bias for the Pt-loaded samples compared with unloaded samples. There is almost no improvement at high bias. This can be understandable by the fact that the overpotential for O₂ evolution in aqueous solution is remarkably decreased by loading the electrocatalysts.

The third exploration focused on NiFe mixed metal oxides which were compared to more expensive RuO₂ and Ni binary oxides/hydroxides such as NiMn, NiCo, and NiCu. Figure T4-7 shows cyclic voltamograms in a N₂ degassed 1M NaOH electrolyte. From this graph it is seen that the addition of RuO₂ or NiCo greatly decreases the overpotential required for oxygen evolution from 670 mV for the bare Fe₂O₃ to 505mV for the electrode with the electrocatalyst. The enhancement in performance by both NiCo and NiFe is shown in Figure T4-8, from this figure we can observe that NiCo shows -0.45 V of onset potential while the FeNi shows -0.30 V and the reference 6% Ti-doped sample -0.11 V. From this graph it can also be observe that NiFe sample has an improved enhancement of photocurrent at low and high applied bias. The zero bias photocurrent is shown in Figure T4-9. An approximately 7 fold improvement in photocurrent was observed due to the addition on the NiFe electrocatalyst as compared to the reference sample. We can also observe that there is a functional relationship between the amount of electrocatalyst deposited and the performance of the sample, which is dependant on the aborption of light by the electrocatalyst as well as the size of the electrocatalys on the surface of the hematite. Different synthesis methods of the NiFe electrocatalyst where tested by electrodepositing the electrocatalyst with different precursors. Very different properties where observed for the electrocatalyst deposited, if was founs that the electrocatalyst deposited with Ni(II)Fe(II) had the highest OER activity which was very similar to those deposited with just Ni(II) (see figure T4-10); however the photoelectrochemical performance of the electrocatalyst-photocatalyst system showed that the Ni(II)Fe(III) and the control sample had the highest performance and that the electrocatalyst with NI(II)Fe(II) and NI(II) had a decrease of the photocurrent (data not shown).

The results from this task have been extremely encouraging, and is being continued under the DOE H₂ contact DE-FG36-05GO15040 due to its promise and possible impact on PEC material system development. This task has been completed as expected and it is believed that the results that have been achieved are of great scientific importance since to our knowledge this is the first report in which NiFe electrocatalyst which are much more economical than RuO₂ have shown its applicability for improved OER on hematite photoelectrodes. It is expected that the results developed in this task will be of general interest to the scientific community.
Task 5: Efficiency of Hydrogen Production From Organic Substrate Oxidation

Our investigations of cost-effective solar hydrogen production suggest that the need for separation of hydrogen and oxygen significantly increases the system cost and the OER further limits the PEC efficiency. Widely available low cost (or negative value) organic substrates including wastewater and biomass analogs have been studied as oxidants for PEC applications. The organic decomposition of substrates is of importance because (1) if the OER catalysis reaction is hindering and a facile oxidant molecule can be found; photocatalyst can be tested in the limit of no OER limitation which could give the upper bound efficiency. (2) Photocatalysis could be used to decompose waste water streams which have a negative value and at the same time increase the overall performance of the system towards H₂ production.

The working hypothesis for this task is that the Oxygen evolution reaction is the rate limiting step in the photocatalytic process due to the higher overpotential required to produce oxygen from water. Electrocatalysts such as RuO₂ which are expensive where also simultaneously being tested to improve the OER reaction (Task 4); however if a facile oxidant can be found, photocatalyst synthesized can be tested in the limit of no overpotential limitation and then the upper bound efficiency of the materials can be reported. Furthermore decoupling the use of electrocatalyst and OER limitation is of great importance because it gives information about the charge generation/charge separation on a photocatalyst with taking in account the overall kinetic rates.

The methodology consisted of screening variety of different biomass analogs in basic media (NaOH). The results were encouraging and it was found that glucose and glycerol can be readily oxidized. Gas chromatography (data not shown) showed that H₂ was produced during the photocatalytic process where the biomass analogs where being oxidized. Figure T5-1 shows the photocurrent of a iron oxide sample as a function of the concentration of glucose in solution at different applied potentials, from this figure we can see that the performance is improved ~3 times when using glucose as compared to NaOH. Figure T5-2 shows the improvement of different biomass analogues, and glycerol is seen to give a 5 fold improvement in performance over NaOH.

Delays in accomplishing this task resulted from redirection of manpower on higher priority areas (Task 6, Task 1, Task 2) where greater hurdles needed attention. Nonetheless, the initial results were very encouraging and further progress is being made under continuing support from DOE award DE-FG36-05GO15040. It is estimated that this task was completed to 60% as reported in FY2008-Q4.

Task 6 Electrochemical deposition of Iron Oxide

Electrodeposition techniques have many advantages over alternative synthesis methods: electrical contact assured, controlled microstructure, dopants readily added, large-scale synthesis commercially practiced, relatively simple process, and cost effective. The electrodeposition solution contains aqueous FeCl₃ stabilized in peroxide. Figure T6-1 shows the principle of the electrodeposition of iron oxide thin films in the presence of H₂O₂ in the electrolyte solution.
During the reduction process, H$_2$O$_2$ is reduced to OH$^-$, then the local pH in the vicinity of working electrode surface increases, leading to depositing iron hydroxides. The other function of H$_2$O$_2$ is to stabilize some doped transition metal precursors in aqueous solution. Figure T6-2 shows the photographs of the deposited films before and after heat-treatment. A yellow/red deposited film is observed before and after heat-treatment. According to Raman spectroscopy, $\alpha$-FeOOH and $\alpha$-Fe$_2$O$_3$ are the corresponding species respectively (Figure T6-3). The temperature of the heat-treatment has a significant effect on the structure and PEC performance of iron oxide thin films.

In order to improve the poor charge transport properties of $\alpha$-Fe$_2$O$_3$, most work has been focusing on doping the iron oxide with heteroatoms as a means of improving performance. We used co-electrodeposition method for the first time to synthesize a serial of doped iron oxide samples. Their PEC performance is presented in Figure T6-4. It can be seen that some dopants such as Pt, Ti, Cr, Mo, etc. exhibit promising PEC performance. In the case of Cr-doping, in contrast to previous report, it is one of the most effective dopant for enhancing the PEC performance after Pt (which is currently being investigated as part of our DOE project proposal). The films deposited without dopant (Figure T6-5a) had the smallest particle size (less sintered after calcination) while at 5 % (Figure T6-5b) and the particles are much bigger and at 10 % Cr the particles are highly sintered (Figure T6-5b c); in the case of Mo the particle sintering is less pronounced at 2 % and 5 % (Figure T6-5b, d and e) but is quite high at 15 % Mo (Figure T6-5b f).

The X-ray diffraction (XRD) patterns of the electrodeposited samples on FTO are shown in Figure T6-6. The XRD data is normalized with respect to the peak of 37.68 corresponding to cassiterite Reference pattern JCPDS 21-1250, while the hematite ($\alpha$-Fe$_2$O$_3$, space group: R3c(167), a=0.5035, b=0.5035, c=1.3748 nm) reference pattern used to index the peaks is JCPDS 33-0664. Figure T6-6a shows the XRD pattern of the undoped and Cr doped samples. In this figure it can be seen that the crystalinity of the undoped is much higher than that of sample at 10%Cr, at 20% doping the crystalinity of the sample was further decreased, no other phases were detected from XRD. The XRD pattern of the samples differs from that of the reference pattern in the intensity of the peaks, the main peak for all samples is the (104), but all electrodeposited samples have a higher intensity for the (012), (104) and (110) than that of the reference pattern. This would suggest that the film grows with no specific orientation and that as we increase the % of dopant in the electrolyte the electrodeposited films become less crystalline.

X-Ray photoelectron spectroscopy (XPS) was utilized for compositional analysis to characterize the Fe, Cr and Mo valance state of the electrodeposited films (data not shown). The Fe$_{2p}$ spectra of all the samples is very similar and is attributed to Fe$^{3+}$, as proposed by Grosvenor et al. The 2 % Cr doped sample only shows Cr$^{4+}$, while the 5% sample shows both Cr$^{4+}$ and Cr$^{3+}$ and the samples with 10 % and 20 % of Cr show Cr$^{6+}$, Cr$^{4+}$ and Cr$^{3+}$ (data not shown). In the case of the Mo doped samples all of the molybdenum corresponded to that of Mo$^{6+}$ in all of the samples. Etching studies to characterize the doping profile of the sample are underway and will be reported next quarter.

The photoelectrochemical performance of the samples was characterized by cyclic voltammetry for the undoped and doped Fe$_2$O$_3$ samples. From Figure T6-7 it can be observed that the photocurrent for the undoped sample at 0 V vs Ag/AgCl is higher than that of the doped
samples, however the photocurrent at this applied potential is very low. At an applied potential of 0.2 V vs Ag/AgCl the photocurrent of the 5 % Cr doped samples is almost doubled with respect to the undoped sample, and the 10 % Cr doped samples is ~0.6 times that of the undoped sample. Doping concentration higher than 5 % showed a negative effect of the photoelectrochemical performance of the samples.

In the case of the samples doped with molybdenum (Figure T6-7b) the photocurrent at an applied bias of 0V vs Ag/AgCl shows an improvement with % of Mo in the sample increasing up ~1.4 times for the 2 % and 10 % and ~1.5 times for the 15 % Mo. At an applied potential of 0.2V vs Ag/AgCl the photocurrent increases 2 times for the 2 % Mo doping and ~3 times for the 10% and 15 % Mo doping.

During this task no insurmountable problems where encountered and the proposed methodology was executed as proposed, the task progress was scheduled and executed as planned without delays. *This is the first report of electrochemical doping of iron oxide and two publications have been accepted for publication based on this work.* Further work is being performed under a different DOE contract. Further, important collaborations have been started in which theoretical and experimental work is being compared to further understand and guide experiment with aims of improving the performance of iron oxide to achieve the 2015 DOE targets.
**Actual accomplishments of goals and objectives of your task**

The table below summarizes the 6 tasks of the subcontract #RF-07-SHGR-011 with UNLV described above and their status.

### UNLV Task Schedule

<table>
<thead>
<tr>
<th>Task Number</th>
<th>Project Milestones</th>
<th>Task Completion Date</th>
<th>Progress Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Original Planned</td>
<td>Revised Planned</td>
</tr>
<tr>
<td>1.2.3</td>
<td>Reduce Fe$_2$O$_3$ Nanorod diameter</td>
<td>10/01/07</td>
<td>5/01/08</td>
</tr>
<tr>
<td>1.2.3</td>
<td>Synthesis of doped Fe$_2$O$_3$ nanorods</td>
<td>12/01/07</td>
<td>7/01/08</td>
</tr>
<tr>
<td>1.3.1</td>
<td>Morphological and photo-electrochemical characterization</td>
<td>10/01/07</td>
<td>10/01/08</td>
</tr>
<tr>
<td>2.3</td>
<td>Deposition of nanoparticle catalysts on Fe$_2$O$_3$ nanorods</td>
<td>08/01/07</td>
<td>08/01/08</td>
</tr>
<tr>
<td>5.1</td>
<td>Efficiency of Hydrogen Production From Organic Substrate Oxidation</td>
<td>07/01/07</td>
<td>08/01/08</td>
</tr>
<tr>
<td>6</td>
<td>Electrochemical deposition of Iron Oxide</td>
<td>12/01/07</td>
<td>07/01/08</td>
</tr>
</tbody>
</table>
Publications and Presentations:

During funding of this subcontract the next publications where published:


Presentations


2. MRS March 24-28th 2008 LL7.5. “Multi-Component Nanostructured Semiconductors for Photoelectrocatalysis - Progress Towards Efficient and Stable Solar-to-Chemical Energy Conversion”

Collaborations:

During this project the several collaboration have been started which are stated below:

- Standard DOE H$_2$- Photoelectrochemical testing group discussion
- Yanfa Yan, NREL (Theoretical Calculations)
- Eric Miller, University of Hawaii (Electrocatalysts for WO3)
- Clemens Heske, UNLV (Characterization of Fe2O3)
- Tom Jaramillo, Stanford (round-robin testing)
- M. Gräztel, Ecole polytechnique fédérale de Lausanne (Fe2O3)
References

(7) Grosvenor, A. P.; Kobe, B. A.; Biesinger, M. C.; McIntyre, N. S. Surface and Interface Analysis 2004, 36, 1564-1574.
Figures.

Task 1.

<table>
<thead>
<tr>
<th>hkl</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(101)</td>
<td>23</td>
<td>18</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(104)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(110)</td>
<td>51</td>
<td>28</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>(113)</td>
<td>21</td>
<td>16</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(024)</td>
<td>21</td>
<td>18</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(300)</td>
<td>27</td>
<td>21</td>
<td>36</td>
<td>43</td>
</tr>
</tbody>
</table>

Figure T1-1 (a). XRD of two different nanorod samples. Sample S1 has a higher intensity for the (110) plane. (b) Table showing 4 samples in which the electrolyte concentration was varied, sample S1 shows the highest peak intensity for the (110) plane while S3 and S4 show the lowest intensity for the peak.

Figure T1-2. Scanning electron micrographs of different growth conditions of Nanorods, the bottom shows the average diameter of the Nanorods.

1) 35 ± 3 nm  2) 21 ± 2 nm  3) 20 ± 3 nm  4) 12 ± 3 nm

Figure T1-3. Transmission electron microscopy of α-Fe₂O₃ nanorods. A) Low magnification TEM. B) High magnification of nanorods. C) TEM showing a top view of α-Fe₂O₃ nanotubes in which the hollow nanotube is shown. D) TEM of a nanorod.
Figure T1-4. UV-VIS absorption of the nanorod samples.
Task 2.

Figure T2-1. Growth time of iron oxide nanorods vs. zero bias photocurrent and photocurrent at 0.4 V vs. Ag/AgCl.

Figure T2-2. Photoelectrochemical performance of control nanorods sample, and Ti-doped samples by Ti sputtering on the surface of iron nanorods followed by surface diffusion and calcination to obtained a Ti-doped nanorods.
Figure T4-1. $\alpha$-Fe$_2$O$_3$ nanorods before (A) and after RuO$_2$ deposition (B)

Figure T4-2. TEM of $\alpha$-Fe$_2$O$_3$ nanorods with RuO$_2$ nanoparticles (nanoparticles are surrounded by a red Circle to signal how should they look like)
Figure T4-3. SEM images of Pt nanoparticles on Ti-doped iron oxides prepared by Electrodeposition under different electrochemical conditions.
Figure T4-4. SEM images of Au nanoparticles on Ti-doped iron oxides prepared by Electrodeposition under different electrochemical conditions.

Figure T4-5. IV curves of Ti-doped iron oxides before and after Pt nanoparticles deposition.
Figure T4-6. Chopped IV curves of Ti-doped iron oxides before and after Pt nanoparticle deposition.

Figure T4-7. Cyclic voltamograms for different substrates with and without electrocatalyst in degassed 1M NaOH.
Figure T4-8. Cyclic voltamograms for 6% Ti Fe₂O₃ prepared by electrochemical methods with and without electrocatalyst in degassed 1M NaOH.

Figure T4-9. 2-electrode Zero bias PEC performance of 6% Ti Fe₂O₃ with and without NiFe electrocatalyst with different electrodeposition times (changes in electrocatalyst loading) under 1M N₂ degassed NaOH. Note NiFe in this case refers to Ni(II)Fe(III)

Figure T4-10. Cyclic Voltamograms in N₂ degassed 1M NaOH in the dark, showing (a) control sample, (b) Ni(II)Fe(III), (c) Ni(II)Fe(II) and (d) Ni(II)
Task 5.

Figure T5-1. Photocurrent as a function of Glucose concentration at different applied bias for a iron oxide electrode.

Figure T5-2. Photocurrent as a function of biomass analogue concentration at 0.3V vs Ag/AgCl bias for a iron oxide electrode
Task 6.

Figure T6-1. Schematic diagram of the setup used for electrodeposition.

Figure T6-2. Photograph of a) electrodeposited film before calcination and b) after calcination.

Figure T6-3. Raman spectroscopy of iron based film before and after calcination.
Figure T6-4. The photocurrent versus different dopants at different applied bias.

Figure T6-5. SEM of electrodeposited samples (a) undoped sample, (b) 5 % Cr in solution (c) 10 % Cr in solution (d) 2 % Mo in Solution (e) 5 % Mo in Solution (f) 10 % Mo in Solution
Figure T6-6. XRD of Samples  
(a) Cr doped samples  
(b) Mo doped samples

Figure T6-7. IV Curves of (a) Cr doping  
(b) Mo Doping
ATTACHMENT C

University of Hawaii

Photoelectrochemical Hydrogen Production

(13 Pages)
Photoelectrochemical Hydrogen Production: UNLV-SHGR at UH Program Subtask Final Report

Robert Perret
The University of Nevada, Las Vegas (UNLV) Research Foundation
4550 Maryland Parkway, Box 452036
Las Vegas, NV 89154-2036
Phone: (702) 630-1542; Fax: (702) 413-0094
E-mail: ntsllc@rperret.com

Eric L. Miller (primary contact)
University of Hawaii at Manoa (UH)
1680 East-West Road, Post 109
Honolulu, HI 96822
Phone: (808) 956-5337; Fax: (808) 956-2336
E-mail: ericm@hawaii.edu

DOE Technology Development Manager: Roxanne Garland
Phone: (202) 586-7260; Fax: (202) 586-9811
E-mail: Roxanne.Garland@ee.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956; Fax: (303) 275-4788
E-mail: David.Peterson@go.doe.gov

Contract Number: DE-FG36-03GO13062

Subcontractors:
University of Hawaii at Manoa, Honolulu, Hawaii (UH)
MVSSystems Inc., Golden, Colorado
Intematix Corp., Fremont, California
National Renewable Energy Laboratory (NREL- integrated through cooperative agreement)

Project Start Date: January 1, 2005

Project End Date: December 31, 2007 (no-cost extension through August 31, 2008)
Objectives

- Identify and develop new Photoelectrochemical (PEC) film materials compatible with high-efficiency, low-cost hydrogen production devices: Target: 1.6 mA/cm²–6.5 mA/cm² AM 1.5 photocurrent
- Demonstrate functional multi-junction device incorporating best-available PEC film materials: Target: 2–8 % STH efficiency under AM 1.5 illumination
- Develop avenues, integrating new theoretical, synthesis and analytical techniques, for optimizing future PEC materials and devices
- Explore avenues toward manufacture scaled devices and systems

Technical Barriers

This project addresses the following technical barriers from the “Photoelectrochemical Hydrogen Production” section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AA) PEC Device and System Auxiliary Material
- (AB) Bulk Materials Synthesis
- (AC) Device Configuration Designs

Technical Targets

As recognized within the PEC Hydrogen research community and the DOE PEC Hydrogen program, the technology is still far from maturity, and the most critical technical issues relate to the development of suitable photoactive semiconductors for water-splitting. Of the four DOE technical characteristics outlined in the Multi-Year RD&D Plan for PEC hydrogen production (see Table 1), targets in the first category (“useable semiconductor band gap”) are the primary focus of this program’s research, with secondary emphasis on the second category targets (“chemical conversion process efficiency”). To address the technical barriers for meeting the DOE targets, the project team has utilized its collective expertise in theoretical materials modeling, materials synthesis, and characterization to study a diverse portfolio of promising PEC thin-film materials classes.

Table 1. DOE Targets for Photoelectrochemical Hydrogen Production

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2006 Status</th>
<th>2013 Target</th>
<th>2018 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Useable semiconductor band gap</td>
<td>eV</td>
<td>2.8</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Chemical conversion process efficiency (EC)</td>
<td>%</td>
<td>4</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Plant solar-to-hydrogen efficiency (STH)</td>
<td>%</td>
<td>N/A</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>plant durability</td>
<td>hrs</td>
<td>N/A</td>
<td>1000</td>
<td>5000</td>
</tr>
</tbody>
</table>

As described in following sections, an important milestone achieved through this project has been the demonstration of 2.6eV useable band gap in tungsten-based films compatible with integration into multi-junction devices with 3-4% chemical conversion efficiency. Even lower band gaps have been demonstrated in silicon-carbide (2.1eV) and copper-chalcopryte (1.6eV) materials, but work is ongoing to render these band gaps “useable” for PEC hydrogen production.
Accomplishments

• Successful Development and Application of New PEC “Tool-Chest” Capabilities
  o Successfully worked with an integrated DOE-PEC Working Group in advancing the use of materials theory, synthesis and characterizations to facilitate the materials discovery and development process for improved PEC devices
  o Versatile modeling, synthesis and characterization tools developed with the DOE-PEC Working Group
  o Comprehensive testing protocols being established by the DOE-PEC Working Group

• Significant Advances in Focus Materials Classes Using the New PEC “Tool-Chest”
  o Further optimization of WO3 films using Wo:Mo-Ox bi-layer approach
  o Demonstration of high levels of stable PEC photocurrents through the modification and optimization of copper-chalcopyrite alloy film
  o Demonstration of enhanced stability in highly-photoactive amorphous silicon carbide films

• Key Milestones Met in Focus Materials Experiments:
  o Photocurrents in excess of 3.5 mA/cm² in tungsten-based bi-layer films
  o Photocurrents in excess of 8 mA/cm² and 18 mA/cm² in Si- and chalcopyrite-based films, respectively (with additional bias constraints to be corrected in band edge alignment modifications)
  o STH Device efficiencies in excess of 3% in WO3-based multi-junction structures under 1 sun

• Further Expansion of Collaborative Research Efforts
  o Continued expansion work with the DOE-PEC Working Group
  o Development of a new International-Energy-Agency (Hydrogen-Implementing-Agreement) Annex on PEC Materials for Hydrogen Production to expand the DOE Working Group efforts on an international scale

• Avenues Developed for Continued Research Funding
  o DOE-funded PEC project at MVSystems Incorporated initiated to continue R&D work on tungsten-oxide, copper-chalcopyrite, and amorphous silicon-carbide based thin-film compounds for PEC hydrogen production

Introduction

The primary objective of this project has been the research and development of semiconductor materials for stable and efficient photoelectrochemical (PEC) hydrogen-production systems. The candidate materials have to be functional (1) as a photoactive layer, absorbing a significant fraction of the incident light; (2) as photoelectrochemical junction with the electrolyte; and (3) as a facilitator of the gas evolution reaction (either hydrogen or oxygen, depending on the n- or p-type nature of the semiconductor, in conjunction with the specific integrated device configuration). The requirements on the material include adequate light absorption over the solar spectrum, high carrier collection efficiency, stability in suitable aqueous electrolytes, and favorable kinetics for the electrode reaction. As candidate materials with suitable properties emerge, additional requirements for the photoelectrode semiconductor device integration become increasingly important, such as process compatibility of the complete multi-junctions devices, as well as long durability and low material cost. Throughout its duration, this project has continually made important progress in the discovery and development of promising PEC thin-film materials classes through the expanded collaborative efforts with the DOE-PEC Working Group, a group offering a broad palate of state-of-the-art theoretical and experimental tools and techniques.
Approach

The general approach of this collaborative effort between the UNLV-SHGR and the DOE PEC Working Group researchers is to integrate state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability and cost. From the application of density-functional theory to calculate band-structures and effects of co-incorporants on valence and conduction band positions; through the use of diverse synthesis techniques, including combinatorial methods, to create tailored materials; and by employment of microstructural, electron spectroscopic, and electrochemical characterization techniques, a comprehensive picture of the materials properties and resulting performance is being developed. Within the UH part of the UNLV-SHGR project, the approach has been applied to three classes of “focus materials” deemed of particular interest for PEC applications. These “focus materials” classes under current investigation include tungsten-based films, copper chalcopyrite-based films, and silicon-carbide-based films.

Results

During the course of this project, extensive studies of the three materials classes under investigation have focused on understanding and improving photovoltaic behavior, specifically by applying our theoretical, synthesis and analytical techniques in identifying relevant aspects of structural, optoelectronic and electrochemical properties. Specific progress in the development of each of the focus materials is detailed in the following subsections.

Tungsten-based films

With an optical band gap of approx. 2.6 eV, tungsten oxide has been selected as a promising candidate for water splitting. For several years now, researches have been conducted at the University of Hawai‘i on this material to develop a low-cost deposition process to fabricate photoactive WO$_3$ films. Progress on deposition parameters, such as temperature and pressure, were done and a saturated photocurrent (measured under simulated AM1.5G illumination in 0.33M H$_3$PO$_4$ electrolyte) of about 3 mA/cm$^2$ was obtained (see Fig. 1a). Mounted over a Si-based PV cell in a so-called mechanical stack (both PEC and PV devices shorted with WO$_3$ PEC electrodes sitting over the PV cell), a solar-to-hydrogen efficiency of 3.1% was demonstrated with these WO$_3$ PEC electrodes (Fig. 1b). However, the DOE target of 12% STH efficiency cannot be achieved with pure WO$_3$ due to its relatively “high” band gap that limits the use of the solar spectrum. To overcome this issue, several experiments were conducted to reduce band gap of the WO$_3$ by incorporating impurities in the material matrix, such as nitrogen. Despite a net band gap reduction of 0.5 eV after N incorporation, a drastic reduction of the maximum photocurrent to approx. 0.6 mA/cm$^2$ was observed, mainly due to lattice distortion and defects creation that trap photogenerated carriers. This indicates that a performance enhancement of tungsten-oxide-based PEC electrodes cannot be easily obtained by “impurity” incorporation solely focusing on reducing the band gap. Recent work has shown however than higher performance can be obtained with the use of bilayer PEC electrodes, where a bottom relatively thick film is used for light absorption and a thin top layer to modify the chemical and electronic surface properties. In the case of Mo-based bilayer WO$_3$ PEC electrodes, where Mo is incorporated only in the near-surface of WO$_3$, approx. 300 nm), a 20% increase of saturation photocurrent ($I_{\text{photo.sat}}=3.6$ mA/cm$^2$) was observed compared to pure WO$_3$-based champion devices ($I_{\text{photo.sat}}=3$ mA/cm$^2$), as presented in Fig. 1a. Experimentally derived band structures of such a bilayer surface versus a pure WO$_3$ surface are shown in Fig. 2. Future research will be focused on further understanding and improvement of bilayer devices, as well as RuO$_2$ nanoparticle deposition to enhance holes transfer in electrolyte.
Copper Chalcopyrite Films

Research at the university of Hawai’i on copper chalcopyrite (copper alloyed with combinations of indium, gallium and selenium) –based PEC electrodes benefits from decades of studies made for this material in the PV filed. One main advantage of this material class is the possibility to tune the band gap by changing the film stoichiometry (from 1.0 eV with CuInSe2 to 2.43 eV with CuGaS2). This makes copper chalcopyrite an ideal candidate for solar-powered water splitting, where current research in PEC aims to find a low-cost and corrosive resistant material with a 2.0 eV band gap. Recent improvements with CuGaSe2 materials have been obtained by varying deposition parameters such as temperature, as illustrated in Fig. 3. With a decrease from 530ºC to 480ºC, a saturation photocurrent increase from 12 to 20 mA/cm² (measured under simulated AM1.5G illumination in 0.5M H2SO4 electrolyte) was observed. Research has been also pursued on sulfur incorporation to increase the material band gap. In addition, it has been demonstrated that the inclusion of sulfur into copper-chalcopyrite material leads to a more favorable band edge alignment with respect to the water-splitting redox reactions. Preliminary results test were conducted on CuInSeS thin-film electrode provided by the Hahn Meitner Institute in Berlin. As presented in Fig. 4, this material shows a more favorable onset potential (validating the theoretical prediction that sulfur incorporation can provide better band edge alignment) but a lower saturation photocurrent and a poor “fill factor” (which correspond to the squareness of the J-V characteristic) when compared to CuInGaSe2. Additional studies on process deposition will be required to optimize this material.

Amorphous silicon carbide-based films

Research conducted at the University of Hawai’i on MVSystem’s a-SiC films were mainly dedicated to surface modification. One example is the use of HF (24%) solution to etch the SiOx native oxide layer grown on top of the a-SiC films. As presented in Fig. 5, the saturation photocurrent increases from -8.5 mA/cm² to -10mA/cm² after a 15 second HF etch (measured under simulated AM1.5G illumination in pH2 buffer solution). In addition, one can note also that the fill factor is improved after HF treatment. More noticeable is the onset potential reduction (toward 0V vs. SCE) after this treatment, indicating that the “naturally” grown SiOx thin layer shifts the band-edges. This finding indicates again that great attention should be paid to surface chemistry and energetic to ensure high performance PEC electrode. Surface passivation is currently being investigated by MVSystems to improve and stabilize PEC performance. Encouraging stability improvements have been realized, as illustrated in Fig. 6. Current research at the university of Hawai’i include the evaluation of palladium and nickel/ion nanoparticles deposition on a-SiC films to enhance surface catalytic activities.

Conclusions and Future Directions

This project’s approach of integrating state-of-the-art theoretical, synthesis and analytical techniques has proved to be invaluable in the identification and development of the most promising materials for practical PEC hydrogen production. Significant progress has been made during the course of the program on several fronts:

- Collaborative Approach has been Successful:
  - The SHGR team, working closely with the DOE PEC Working Group, has developed an extensive “Tool Chest” of theoretical, synthesis and
characterization techniques and successfully applied it in the R&D of important focus PEC materials systems

• Major Technical Targets Met in Focus Materials Research:
  o Photocurrent target (>1.6mA/cm²) met in several films:
    ▪ 3.5 mA/cm² demonstrated in low temperature WO₃ films
    ▪ >9.0 mA/cm² demonstrated in amorphous silicon carbide
    ▪ >18 mA/cm² demonstrated in copper chalcopyrite films
  o Conversion efficiency target (2-8% STH) met in multi-junction devices:
    ▪ 3.1% STH efficiency demonstrated using 2006 WO₃
    ▪ 4% STH efficiency expected using recent bi-layer WO₃
  o Stability target (100 hour durability) met:
    ▪ >100 hour stable operation demonstrated using WO₃

Continued development along this pathway is expected to greatly facilitate the discovery and optimization of material systems and device configurations capable of meeting the DOE PEC production targets.

Specific future directions for the work initiated in this program include:

• Continue Current PEC R&D and Optimization Efforts Under New Funding Umbrellas
  o Focus material R&D: tungsten-, silicon-, and chalcopyrite-compounds
  o Accelerate interface, device and system development work
• Continue DOE PEC Working Group Efforts
  o Further PEC “Tool-Chest” development efforts
  o Standardization of materials and device testing protocols
  o Refinement of materials selection and prioritization criteria
• Expansion of Collaboration Efforts: Nationally and Internationally
  o DOE PEC Working Group Expansion
  o USA-led “International Energy Agency PEC Annex-26” offshoot of SHGR work
  o “International Partnership for a Hydrogen Economy” program proposal

The ultimate aim is to make the materials & device breakthroughs necessary for high-efficiency, low-cost PEC hydrogen production.

Special Recognitions & Awards/Patents Issued

2. 2008 DOE Hydrogen Program R&D Award: E. Miller
3. IEA-HIA PEC Annex-26 Operating Agent Appointment: E. Miller

Publications/Presentations


E. L. Miller, “Photoelectrochemical Hydrogen Production”, presented at 2007 IMRC (Cancun, Mexico, August 2007).


**Acronyms**

- **a-Si** Amorphous Silicon
- **a-SiC** Amorphous Silicon Carbide
- **CGSe2** Copper Gallium Diselenide
- **CIGSe2** Copper Indium Gallium Diselenide
- **DOE** Department of Energy
- **IEA-HIA** International Energy Agency Hydrogen Implementing Agreement
- **LSV** Linear Sweep Voltammetry
- **NREL** National Renewable Energy Laboratory
- **PEC** Photoelectrochemical
- **PECVD** Plasma Enhanced Chemical Vapor Deposition
- **PV** Photovoltaic
- **SHGR** Solar Hydrogen Generation Research
- **STH** Solar-to-Hydrogen (conversion efficiency)
- **UNLV** University of Nevada, Las Vegas
- **UH** University of Hawaii at Manoa
$\text{WO}_3$  Tungsten Trioxide
### Task Schedule

<table>
<thead>
<tr>
<th>Task Number</th>
<th>Project Milestones</th>
<th>Task Completion Date</th>
<th>Progress Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Original Planned</td>
<td>Revised Planned</td>
</tr>
<tr>
<td>1</td>
<td>PEC Materials R&amp;D</td>
<td>12/31/07</td>
<td>10/31/08</td>
</tr>
<tr>
<td></td>
<td>milestones</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>WO₃: 3.7mA/cm²</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>photocurrent at 1.6V&lt;sub&gt;SCE&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(O₂ reaction)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CGS: 22.8mA/cm²</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>photocurrent at -0.9V&lt;sub&gt;SCE&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(H₂ reaction)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A-Si:C: 9 mA/cm²</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>photocurrent at -1.5V&lt;sub&gt;SCE&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(H₂ reaction)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Combinatorial library for molybdenum doped WO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>with and without sulfurization initiated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Multi-junction Auxiliary Materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>milestones</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Single junction a-Si PV cells demonstrating Voc close to 1V on stainless-steel substrates</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Initial demonstration of micro-morph PV cells on stainless-steel substrates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>System Engineering</td>
<td>12/31/07</td>
<td>10/31/08</td>
</tr>
<tr>
<td></td>
<td>milestones</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>WO₃/tandem-a-Si hybrid photoelectrode stacked device continues to perform at 3.3% STH without degradation.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Project Spending

<table>
<thead>
<tr>
<th>Quarter</th>
<th>From</th>
<th>To</th>
<th>Estimated Federal Share of Outlays*</th>
<th>Actual Federal Share of Outlays</th>
<th>Estimated Recipient Share of Outlays*</th>
<th>Actual Recipient Share of Outlays</th>
<th>Cumulative</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Q05</td>
<td>1/1/05</td>
<td>3/31/05</td>
<td>100,000</td>
<td>100,000</td>
<td>27,150</td>
<td>27,150</td>
<td></td>
</tr>
<tr>
<td>2Q05</td>
<td>4/1/05</td>
<td>6/30/05</td>
<td>100,000</td>
<td>100,000</td>
<td>27,150</td>
<td>27,150</td>
<td></td>
</tr>
<tr>
<td>3Q05</td>
<td>7/31/05</td>
<td>9/30/05</td>
<td>100,000</td>
<td>100,000</td>
<td>27,150</td>
<td>27,150</td>
<td></td>
</tr>
<tr>
<td>4Q05</td>
<td>10/1/05</td>
<td>12/31/05</td>
<td>100,000</td>
<td>100,000</td>
<td>27,150</td>
<td>16,746.18</td>
<td></td>
</tr>
<tr>
<td>1Q06</td>
<td>1/1/06</td>
<td>3/31/06</td>
<td>133,965.25</td>
<td>133,965.25</td>
<td>37,044.75</td>
<td>37,044.75</td>
<td></td>
</tr>
<tr>
<td>2Q06</td>
<td>4/1/06</td>
<td>6/30/06</td>
<td>133,965.25</td>
<td>133,965.25</td>
<td>37,044.75</td>
<td>37,044.75</td>
<td></td>
</tr>
<tr>
<td>3Q06</td>
<td>7/31/06</td>
<td>9/30/06</td>
<td>133,965.25</td>
<td>133,965.25</td>
<td>37,044.75</td>
<td>37,044.75</td>
<td></td>
</tr>
<tr>
<td>4Q06</td>
<td>10/1/06</td>
<td>12/31/06</td>
<td>133,965.25</td>
<td>133,965.25</td>
<td>37,044.75</td>
<td>11,370.81</td>
<td></td>
</tr>
<tr>
<td>1Q07</td>
<td>1/1/07</td>
<td>3/31/07</td>
<td>187,500</td>
<td>187,500</td>
<td>52,042.50</td>
<td>44328.00</td>
<td></td>
</tr>
<tr>
<td>2Q07</td>
<td>4/1/07</td>
<td>6/30/07</td>
<td>187,500</td>
<td>187,500</td>
<td>52,042.50</td>
<td>52,000</td>
<td></td>
</tr>
<tr>
<td>3Q07</td>
<td>7/31/07</td>
<td>9/30/07</td>
<td>187,500</td>
<td>125,000</td>
<td>52,042.50</td>
<td>52,000</td>
<td></td>
</tr>
<tr>
<td>4Q07</td>
<td>10/1/07</td>
<td>12/31/07</td>
<td>187,500</td>
<td>125,000</td>
<td>52,042.50</td>
<td>20,000</td>
<td></td>
</tr>
<tr>
<td>1Q08</td>
<td>1/1/08</td>
<td>3/31/08</td>
<td>-</td>
<td>100,000</td>
<td>-</td>
<td>20,000</td>
<td></td>
</tr>
<tr>
<td>2Q08</td>
<td>4/1/08</td>
<td>6/30/08</td>
<td>-</td>
<td>15,000</td>
<td>-</td>
<td>20,000</td>
<td></td>
</tr>
<tr>
<td>3Q08</td>
<td>7/1/08</td>
<td>8/31/08</td>
<td>-</td>
<td>10,000</td>
<td>-</td>
<td>15,000</td>
<td></td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td></td>
<td></td>
<td><strong>1,685,861</strong></td>
<td><strong>1,685,861</strong></td>
<td><strong>464,949</strong></td>
<td><strong>467,029</strong></td>
<td></td>
</tr>
</tbody>
</table>

* Update quarterly – Previous quarters should show actual expenditures and should coincide with the SF269 numbers; future quarters should show estimates. Estimates need to be provided for the entire project. If spending for a given quarter is different than estimated, then the remaining quarter’s estimates should be updated to account for the difference. Total DOE and Cost Share Estimate amounts should be the same as the Award amount.

**General Notes:**
1) DOE Laboratory partner spending should not be included in the above table.
2) The information in this table should be consistent with the information provided in section 10 of the quarterly financial status reports (SF269 or SF269A).
Fig. 1. (a) Current density-vs-potential characteristics measured in 0.33M H₃PO₄ solution under simulated AM1.5G illumination on WO₃-based PEC electrodes fabricated at different stages of the project. This figure presents improvements made from the first deposition (2004, $I_{\text{photo,sat}}=1$ mA/cm²) to the current bilayer-based (WO₃:Mo/WO₃) PEC champion device (present, $I_{\text{photo,sat}}=3.6$ mA/cm²). (b) Current density-vs-time obtained in a mechanical stack configuration using Si-based PV underlying cell. The resulting stabilized solar-to-hydrogen efficiency is 3.1%STH.

Figure 2: Surface energy band diagram of (a) WO₃ and (b) Mo:WO₃ films deposited using a reactive sputtering process. Data are compared with $H^+/H_2$ and $H_2O/O_2$ energy levels.
Figure 3: Photocurrent generated by 8 PEC electrodes made of CGSe films deposited during the same run. X/Y plane corresponds to the special repartition of samples over the 3x3 substrate holder and the bars represent the saturated current density produced by each sample. Samples from row 3 routinely performed poorly. Note that sample seated at the center position is commonly used as witness sample and note wired as PEC electrode.

Fig. 4. Current density-vs-potential curves under AM1.5 simulated solar irradiance in 0.5M H2SO4 plotting $J_{\text{light}} - J_{\text{dark}}$ versus potential for (a) an optimized CGSe film and (b) a CISeS film.
Figure 5: Current density-vs-potential curves measured under simulated AM1.5G illumination in pH2 buffer solution on a-SiC before and after HF 24% etch performed for 15 seconds.

Figure 6: Stability experiments of a-Si PEC photoelectrodes deposited on (a) stainless steel and (b) tin oxide substrates, shown before and after PEC hydrogen production testing.
ATTACHMENT D

University of Nevada, Las Vegas (UNLV)

High Temperature Rotary Drum

(33 Pages)
Project Objective: To study the effects of thermal and dynamic effects on attrition that the alumina-based particles is expected to experience at the solar particle receiver located at Sandia National Laboratories. Our tasks at UNLV consisted of constructing a high temperature rotary drum that can closely simulate the motion the particle endures.

Abstract: A testing apparatus was completely designed built and tested at UNLV for the study of attrition effects at high temperature of the Solar Particle Receiver (SPR) bauxite particles. The testing temperature that is targeted is around 850-900 °C similar to the conditions that are expected in the eventual operation of an industrial SPR. The experimental results were initially for attrition of these particles at ambient temperatures. The initial results show a decrease of about 20% in the statistically averaged size of the sampled particles over a testing period from 2 to 6 hour duration.

Tests on attrition of these particles at high temperature is being conducted now and the preliminary results indicate that with a test duration of one hour at high temperature there is a reduction of 14% in the statistical size of the particles which indicates a faster rate of attrition at these temperatures. It is to be noted that one of the aims of the experimental work is to eventually scale those results with a ‘scaling time factor” that would reasonably simulate the rate of impacts that take place in a real SPR. Once this factor can be estimated then the factor can be essentially multiplied by the actual testing times in the current testing setup to obtain a qualitative estimate of the length of time that is needed in an SPR environment to reach to the attrition rates found in the current test section.

TABLE OF CONTENTS

Project Objective................................................................. 1
Abstract.................................................................................... 1
Table of Contents................................................................. 2
List of Figures.......................................................................... 3
List of Tables............................................................................ 4
Background................................................................................ 5
Experimental Setup............................................................... 7
LIST OF FIGURES

Figure 1  Solar Hydrogen Production Plant........................................  5
Figure 2  General view of particles.....................................................  6
Figure 3  Diagram of the test facility..................................................  7
Figure 4  Schematic of the test facility...............................................  7
Figure 5  High Temperature Rotating Drum (HTRD)..............................  8
Figure 6  Heater's k-type thermocouple..............................................  9
Figure 7  TPC user panel revealing heater temperature......................... 10
Figure 8  System's motor with speed reducer................................. 10
Figure 9  Tachometer measuring shaft's RPM................................. 11
Figure 10 Manner in which the particles enter and exit the drum......... 11
Figure 11 Motor Speed vs. Shaft RPM........................................... 12
Figure 12 System of sieves........................................................... 13
Figure 13 Particles in test drum before cold run.......................... 13
Figure 14 Untested particle distribution (Standard)......................... 14
Figure 15 Cold Test No.1............................................................... 17
Figure 16 Cold Test No. 2.............................................................. 19
Figure 17 Cold Test No. 3.............................................................. 21
Figure 18 Cold Test No. 4.............................................................. 23
Figure 19 Cold Test No. 5.............................................................. 25
Figure 20 Cold Test No. 6.............................................................. 27
Figure 21 Particle distributions with various sieving times.............. 30
Figure 22 Hot Test.......................................................... 31

LIST OF TABLES

Table 1  Fundamental Properties of k-type Thermocouple.................. 9
Table 2  System's Power Cord Physical Properties.......................... 10
Table 3  Tests determining shaft RPM relative to speed controller percentage 12
Table 4  Non-rotated Particle Sieve Distribution.............................. 15
Table 5  Cold Testing Configurations.......................................... 16
Table 6  Cold Test No. 1 Particle Distribution................................ 18
Table 7  Cold Test No. 2 Particle Distribution................................ 20
Table 8  Cold Test No. 3 Particle Distribution................................. 22
Table 9  Cold Test No. 4 Particle Distribution................................. 24
Table 10 Cold Test No. 5 Particle Distribution................................. 26
Table 11 Cold Test No. 6 Particle Distribution................................. 28
Table 12 ACPS of Standard vs. Cold Tests....................................... 29
Table 13 Various Sieving Time Conditions....................................... 29
Table 14 Hot Testing Conditions...................................................... 30
Table 15 Hot Test Particle Distribution.............................................. 32

Background: A Solid particle solar receiver is employed to receive concentrated solar energy from a field of heliostats to heat ceramic particles. Thus the heated ceramic particle can serve as a heat transfer and storage medium or as a substrate on which chemical reaction may be performed directly. The solid particles are enclosed in a cavity called receiver to absorb concentrated solar radiation and can provide efficient absorption of concentrated sunlight. Studies [1, 2] show that by utilizing a large-scale production of hydrogen using solar energy at comparatively lower cost is feasible with a solid particle solar energy receiver concept. Spherical particles of
697 µm size were used as a working medium. The particles used in this work were commercially available sintered bauxite “proppants” from Carbo-Ceramics [4].

Attrition of particles is left behind as an unnoticed parameter. For the design of real world receiver (Fig. 1), attrition of particles is certainly required in a quantitative way of assessment. This could possibly help in continuous running of the real world receiver by removing the attired or fine particles and refeeding the assessed amount [4].

In a real world receiver the following factors are considered as influencing on particle attrition.

1. Particles falling with zero start velocity and ending with terminal velocity (6 to 10 m/s).
2. Inter-particle collisions which is mostly expected at the hopper discharge, movement of particle bed in hot and cold storage tanks (Fig.1).
3. Particle impact on metal surface which includes (Fig.1).
   a) hot storage tank (~ 950 °C)
   b) heat exchangers,
   c) cold storage tank (~ 550 °C)
   d) bucket elevators

Hruby [3] reported about ‘Material Characterization and Agglomeration Behavior” and “Fracture Resistance” in her report. Studies on agglomeration behavior of the ceramic particles had been carried out by heating in a 4 cm diameter by 3 cm high powder bed in air at temperatures ranging from 800 to 1500 °C for one hour.

Particle sizes of 100 µm were used for these tests because the smallest particles are the most likely to demonstrate agglomeration. The effect of agglomeration on storage was also performed by applying load to the particles at higher temperatures. Pressures as high as 200 psi were applied to the packed particle samples of the materials and it was concluded that the particles did not agglomerate except for time duration greater than 12 hours. The result showed that, for temperatures between 1000 °C and 1100 °C, the alumina particles are free flowing. Since it is anticipated that the solid particle receiver will operate at approximately 1000 °C, the effect of agglomeration cannot be seen as significant. The author also reported some work related to Mechanical Fracture and Thermal Fracture. It was concluded that the Mechanical Fracture, which is mainly impact-induced, cannot contribute much when the impact velocity of the particles is lower than the critical impact velocity [1].

Figure 2 - General view of particles
In the case of Thermal Fracture, the author discussed about compressive strength of the particles. The packed particle samples were cycled in the solar furnace. Samples were exposed to 1.5 MW/m² solar flux until it reached 1200 °C, and then were exposed to cool to at least 700 °C before another solar flux exposure. Particle temperature was recorded optically during these tests with a solar blind pyrometer operating at 3.4 µm. The compressive strength was measured using Instron machine. It was concluded that the measurement of compressive strength on particles resulted in slight decrease in strength of particles cycled less than 50 times and an increase in strength when the particles were exposed to 100 or more cycles. The reason for the decrease is explained to be a result of chemical phase changes, or initial cracking which is healed with continued cycling. Both the increase and decrease were not appreciable; hence the thermal fracture of the particle could be small or negligible. Clearly, studies on agglomeration, mechanical fracture and thermal fractures and its effects have been reported to an appreciable extent. But the studies on attrition behavior of the particles are not reported.

The literature review on attrition/abrasion reveals some possible experimental methods to evaluate solid particle attrition. Pis et al. [5] gives explanation for the phenomenon of attrition in a fluidized bed. Two types of mechanism encountered in attrition are explained as follows

(i) Abrasion: A wearing down by friction. Particles of much smaller size break away from the original particle. The resulting particles are slightly smaller than the original one.

(ii) Fragmentation: The breaking-away process gives rise to a number of particles of a smaller size than the original one.

**Experimental Setup:**

*Preliminary Setup*

Fluidization of a bed (Fig. 3) of solid particles occurs when an evenly distributed flow of gas passes upwards through it at a sufficient velocity such that the particles begin to levitate. The bed is said to be fluidized because it behaves in many ways like a liquid; the mixture will flow from a higher to a lower level, and heavier objects will sink within it while lighter objects will rise. If the mean particle size and superficial velocity are large enough, the bed will be in a stable regime in which bubbles form near the gas distributor at the bottom of the bed and grow by coalescence as they rise towards the top. In this way, the bed rather resembles a boiling liquid [1].

Fluidized bed attrition studies have some potential advantages over other methods. Standard empirical methods developed from basic

![Figure 3 - Diagram of the Test Facility]
principles are available. These methods were tested and validated for fluidized bed attrition data available from the literature. Attrition studies through fluidized bed might be closely related to real world particle receiver systems. After discovering the amount of power this setup was calling for, the sizing of the reactor column is beyond the scope of laboratory scale design. Also, the fines produced by attrition might leave the system through the exhaust, thus adversely affecting the accurate measurement of particle attrition. Another constraint is the convective heat losses that will be encountered during particle fluidization.

**Chosen Design**

The above demerits can be overcome in the new design of high temperature rotating drum developed for attrition studies built at UNLV Mechanical Engineering shop. The particle terminal velocity can be simulated in the rotating drum by a simple relation,

\[
V = \omega r
\]

Solving for the number of revolutions per minute, it was determined that the drum had to be rotated approximately 500 RPM.

Test section, such as the drum and shaft (Figs. 9, 10), is made up of Inconel alloy 625 (Fig. 5). This nickel-chromium-molybdenum wrought alloy is an excellent general purpose material for elevated temperature use in high strength, oxidation problem applications. It also has excellent corrosion resistance to many acids and resists intergranular attack and stress-corrosion cracking. The alloy finds use in high temperature applications such as heat exchangers and gas turbine components. Because of its good corrosion resistance, it is also used in wet scrubbers and some acid process equipment. Its outstanding strength and toughness in the temperature range cryogenic to 2000°F (1093°C) are derived primarily from the solid solution effects of the refractory metals, columbium and molybdenum, in a nickel-chromium matrix. The alloy has excellent fatigue strength and stress-corrosion cracking resistance to chloride ions. Some typical applications for alloy 625 have included heat shields, furnace hardware, gas turbine engine ducting, combustion liners and spray bars, chemical plant hardware, and special seawater applications [1].
The couplings are used on either side of the shaft to accommodate any thermal expansion which would occur when one end of the shaft is exposed to 1000 °C. The couplings are made up of super tough glass reinforced nylon of sleeve with a snap ring. The sleeve measures 11.25cm in length. The thermal expansion can be calculated from

\[ \text{Elongation} = L \times \alpha \times \Delta T. \]

The average possible elongation estimated from the above relation is 15-16 mm. Where \( \alpha \) is the coefficient of thermal expansion of Inconel at 982 °C is \( 17.3 \times 10^{-6} \text{ m/m °C} \). A DC, 1.5 HP, 2500 RPM fan cooled motor is shown in Fig. 8. A Speed control is attached in order to regulate speeds within 5% of nameplate RPM and provides full-wave rectification. Built-in features include minimum and maximum adjustable speed, current/torque limit, and fixed IR compensation.

The heater consist two parts: the top and bottom (Fig. 9). As a result, two sets of wiring were implemented and connected to the heater’s power box. A 10-gage, 3-conductor cable was utilized in connecting the heater to the power box. Two terminal block was added into the power box in order to accommodate the second heater cable. The 30 A cable is made of copper, resistant to high heat (up to 105 °C), and is able to endure voltage up to 300 VAC.

In order to ensure that the drum is heated to approximately 1,000 °C (1,832 °F), thermocouples were added to top and bottom portions of the heater (Fig. 6). Due to the extreme heat that the heater may provide, the thermocouple will need to endure such high temperatures. As a result, the popular \( k \)-type thermocouple is chosen due to its durability under extreme

---

Figure 5 - High Temperature Rotating Drum (HTRD)

Figure 6 - Heater’s k-type thermocouple
conditions. The following table reveals standard properties for the k-type thermocouple:

<table>
<thead>
<tr>
<th>Type</th>
<th>Metals Utilized</th>
<th>Temperature Range (°C)</th>
<th>Sensativity</th>
<th>Std. Limits of Error</th>
<th>Spec. Limits of Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>Chromel/Alumel</td>
<td>-200-1250 (-328 °F to 2282 °F)</td>
<td>41μV/°C</td>
<td>Greater of 2.2 °C or 0.75%</td>
<td>Greater of 1.1 °C or 0.4%</td>
</tr>
</tbody>
</table>

The bottom thermocouple will be connected to the Temperature and Process Controller (TPC) as an input while the top thermocouple can be connected to a standard multimeter. This is to ensure that both halves of the boxes are generating nearly the same amount of heat if manually checked.

The power cord was installed into the system; the heater calls for a power cord that’s able to plug into a 3-phase outlet since the power box is capable to use up to 240 volts during operation. The length was ordered at 50 feet since the operation will be held outside while the outlet is located inside the engineering building. In order to ensure that the system is grounded, the green conductor was attached to the side of the power box. As a result, the power box is connected to the portable cart that the system sits on. The following table discloses standard properties for the system’s power cord:

<table>
<thead>
<tr>
<th>Volts</th>
<th>Amps</th>
<th>Gauge (AWG)</th>
<th>No. of Conductors</th>
<th>Conductor Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 VAC</td>
<td>30</td>
<td>10</td>
<td>4</td>
<td>Copper</td>
</tr>
</tbody>
</table>

In an effort to maintain a target temperature declared by the user, the Temperature and Process Controller (TPC) was purchased and installed onto the system (Fig. 7). The TPC is a device that regulates the power given to the heater box in order to control the temperature the heater box generates. The panel consists of an on/off toggle switch and a 250 mA fuse. Its input will be the temperature
while the output will be the voltage. Once the TPC is on, the user is able to set their desired temperature limits.

The TPC will allow the power box to reach the desired temperature; once the temperature is reached and continue to climb, the TPC will disallow the power box to power the heater, thus in essence cutting off power to the heater box momentarily. As mentioned earlier, the bottom half of the heater box has a thermocouple that is connected to the TPC while the top half can be connected with a multimeter.

To acquire the working relationship between the speed controller and motor, it was imperative to determine the shaft’s RPM relative to what percentage the speed controller was placed on. By using a tachometer, determining the shaft’s RPM was straightforward by simply placing the device approximately 3 inches (7.62 centimeters) from the top of the shaft. Figure 9 reveals the tachometer measuring the shaft’s actual RPM.

The speed controller was increased in increments of 5 percent, and after recording the shaft’s RPMs from 0 to 65 percent, the speed controller was shut off. It was established that after reaching 65 percent of the speed controller’s capacity, the vibration of the system’s foundation could not be disregarded, thus ceasing the determination of the shaft’s RPMs after 65 percent.

After obtaining RPM values on three separate occasions, a table (Table 3) was created in order to discover if the motor would allow the drum to rotate at the intended target of 400 RPM. RPMs for speed controller percentages 70 through 100 were received after plotting the known data (speed controller percentages 0-65), and they are denoted via highlight. The three separate tests produced their distinct linear equation, and having each of their R² values at over 99 percent, in theory, the drum is able to reach close to 400 RPM at 100 percent motor capacity.

Table 1 reveals the RPM data that was collected relative to the speed controller percentage. Figure 11 confirms the linearity of the three speed controller-shaft RPM tests.
Figure 11 - Motor Speed vs. Shaft RPM

Table 3 - Tests to determine shaft RPM relative to percentage of speed controller

<table>
<thead>
<tr>
<th>Shaft Speed Controller %</th>
<th>TEST 1 RPM</th>
<th>TEST 2 RPM</th>
<th>TEST 3 RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>17.8</td>
<td>18.9</td>
<td>17.9</td>
</tr>
<tr>
<td>20</td>
<td>37.5</td>
<td>39</td>
<td>38.9</td>
</tr>
<tr>
<td>25</td>
<td>60.2</td>
<td>62</td>
<td>61.6</td>
</tr>
<tr>
<td>30</td>
<td>82.4</td>
<td>81.8</td>
<td>82.2</td>
</tr>
<tr>
<td>35</td>
<td>103.2</td>
<td>105.1</td>
<td>103.3</td>
</tr>
<tr>
<td>40</td>
<td>126.1</td>
<td>125.6</td>
<td>127.7</td>
</tr>
<tr>
<td>45</td>
<td>148.2</td>
<td>148.5</td>
<td>148.7</td>
</tr>
<tr>
<td>50</td>
<td>171.7</td>
<td>173.2</td>
<td>172</td>
</tr>
<tr>
<td>55</td>
<td>190</td>
<td>195.3</td>
<td>195.4</td>
</tr>
<tr>
<td>60</td>
<td>218.2</td>
<td>218.6</td>
<td>221.2</td>
</tr>
<tr>
<td>65</td>
<td>240</td>
<td>240.7</td>
<td>243</td>
</tr>
<tr>
<td>70</td>
<td>260.305</td>
<td>261.89</td>
<td>263.688</td>
</tr>
<tr>
<td>75</td>
<td>282.5485</td>
<td>284.1945</td>
<td>286.2435</td>
</tr>
<tr>
<td>80</td>
<td>304.792</td>
<td>306.499</td>
<td>308.799</td>
</tr>
<tr>
<td>85</td>
<td>327.0355</td>
<td>328.8035</td>
<td>331.3545</td>
</tr>
<tr>
<td>90</td>
<td>349.279</td>
<td>351.108</td>
<td>353.91</td>
</tr>
<tr>
<td>95</td>
<td>371.5225</td>
<td>373.4125</td>
<td>376.4655</td>
</tr>
<tr>
<td>100</td>
<td>393.766</td>
<td>395.717</td>
<td>399.021</td>
</tr>
</tbody>
</table>
TESTING

Standard Testing

Results were obtained from initial cold testing. Before testing, a standard was needed to be established. Its conditions consist of sieving the non-tested particles in order to see the distribution of the particles through the system of sieves (Fig. 12). After sieving for one hour, each sieve-group of particles was weighed.

The graph on the next page (Fig. 14) illustrates the particles distribution throughout the system of sieves. The average calculated particle size (ACPS) was determined by summing the product of the sieve size by its percentage of particles in that sieve. As a result, the non-rotated particles had an average particle size of 654 µm, whereas the rotated particles, depending on the time duration and drum RPM, varied. Hence, attrition by dynamic forces cannot be neglected.

Figure 12 - System of sieves

Figure 13 – Particles in test drum before cold run
Figure 14 - Untested Particle Distribution (Standard)
<table>
<thead>
<tr>
<th>Sieve Size (microns)</th>
<th>Mass (g)</th>
<th>Percentage of Total Particles</th>
<th>Sieves * %</th>
</tr>
</thead>
<tbody>
<tr>
<td>710</td>
<td>1447.8</td>
<td>56.7</td>
<td>402.4</td>
</tr>
<tr>
<td>600</td>
<td>893.4</td>
<td>35.0</td>
<td>209.9</td>
</tr>
<tr>
<td>500</td>
<td>204.3</td>
<td>8.0</td>
<td>40.0</td>
</tr>
<tr>
<td>425</td>
<td>7.2</td>
<td>0.3</td>
<td>1.2</td>
</tr>
<tr>
<td>300</td>
<td>1.4</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>212</td>
<td>0.0931</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>106</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>53</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

| Intended Mass (g)    | 2550.0   | Mass Lost (g)                | 0.1        |
| Actual Mass (g)      | 2549.7   | ACPS                         | 653.6      |
| Mass After Rotation (g) | 2554.3 | Percentage of Particles After Rotation | 99.9      |
Cold Testing

Cold testing was performed in order to further study the influence of attrition solely by rotation. A total of six cold runs were performed. Three sets of cold runs are distinct from one another by time duration. Table 5 shows the cold testing configurations.

Table 5 - Cold Testing Configurations

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Time Duration</th>
<th>Drum RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test No. 1</td>
<td>2</td>
<td>125</td>
</tr>
<tr>
<td>Test No. 2</td>
<td>2</td>
<td>218</td>
</tr>
<tr>
<td>Test No. 3</td>
<td>4</td>
<td>125</td>
</tr>
<tr>
<td>Test No. 4</td>
<td>4</td>
<td>218</td>
</tr>
<tr>
<td>Test No. 5</td>
<td>6</td>
<td>125</td>
</tr>
<tr>
<td>Test No. 6</td>
<td>6</td>
<td>218</td>
</tr>
</tbody>
</table>

Results have been attained from initial cold testing. All six of the cold runs were compared to the standard that was created in August (the non-rotated particle distribution through the system of sieves). It was believed that the longer (in time) and faster (RPM) the particles experienced in the rotating drum that the attrition rate would increase, and that belief held true. The following six graphs and their respective data charts reveal the particle results after experiencing attrition in these six distinctive cold runs.
Particle Distribution Through Sieves

Figure 15 – Cold Test No.1
## Table 6 - Cold Test No. 1 Particle Distribution

**TEST No. 1**

2 hr., ≥ 125 RPM

<table>
<thead>
<tr>
<th>Sieve Size (microns)</th>
<th>Mass (g)</th>
<th>Percentage of Total Particles</th>
<th>Sieves * %</th>
</tr>
</thead>
<tbody>
<tr>
<td>710</td>
<td>1001.3</td>
<td>39.3</td>
<td>278.8</td>
</tr>
<tr>
<td>600</td>
<td>789.2</td>
<td>31.0</td>
<td>185.7</td>
</tr>
<tr>
<td>500</td>
<td>586.3</td>
<td>23.0</td>
<td>115.0</td>
</tr>
<tr>
<td>425</td>
<td>74.7</td>
<td>3.0</td>
<td>12.4</td>
</tr>
<tr>
<td>300</td>
<td>27.3</td>
<td>1.1</td>
<td>3.2</td>
</tr>
<tr>
<td>212</td>
<td>11.7</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>106</td>
<td>8.9</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>53</td>
<td>3.3</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Intended Mass (g)</strong></th>
<th>2550.0</th>
<th><strong>Mass Lost (g)</strong></th>
<th>47.2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Actual Mass (g)</strong></td>
<td>2549.7</td>
<td><strong>ACPS</strong></td>
<td>596.6</td>
</tr>
<tr>
<td><strong>Mass After Rotation (g)</strong></td>
<td>2502.5</td>
<td><strong>Percentage of Particles After Rotation</strong></td>
<td>98.1</td>
</tr>
</tbody>
</table>
Figure 16 - Cold Test No. 2
Table 7- Cold Test No. 2 Particle Distribution

<table>
<thead>
<tr>
<th>Sieve Size (microns)</th>
<th>Mass (g)</th>
<th>Percentage of Total Particles</th>
<th>Sieves * %</th>
</tr>
</thead>
<tbody>
<tr>
<td>710</td>
<td>991.2</td>
<td>38.9</td>
<td>276.1</td>
</tr>
<tr>
<td>600</td>
<td>787.7</td>
<td>30.9</td>
<td>185.4</td>
</tr>
<tr>
<td>500</td>
<td>577.4</td>
<td>22.7</td>
<td>113.3</td>
</tr>
<tr>
<td>425</td>
<td>62.6</td>
<td>2.5</td>
<td>10.4</td>
</tr>
<tr>
<td>300</td>
<td>37.2</td>
<td>1.5</td>
<td>4.4</td>
</tr>
<tr>
<td>212</td>
<td>19.9</td>
<td>0.8</td>
<td>1.7</td>
</tr>
<tr>
<td>106</td>
<td>12.0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>53</td>
<td>6.4</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Intended Mass (g)</strong></td>
<td>2550.0</td>
<td>Mass Lost (g)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>54.3</td>
</tr>
<tr>
<td><strong>Actual Mass (g)</strong></td>
<td>2548.5</td>
<td>ACPS</td>
<td>592.0</td>
</tr>
<tr>
<td><strong>Mass After Rotation (g)</strong></td>
<td>2494.2</td>
<td>Percentage of Particles After Rotation</td>
<td>97.9</td>
</tr>
</tbody>
</table>
Particle Distribution Through Sieves

![Graph showing particle distribution through sieves.]

Figure 17 - Cold Test No. 3
Table 8 - Cold Test No. 3 Particle Distribution

<table>
<thead>
<tr>
<th>Sieve Size (microns)</th>
<th>Mass (g)</th>
<th>Percentage of Total Particles</th>
<th>Sieves * %</th>
</tr>
</thead>
<tbody>
<tr>
<td>710</td>
<td>976.4</td>
<td>38.3</td>
<td>271.7</td>
</tr>
<tr>
<td>600</td>
<td>748.7</td>
<td>29.3</td>
<td>176.1</td>
</tr>
<tr>
<td>500</td>
<td>561.7</td>
<td>22.0</td>
<td>110.1</td>
</tr>
<tr>
<td>425</td>
<td>75.0</td>
<td>2.9</td>
<td>12.5</td>
</tr>
<tr>
<td>300</td>
<td>46.7</td>
<td>1.8</td>
<td>5.5</td>
</tr>
<tr>
<td>212</td>
<td>42.1</td>
<td>1.7</td>
<td>3.5</td>
</tr>
<tr>
<td>106</td>
<td>23.7</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>53</td>
<td>12.5</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Intended Mass (g)</strong></td>
<td>2550.0</td>
<td><strong>Mass Lost (g)</strong>: 64.7</td>
<td></td>
</tr>
<tr>
<td><strong>Actual Mass (g)</strong></td>
<td>2551.3</td>
<td><strong>ACPS</strong>: 580.6</td>
<td></td>
</tr>
<tr>
<td><strong>Mass After Rotation (g)</strong></td>
<td>2486.6</td>
<td><strong>Percentage of Particles After Rotation</strong>: 97.5</td>
<td></td>
</tr>
</tbody>
</table>
Particle Distribution Through Sieves

Sieve Size (micrometer)

Percentage of Particles

- 4 hrs.
- Untested 2554.4

Figure 18 - Cold Test No. 4
<table>
<thead>
<tr>
<th>Sieve Size (microns)</th>
<th>Mass (g)</th>
<th>Percentage of Total Particles</th>
<th>Sieves * %</th>
</tr>
</thead>
<tbody>
<tr>
<td>710</td>
<td>943.6</td>
<td>37.0</td>
<td>262.5</td>
</tr>
<tr>
<td>600</td>
<td>732.7</td>
<td>28.7</td>
<td>172.2</td>
</tr>
<tr>
<td>500</td>
<td>548.7</td>
<td>21.5</td>
<td>107.5</td>
</tr>
<tr>
<td>425</td>
<td>70.2</td>
<td>2.8</td>
<td>11.7</td>
</tr>
<tr>
<td>300</td>
<td>53.3</td>
<td>2.1</td>
<td>6.3</td>
</tr>
<tr>
<td>212</td>
<td>41.8</td>
<td>1.6</td>
<td>3.5</td>
</tr>
<tr>
<td>106</td>
<td>34.3</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>53</td>
<td>25.6</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Intended Mass (g)</strong></td>
<td>2550.0</td>
<td><strong>Mass Lost (g)</strong></td>
<td>101.9</td>
</tr>
<tr>
<td><strong>Actual Mass (g)</strong></td>
<td>2552.1</td>
<td><strong>ACPS</strong></td>
<td>565.6</td>
</tr>
<tr>
<td><strong>Mass After Rotation (g)</strong></td>
<td>2450.2</td>
<td><strong>Percentage of Particles After Rotation</strong></td>
<td>96.0</td>
</tr>
</tbody>
</table>
Figure 19 - Cold Test No. 5
### Table 10 - Cold Test No. 5 Particle Distribution

**TEST No. 5**  
6 hr., ≥ 125 RPM

<table>
<thead>
<tr>
<th>Sieve Size (microns)</th>
<th>Mass (g)</th>
<th>Percentage of Total Particles</th>
<th>Sieves *</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>710</td>
<td>804.3</td>
<td>31.4</td>
<td>223.2</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>621.2</td>
<td>24.3</td>
<td>145.7</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>406.0</td>
<td>15.9</td>
<td>79.4</td>
<td></td>
</tr>
<tr>
<td>425</td>
<td>202.5</td>
<td>7.9</td>
<td>33.7</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>149.7</td>
<td>5.9</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td>212</td>
<td>127.3</td>
<td>5.0</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>106</td>
<td>84.7</td>
<td>3.3</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>67.7</td>
<td>2.6</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td><strong>Intended Mass (g)</strong></td>
<td>2550.0</td>
<td><strong>Mass Lost (g)</strong></td>
<td>94.8</td>
<td></td>
</tr>
<tr>
<td><strong>Actual Mass (g)</strong></td>
<td>2558.1</td>
<td><strong>ACPS</strong></td>
<td>515.0</td>
<td></td>
</tr>
<tr>
<td><strong>Mass After Rotation (g)</strong></td>
<td>2463.3</td>
<td><strong>Percentage of Particles After Rotation</strong></td>
<td>96.3</td>
<td></td>
</tr>
</tbody>
</table>
Particle Distribution Through Sieves

Figure 20 - Cold Test No. 6
Table 11 - Cold Test No. 6 Particle Distribution

<table>
<thead>
<tr>
<th>Sieve Size (microns)</th>
<th>Mass (g)</th>
<th>Percentage of Total Particles</th>
<th>Sieves * %</th>
</tr>
</thead>
<tbody>
<tr>
<td>710</td>
<td>759.7</td>
<td>29.7</td>
<td>211.1</td>
</tr>
<tr>
<td>600</td>
<td>580.2</td>
<td>22.7</td>
<td>136.3</td>
</tr>
<tr>
<td>500</td>
<td>386.3</td>
<td>15.1</td>
<td>75.6</td>
</tr>
<tr>
<td>425</td>
<td>197.3</td>
<td>7.7</td>
<td>32.8</td>
</tr>
<tr>
<td>300</td>
<td>145.7</td>
<td>5.7</td>
<td>17.1</td>
</tr>
<tr>
<td>212</td>
<td>139.7</td>
<td>5.5</td>
<td>11.6</td>
</tr>
<tr>
<td>106</td>
<td>129.3</td>
<td>5.1</td>
<td>5.4</td>
</tr>
<tr>
<td>53</td>
<td>94.7</td>
<td>3.7</td>
<td>2.0</td>
</tr>
</tbody>
</table>

| Intended Mass (g)    | 2550.0   | Mass Lost (g)                 | 123.4      |
| Actual Mass (g)      | 2556.1   | ACPS                          | 491.6      |
| Mass After Rotation (g) | 2432.7 | Percentage of Particles After Rotation | 95.2      |
After reviewing the graphs, two observable facts can be seen. First, the percentage of particles in sieves 710 decreased nearly 10 percent. As a result, the rest of the particles were distributed into the remaining sieves. Comparing between the dry runs of “2 hours at 125 RPM” to “6 hours at 218 RPM”, the distribution of particles throughout the sieves is clearly visible, in other words, the particles are beginning to collect into each sieve in an evenly manner. Second, the average calculated particle size (ACPS) decreased as the time duration and RPM increased. Table 12 reveals this phenomenon.

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Average Calculated Particle Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-rotated Particles (Standard)</td>
<td>653.6</td>
</tr>
<tr>
<td>Test No. 1: 2 hr, ≥ 125 RPM</td>
<td>596.6</td>
</tr>
<tr>
<td>Test No. 2: 2 hr, ≥ 218 RPM</td>
<td>592.0</td>
</tr>
<tr>
<td>Test No. 3: 4 hr, ≥ 125 RPM</td>
<td>580.6</td>
</tr>
<tr>
<td>Test No. 4: 4 hr, ≥ 218 RPM</td>
<td>565.6</td>
</tr>
<tr>
<td>Test No. 5: 6 hr, ≥ 125 RPM</td>
<td>515.0</td>
</tr>
<tr>
<td>Test No. 6: 6 hr, ≥ 218 RPM</td>
<td>491.6</td>
</tr>
</tbody>
</table>

Given that that sieve shaker itself imposes a repetitive force onto the sieves and particles, it is possible that the particles may break up into even smaller sizes, thus compromising the system’s data. The chart below reveals describes various sieving time, while the untested particle time acts as a “measuring stick” in how much the system broke down the size of the particles.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Mass (g)</th>
<th>Sieve Time (hr.)</th>
<th>Duration in Drum</th>
<th>Drum RPM</th>
<th>Average Calculated Particle Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>2554.4</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>653.6</td>
</tr>
<tr>
<td>1</td>
<td>2549.7</td>
<td>2</td>
<td>1</td>
<td>60</td>
<td>570.6</td>
</tr>
<tr>
<td>2</td>
<td>2601.2</td>
<td>1</td>
<td>1</td>
<td>60</td>
<td>596.6</td>
</tr>
<tr>
<td>3</td>
<td>2441.7</td>
<td>3</td>
<td>1</td>
<td>60</td>
<td>541.2</td>
</tr>
</tbody>
</table>
As shown in Figure 21, as the particles spend more time in the shaker, the particles begin to drop into the smaller sieves, giving a more even particle distribution throughout the sieves. As mentioned earlier, one reason may be that the shaker’s motion may break the particles into smaller sizes. Another reason may be that the particles are given more time to actually reach the bottom of each sieve, thus giving them an opportunity to go into their respective sieve.

**Hot Testing**

One test was performed in order to see preliminary results of attrition and also to observe if any system failures occurred. Table 14 below reveals the testing parameters the hot experiment followed and the particle distribution throughout the system of sieves located on the next page. Table 15 reveals that the ACPS was recorded at 437.7.

**Table 14 - Hot Testing Conditions**

<table>
<thead>
<tr>
<th>Test Time (Min.)</th>
<th>Test Temperature (°C)</th>
<th>Test Drum RPM</th>
<th>Sieving Time (Min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>820.0-830.0</td>
<td>≥ 218</td>
<td>90</td>
</tr>
</tbody>
</table>
Particle Distribution Through Sieves

Figure 22 - Hot Test
### Table 15 - Hot Test Particle Distribution

**Hot Test No. 1**  
1.5 hr., ≥ 218

<table>
<thead>
<tr>
<th>Sieve Size (microns)</th>
<th>Mass (g)</th>
<th>Percentage of Total Particles</th>
<th>Sieves * %</th>
</tr>
</thead>
<tbody>
<tr>
<td>710</td>
<td>573.6</td>
<td>22.8</td>
<td>161.7386316</td>
</tr>
<tr>
<td>600</td>
<td>449.7</td>
<td>17.9</td>
<td>107.1377889</td>
</tr>
<tr>
<td>500</td>
<td>325.6</td>
<td>12.9</td>
<td>64.65890318</td>
</tr>
<tr>
<td>425</td>
<td>279.6</td>
<td>11.1</td>
<td>47.19661961</td>
</tr>
<tr>
<td>300</td>
<td>247.7</td>
<td>9.8</td>
<td>29.50594472</td>
</tr>
<tr>
<td>212</td>
<td>216.4658</td>
<td>8.6</td>
<td>18.2236318</td>
</tr>
<tr>
<td>106</td>
<td>159.8642</td>
<td>6.3</td>
<td>6.729253117</td>
</tr>
<tr>
<td>53</td>
<td>117.6498</td>
<td>4.7</td>
<td>2.476149392</td>
</tr>
</tbody>
</table>

**Intended Mass (g)**  
2550  

**Mass Lost (g)**  
147.9  

**Actual Mass (g)**  
2518.2  

**ACPS**  
437.7  

**Mass After Rotation (g)**  
2370.3  

**Percentage of Particles After Rotation**  
94.1
**Conclusion:** An experimental facility designed, fabricated and tested at UNLV Mechanical Engineering Department is now available for performing high temperature attrition tests on SPR particles. This facility can produce a high temperature at nearly 850-900 °C. Several tests have been conducted in the cold flow mode to see the preliminary effects of attrition on these particles. From the initial results it seems that there is a reduction of about 20% in the statistical particle size for an attrition time duration between 1 to 6 hours. Tests are being conducted in the high temperature range and the preliminary result is that for a test duration result of 1 hour attrition test showed about a 14% decrease in the statistical size of these particles.

More tests will be conducted for a longer period of attrition which will have a maximum duration of one day continuous testing in the drum. It is important to recognize that the actual mechanical impact conditions and their frequency may not be the same in this test as opposed to the actual operation of a SPR system. It is anticipated that the frequency of impacts is going to be somewhat higher in the current attrition test due to the fact that the rpm and the proximity of the particles inside the drum could increase significantly the collisions between these particles resulting in a faster reduction of particle size than might be envisioned in a real SPR operation. As hot testing continues, an agreeable sieving time will be established and microscopic images of tested and untested particles will be revealed.

Hence it is imperative to shed some light on the fact that a “scaling time factor” needs to be estimated by looking more carefully as how to estimate the collision frequency in this test vs. an estimated collision frequency in a typical SPR. Having obtained this scaling factor one can then multiply by the duration of tests performed in the present work to try to obtain a more realistic estimate of how long it would take the particles to reach the same level of attrition when the SPR is in operation. It is felt that this is fairly important in eventually trying to estimate in the SPR operation how often should one remove a certain percentage of these particles and replenish them with a new batch to try to keep the statistical particle size as close to the original (untested) as possible.
References


ATTACHMENT E

Argonne National Laboratory (ANL)

Status of the R&D Program for the Cu-Cl Thermochemical Cycle for Hydrogen Production

(50 Pages)
STATUS OF THE R&D PROGRAM FOR THE Cu-CI THERMOCHEMICAL CYCLE FOR HYDROGEN PRODUCTION

SUMMARY REPORT
NOVEMBER, 2009

CONTRACT INFORMATION:

Contract Numbers

Contractor: Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL  60439

Principal Investigator: Michele Lewis
Contact Information: (630) 252-6603; lewism@cmt.anl.gov

Project Management: Richard Farmer
Email: Richard.Farmer@doe.ee.gov
Thermochemical cycles were proposed in the 1970’s as an alternative to and a potentially more efficient method of producing hydrogen from water than electrolysis. The rationale remains the same today. Heat and water are the only inputs in a thermochemical cycle; all chemicals are recycled. Electrolytic processes are substituted for thermal processes in a hybrid cycle. McQuillan et al. [1] and Carty et al. [2] have published very extensive summary reports on thermochemical cycles. The two that had the most attention recently are the thermochemical sulfur-iodine (S-I) and the hybrid sulfur cycles, which require process heat at or above 825°C. Other thermochemical cycles that operate at higher temperatures and that require solar heat sources are also being studied in the Solar Generation of Hydrogen Research Program (SHGR) in the Department of Energy-Energy Efficiency and Renewable Energy (DOE-EERE). These include zinc oxide, reactive and Atomic Layer Deposition (ALD) ferrite, sulfur ammonia, sodium manganese, among others [McQuillan].

DOE recognized that the higher temperatures required for these cycles placed a heavy burden on currently available materials of construction and DOE subsequently supported a program which identified and evaluated thermochemical cycles that could operate with lower temperature heat that could be obtained from new heat sources that are near commercialization, i.e., the power tower for solar heat and the sodium-cooled and the super critical water nuclear reactors. These produce process heat near 550°C. Several potentially high efficiency cycles were identified. Based on various analyses, the copper-chlorine (Cu-Cl) was selected as one of the most promising.

Argonne National Laboratory led the effort to reexamine the potential of the Cu-Cl cycle in 2004. The goal of the program was to evaluate the efficiency and cost of hydrogen production using the Cu-Cl cycle. During this time, proof-of-concept work was completed for the major reactions in the cycle, an AspenPlus® flowsheet was prepared and a conceptual process design was proposed. These were used as the basis of an H2A cost analysis.

Two challenges were identified early in the experimental program, i.e., the need for excess steam to drive the hydrolysis reaction to completion and poor electrolyzer performance due to copper crossover from the anode to the cathode in the electrolyzer. The experimental program has been focused on meeting these challenges and significant progress has been made. For example, we have recently demonstrated that operating the hydrolysis reactor at subatmospheric pressure reduces the need for steam. The impact of the lower amount of steam is greater efficiency and lower capital costs. Two methods to
eliminate copper crossover during electrolysis are also being investigated, (1) identification of a suitable membrane and (2) development of an engineering design. The electrolyzer work has been done primarily by the INERI and NERI-C partners, described below.

DOE also supported research outside of Argonne National Laboratory. An International Nuclear Energy Research Initiative (INERI) was established with Atomic Energy of Canada Limited (AECL). AECL’s work was focused on the development of the electrolyzer in the cycle. AECL also showed that the anode reaction was mass transfer limited and stirring and/or higher operating temperatures reduced the cell voltage from values obtained without stirring and at room temperature. AECL has shown that an electrolyzer with a gap design can also reduce copper crossover significantly. They recently reported that their latest cell design provided 2-3 days of operation with a stable voltage of 0.6 to 0.7 V in a flow-through cell. AECL provided seed money to the University of Ontario Institute of Technology (UOIT) that was used to obtain a $5.5M grant from the Ontario Research Foundation. This grant funded research on various aspects of the Cu-Cl cycle at UOIT and several other universities.

A Nuclear Energy Research Initiative-Consortium (NERI-C) with Pennsylvania State University (PSU), the University of South Carolina (USC), and Tulane University was funded to develop advanced electrochemical technologies primarily for the Cu-Cl cycle. The highlights of the NERI-C research results were the development of the new class of anion exchange membranes and identification of a cation exchange membrane coupled with the development of a special procedure for running the electrolyzer. Both approaches prevented copper crossover for 2-4 hours. (Longer term tests were not possible due to funding limitations.) The latter approach was deemed more successful in that the current efficiency was about ~98%. Corresponding voltage efficiencies were 80% at 0.5 V & 100 mA/cm², 50% at 0.8 V & 350 mA/cm², and 40% at 1.0 V & 550 mA/cm². The current efficiency of 98% means that all but 2% of the current was used to produce hydrogen and a voltage efficiency of 50% means that the applied potential was about 0.8 V when the decomposition potential was about 0.4 V. The theoretical decomposition potential was very close to the experimental value. While this cell voltage is above our target, these experiments were run at room temperature. Other experiments at AECL and PSU have shown that higher temperature operation reduces the applied potential. Other notable accomplishments were the development of a model for the electrolysis process and a determination of the speciation at various conditions.

An information exchange was established with Commissariat à l'Energie Atomique (CEA). CEA has specialized equipment that allows identification of the effluent gases from the hydrolysis reactor. They showed that no chlorine was produced during hydrolysis when the operating temperature was less than 400C.

This report summarizes the status of the R&D effort at Argonne National Laboratory, the NERI-C universities, AECL and CEA. Early work is very briefly described. Details can be found in the references. Recent work is described more fully. Remaining challenges are identified and possible pathways forward are presented.
# TABLE OF CONTENTS

## I. INTRODUCTION .................................1

A. Cycle definition........................................1
B. Cycle evaluation......................................1
C. Experimental research program ..................3
D. Modeling activities.................................4
E. Collaborations .......................................4

## II. RESULTS AND DISCUSSION-EXPERIMENTAL WORK ..........5

A. Hydrolysis reaction ....................................5
   1. Background........................................5
   2. Tests at atmospheric pressure .................6
   3. Tests at subatmospheric pressure .............9
   4. CuCl formation ..................................12
   5. Spectroscopic and conductivity measurements at CEA 13
B. Copper oxychloride decomposition reaction ..........15
   1. Thermogravimetric analyses ..................15
   2. Kinetics and mechanistic study ..............16
C. The electrolysis reaction ................................17
   1. Background ......................................17
   2. Development and testing of anion exchange membranes 17
   3. Electrolysis model development ............19
   4. Further development of the electrolyzer system 21
   5. Summary of results at AECL ..................24
D. Separations .........................................27
   1. Background ......................................27
   2. HCl handling ...................................27
   3. Crystallization ..................................28

## III. RESULTS AND DISCUSSION-MODELING ACTIVITIES ........28

A. Flowsheet development ............................28
B. Conceptual process development .................29
   1. Hydrolysis/oxychloride decomposition reactors 29
   2. Direct heat exchanger ..........................31
   3. Electrolyzer .....................................32
   4. Anode and crystallizer ..........................34
   5. Cathode and hydrogen generator .............35
   6. Efficiency and cost of H₂ production ........36
   7. Modeling activities within the NERI-C program 38

## IV. CONCLUSIONS ........................................39

## V. FUTURE WORK .........................................40

## VII. REFERENCES ........................................40
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Reactions in the Cu-Cl cycle</td>
<td>1</td>
</tr>
<tr>
<td>2.</td>
<td>Some results from fixed bed experiments</td>
<td>5</td>
</tr>
<tr>
<td>3.</td>
<td>Summary of test results for anion exchange membranes</td>
<td>18</td>
</tr>
<tr>
<td>4.</td>
<td>Properties of membranes tested in the electrolyzer</td>
<td>18</td>
</tr>
<tr>
<td>5.</td>
<td>Assumptions in the efficiency/cost estimate for H₂ production</td>
<td>37</td>
</tr>
<tr>
<td>6.</td>
<td>Results of efficiency and H₂A cost analysis for H₂ production</td>
<td>38</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

1a. Schematic of the spray reactor with a pneumatic nebulizer ........................................6  
1b. Second generation hydrolysis reactor ........................................................................7  
2. XRD pattern of a solid product produced with the nebulizer ........................................8  
3. XRD pattern of the solid product produced with an ultrasonic nozzle ......................9  
4. A sensitivity study showing the effect of pressure on steam demand .......................9  
5. XRD patterns of hydrolysis products obtained at 1 and 0.4 bar with the spray reactor/ultrasonic nozzle ..................................................................................10  
6. XRD patterns of hydrolysis products with two preflushing methods .......................11  
7. Concentrations of CuCl and Cu₂OCl₂ in hydrolysis products obtained at 1, 0.7 and 0.4 bar vs. the H₂O/CuCl₂ molar ratio ........................................................................12  
8a. Integrated conductivity of the condensed effluent produced from the hydrolysis reaction vs. temperature ........................................................................14  
8b. Detection of Cl₂ gas during the hydrolysis reaction using UV-VIS spectroscopy vs. temperature ..................................................................................14  
9. Thermogravimetric analysis of CuCl₂ decomposition in Ar (a) and Cu₂OCl₂ decomposition in Ar (b,c) and Ar/steam (d) ........................................................................15  
10. A mass spectrum showing the evolution of O₂ from Cu₂OCl₂ decomposition as a function of temperature in flowing Ar (50mL/min) ..................16  
11a. Speciation diagrams for Cu(1) to Cu(II) in equilibrium electrolysis 0.2 M CuCl + 2M HCl (aq) ..................................................................................19  
11b. Speciation diagrams for Cu(1) to Cu(II) in equilibrium electrolysis 1 M CuCl + 6 M HCl (aq) ..................................................................................20  
12. Single cell polarization curves for the CuCl-HCl electrolysis obtained with the AHA membrane at three temperatures ..............................................21  
13. Schematic diagram of the CuCl-HCl electrolyzer system ........................................22  
14. Polarization curves for CuCl electrolysis using the HYDRion Nafion-based MEAs and two anolyte flow rates at 30C ..................................................23  
15. Voltage efficiency of the CuCl-HCl electrolysis at 26C ...........................................24  
16. The increase in cell voltage with time due to copper crossover ................................25  
17. Schematic of the single cell set-up used to study the electrolysis reaction at Atomic Energy of Canada Limited .................................................................26  
18. Cell voltage vs. time for CuCl electrolyzer ................................................................27  
19. Simplified AspenPlus® flow sheet of the CuCl cycle ..............................................29  
20. Schematic of the hydrolysis/oxychloride decomposition reactors .............................31  
21. Schematic of the granulation of the CuCl with direct heat exchange .......................32  
22. Schematic of the electrolyzer ....................................................................................32  
23. Schematic of PEM electrolyzer cell, single-cell and double-cell ...........................33  
24. Electrolyzer configuration: Individual cells combined in a stack with multiple stacks combined in a module; 3-modules for 3 electrolyte trains ...34  
25. Schematic of the proposed crystallizer .....................................................................35
I. INTRODUCTION

A. Cycle definition

Two versions of the Cu-Cl cycle were reported in the literature [Carty, Dokiya]. Argonne National Laboratory initially studied both of these versions but determined that combining features of both led to a more efficient cycle with a potentially lower cost for H₂ production and a lower maximum process temperature.

Table 1. Reactions in the Cu-Cl cycle

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td>2CuCl₂ + H₂O → Cu₂OCl₂ + 2HCl</td>
</tr>
<tr>
<td>Decomposition</td>
<td>Cu₂OCl₂ → ½O₂ + 2CuCl</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>CuCl + HCl → CuCl₂ + ½H₂</td>
</tr>
</tbody>
</table>

The hydrolysis reaction involves contacting CuCl₂ with steam, i.e., this is a gas-solid reaction for which mass and heat transfer is critically important. The products of the hydrolysis reaction are copper oxychloride, Cu₂OCl₂, which is found in nature as the mineral melanothallite, and HCl + steam. The HCl and steam mixture is subsequently condensed and transferred to the electrolyzer feed tanks. The Cu₂OCl₂ solid product is transferred to a higher temperature reactor where it decomposes to oxygen and molten CuCl salt. The CuCl salt is cooled and its enthalpy is recovered for use in the process elsewhere. The CuCl is then dissolved in HCl solution prior to transfer to the electrolyzer. By conducting the hydrolysis and decomposition reactions separately, the HCl and O₂ gases are generated in different reactors eliminating any mixing of these two gases. In the electrolysis reaction, Cu(I) is oxidized to Cu(II) at the anode while the hydrogen ion is reduced at the anode.

Argonne National Laboratory developed a methodology to evaluate the efficiency of a cycle, when comparatively little information is available. This methodology is summarized below, using the Cu-Cl cycle as an example. More details are found elsewhere [Lewis-1, -2, and -3].

B. Cycle evaluation

Cycle evaluation proceeds through a series of increasingly difficult steps. Chemical viability and thermodynamic feasibility are investigated initially. After these have been demonstrated, other factors, e.g., engineering feasibility, meeting targets for efficiency and costs of hydrogen production are investigated. These evaluations correspond to various levels of process knowledge for which efficiencies can be calculated. The simplest calculation for efficiency, a Level 1 efficiency, is based on the most simplistic representation of the chemistry. Because of the cyclic nature of the chemistry, individual reactions must have high yields of the desired products, no competing or side reactions, and reasonable kinetics to be chemically viable. Thermodynamic feasibility is determined by the enthalpy and free energy changes that correspond to the chemical reactions. For example, free energy changes that are positive suggest that the yields of
the desired products for that reaction will not be high. Thus, Level 2 efficiency is based on more complex chemistry. For example, competing products are allowed and optimization of process conditions is used to improve yields. These concepts are explained in more detail [Lewis-1, -2].

Thermodynamic feasibility is determined by the efficiency calculated for the cycle. Because cycle efficiency is a DOE target, the definition of cycle efficiency used in our calculations is summarized here and is described in more detail elsewhere. Equation 1 gives the thermal efficiency, \( \eta \), as first proposed by Beghi [Beghi]. This is the accepted definition for calculating the efficiency of a thermochemical cycle.

\[
\eta = \frac{-\Delta H^\circ_{298} (H_2O)}{Q_{\text{hot}} + \frac{W}{0.4}}.
\]

Equation 4

The numerator is the standard enthalpy of the formation of (a) liquid water at 25°C, 285.83 kJ/mol, for calculating the efficiency for the higher heating value (HHV), or (b) water vapor at 25°C and 1 atm, 241.83 kJ/mol, for calculating the efficiency for the lower heating value (LHV) of hydrogen. The \( Q_{\text{hot}} \) in the denominator is the heat supplied to the process from external sources. The \( W/0.4 \) is the thermal equivalent of different types of work (chemical, electrochemical, mechanical, electrical, separation, etc.) input into the process. This 40% conversion factor is used to be consistent with other workers. However, if the heat source is the high-temperature gas-cooled nuclear reactor, this factor is expected to be closer to 50% [Brown].

In order to determine the heat requirements for the thermal reactions, the enthalpy and free energy changes are calculated for each of the reactions. The data for all of the chemicals except copper oxychloride were available in the literature. The most reliable data were incorporated into the model [O’Hare]. Since data for copper oxychloride were not available in the literature, they were first estimated and then subsequently measured [Parry]. Heat from exothermic reactions was recovered and used for endothermic processes where integration was possible. The Cu-Cl cycle contains an electrolytic reaction and the electrical work required is significant. Electrochemical work is defined by the free energy change of the electrochemical reaction, \( \Delta G = -nFE^\circ \), where \( n \) is the number of electrons transferred, \( F \) is Faraday’s constant, and \( E^\circ \) is the electrochemical cell’s reversible emf at standard conditions. The Nernst equation, \( E = E^\circ - 2.303 (RT/nF) \ln (K) \), allows the calculation of the reversible cell emf as a function of reactant and product concentrations. However, for the initial calculations when very little process knowledge was available, a value of 0.5 V was used for the cell voltage and overpotentials due to kinetic, mass transfer, and ohmic losses to the thermodynamic cell potential, \( E^\circ \). This value of 0.5 V was measured experimentally but the design of the electrolysis cell was very simple and the concentrations of the CuCl and HCl were not realistic for a commercial application.

For the thermal energy balance and recovery within the thermochemical process, either pinch analysis and/or a heat exchanger network can be used to establish the maximum
amount of heat that can be recovered and recycled internally. In our initial calculations, we used pinch analysis to match the various hot and cold streams, based on the available heat loads and a minimum practical temperature difference driving force of 10°C (for analyses at Levels 1 and 2, see below) for heat transfer. These analyses, then, provided an estimate of the minimum external heat input required for the overall thermally integrated process. The current Aspen flowsheet uses a heat exchanger network.

Efficiency changes with process knowledge. As a result, efficiency values are not static and are frequently updated in practice. For example, before starting work on the development of the Cu-Cl cycle, Argonne National Laboratory completed two types of evaluations, referred to as Level 1 and Level 2. The Level 1 calculations considered only stoichiometric reactions and no separations other than ideal separations. Level 2 calculations for efficiency included the effect of lower yields of the desired products and competing reactions. Level 3 calculations are much more complex, requiring a process simulator, but are more realistic. This work is being done as part of the modeling activities.

C. Experimental research program

The experimental program at Argonne National Laboratory was initially concerned with obtaining proof-of-concept for the two thermal reactions, hydrolysis of CuCl₂ and Cu₂OCl₂ decomposition. For example, we learned that high yields of Cu₂OCl₂ could be obtained in the hydrolysis reaction if an excess of steam was used. Other experiments showed that the decomposition of Cu₂OCl₂ was complete at <550°C and that oxygen was the only gaseous product [Lewis-2, Serban, Carty]. During the second phase of the hydrolysis reactor studies, the experimental program was designed to identify optimum operating conditions and reactor designs to achieve 100% yields of the desired products while minimizing the amount of excess steam and eliminating any competing product formation [Ferrandon-1, -2, -3].

The electrolysis reaction, \(2\text{CuCl} + 2\text{HCl} \Leftrightarrow 2\text{CuCl}_2 + \text{H}_2\text{(g)}\), was demonstrated at Atomic Energy of Canada Limited, Pennsylvania State University (PSU)), and the University of South Carolina (USC). In its simplest form, the electrolyzer is comprised of an anode, cathode, and a membrane that separates the two compartments. At the anode, Cu(I) is oxidized to Cu(II) and at the cathode, hydrogen ion is reduced to H₂. The anolyte is a solution of CuCl and HCl. The HCl is required in the anode because CuCl is nearly insoluble in water but is readily soluble in HCl and/or CuCl₂ solutions due to the common ion effect. The catholyte is an HCl solution.

Two types of membranes have been examined. AECL has focused on proton exchange membranes (PEM) as typically used in fuel cells while Penn State has focused primarily on anion exchange membranes. With a proton exchange membrane, hydrogen ion is transferred from the anode to the cathode while with an anion exchange membrane, chloride ion is transferred from the cathode to the anode. In the first phase of the work at PSU, commercially available anion exchange membranes were characterized and then tested in the electrolyzer. In the second phase, new anion exchange membranes were
designed and fabricated and are now being tested specifically for this application. Copper crossover from the anode to the cathode was observed in most of the past work at both AECL and PSU. When copper deposits in/on the membrane or on the cathode, the performance of the electrolyzer becomes unstable and the cell voltage increases. Much of the most recent work has therefore been concerned with identifying membrane materials and/or improving the electrolyzer design such that copper crossover is either minimized or eliminated. Significant progress has been made recently. PSU has developed a novel anion exchange membrane that prevented copper crossover for two hours while AECL developed a new electrolyzer design that kept the cell voltage constant for 2-3 days.

D. Modeling activities

The modeling program was structured to obtain Level 3 efficiency values and was initiated at the University of Illinois-Chicago (UIC). This work included the design of a flowsheet using Aspen Plus® and the development of a heat exchanger network. This work provided a more realistic assessment of the heat and work demands of the reactions within the cycle. Subsequent work included a more refined conceptual process design by D. Tatterson. Since this process design was based on commercially practiced processes, this exercise also provided an indication of engineering feasibility. The equipment and energy needs for the cycle as a commercial process were estimated using this process design. The Level 3 efficiency was calculated and hydrogen production costs were estimated using the H2A methodology. Optimization work is still ongoing. Alternate flowsheets are being developed under the NERI-C program described below.

E. Collaborations

DOE supported research through an International Nuclear Energy Research Initiative (INERI) with Atomic Energy of Canada Limited (AECL). AECL’s work was focused on the development of the electrolyzer. DOE also supported a Nuclear Energy Research Initiative-Consortium (NERI-C) with three universities, Pennsylvania State University (PSU), the University of South Carolina (USC) and Tulane University. This funding was provided to develop advanced electrochemical technologies primarily for the Cu-Cl cycle. Other tasks for the NERI-C universities include modeling the electrolysis process and identifying the electrochemically active species. The goal is to identify how the electrolyzer’s performance can be optimized theoretically. When the program was first started, there was little knowledge of the species involved in the electrochemical reaction and the kinetics/mechanism was not known. This work is ongoing at Pennsylvania State University and the University of South Carolina.

The remainder of the report is divided into two sections. The first section includes a summary of the most recent experimental work and is divided into four subsections, corresponding to each of the three reactions in Table 1 and to a proposed separation process for removing HCl and unreacted CuCl from the spent anolyte of the electrolyzer. Experimental results from the INERI and NERI-C programs and work conducted at CEA
are included in the appropriate subsection. The second section includes a summary of the modeling activities and a brief description of the current conceptual process design.

II. RESULTS AND DISCUSSION-EXPERIMENTAL WORK

A. The hydrolysis reaction

1. Background
The hydrolysis reaction, \(2\text{CuCl}_2(s) + \text{H}_2\text{O}(g) \rightarrow \text{Cu}_2\text{OCl}_2(s) + 2\text{HCl}(g)\) has been studied for several years. The two major challenges for the hydrolysis reaction are: (1) identification of a reactor design that provides the needed mass and heat transfer required and (2) the need for excess steam to drive the reaction to the right. Both challenges must be met to obtain essentially 100% yields of the desired products, a must for a cyclic process. In addition, to have an efficient and a cost effective process, the steam to \(\text{CuCl}_2\) molar ratio must be as low as possible since heating and vaporizing massive amounts of water is energy and capital intensive.

Several types of reactor designs were tested at Argonne National Laboratory. Our earliest fixed bed reactors comprised of a quartz basket did not provide sufficient mass and heat transfer to obtain high yields of the desired products. The interior of the bed consisted primarily of unreacted \(\text{CuCl}_2\). When very high flow rates of the carrier gas (as measured by the gas hourly space velocity (GHSV)) were used, yields of the desired products were higher as shown in Table 2. In the experiments with a GHSV of 43000 h\(^{-1}\), \(\text{Cu}_2\text{OCl}_2\) represented 87-89 wt% of the product while in experiments with GHSV’s of 8900 and 26000 h\(^{-1}\), \(\text{Cu}_2\text{OCl}_2\) represented 48 and 66 wt%, respectively of the product. Significant amounts of \(\text{CuCl}_2\) also remained in the tests with the lower GHSV. (The amount of \(\text{CuCl}_2\) is not shown but is equal to 100 minus the weight percent \(\text{Cu}_2\text{OCl}_2\) and \(\text{CuCl}\).) Comparison of these data also shows that the \(\text{Cu}_2\text{OCl}_2\) was essentially independent of the percentage of water vapor in the carrier gas for experiments with GHSV of 43000h\(^{-1}\). These results confirmed the need for a reactor design that would provide extremely good mass and heat transfer.

Table 2. Some results from fixed bed experiments

<table>
<thead>
<tr>
<th>S/Cu</th>
<th>Time (min)</th>
<th>GHSV (h(^{-1}))</th>
<th>H(_2)O (%)</th>
<th>Cu(_2)OCl(_2) (wt%)</th>
<th>CuCl (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>60</td>
<td>43300</td>
<td>8</td>
<td>87</td>
<td>12</td>
</tr>
<tr>
<td>52</td>
<td>30</td>
<td>43100</td>
<td>26</td>
<td>89</td>
<td>8</td>
</tr>
<tr>
<td>17</td>
<td>60</td>
<td>8900</td>
<td>26</td>
<td>48</td>
<td>27</td>
</tr>
<tr>
<td>17</td>
<td>60</td>
<td>26000</td>
<td>8</td>
<td>66</td>
<td>17</td>
</tr>
</tbody>
</table>

GHSV = gas hourly space velocity or the carrier gas flow rate divided by the volume of the sample in the fixed bed.
Fluidized bed and rotary reactors were not considered viable options. Early experiments with fluidized bed reactors showed very high flow rates of a carrier gas were necessary and residence times were too long. The rotary reactor available for testing was not suitable for this application because of the corrosiveness of HCl and unreacted steam in the effluent gas and difficulty in removing the solid products.

2. Tests at atmospheric pressure (Magali Ferrandon, ferrandon@anl.gov)

The design that appears the most promising is a spray reactor. Such a reactor provides high mass and heat transfer and is suitable for injecting liquids into a hot environment [Wikipedia]. Spray reactors are used commercially in the recovery of HCl from spent pickling solutions and in pyrohydrolysis. Several different versions of a laboratory-scale spray reactor have now been tested. The first design is shown in Figure 1A. Details of the apparatus are given elsewhere [Ferrandon-2]. It used a ‘pneumatic’ nebulizer, in which the solution of CuCl₂ is injected through a capillary tube and is then atomized at its tip by an inert gas flowing through a concentric outer tube. The mist of CuCl₂ formed as a cone passes into the reactor heated by an external furnace. Superheated steam with an Ar carrier gas was injected either co-currently or counter-currently to the CuCl₂ solution. After optimizing the operating variables, described below, products that contained high yields of Cu₂OCl₂ were obtained only when the solution was injected counter currently to the superheated steam. The second generation reactor is shown in Figure 1B.

Figure 1a. Schematic of the spray reactor with a pneumatic nebulizer as the injector
Figure 1b. Second generation hydrolysis reactor

Figure 2 is an XRD pattern of a sample that contains lines identified as melanothallite, the mineral form of Cu$_2$OCl$_2$, lines identified as CuCl$_2$ and one line characteristic of CuCl at d-spacing 3.14Å. The relative intensities of the lines for CuCl$_2$ and CuCl are small compared to those for Cu$_2$OCl$_2$ and can be used for a qualitative assessment. This sample was obtained under the following conditions, which are shown below to illustrate the large number of variables:
1. CuCl$_2$ solution concentration of 1.2 m.
2. Overall test duration of 75 min.
3. Superheated steam temperature of 450°C.
4. Ar flow rate through nebulizer of 200 mL/min.
5. Ar flow rate through superheated steam line of 200 mL/min.
6. Furnace temperature of 370°C with an internal temperature of 400°C.
7. Flowrate of water to nebulizer during preheat of 1 mL/hour
8. Flowrate of water through superheated steam line during preheat of 0.25 mL/h.

In counter-current operation, most of the steam associated with the solution appeared to escape near the top of the reactor before it could react in the body of the furnace. It was therefore impossible to quantify the steam to CuCl$_2$ molar ratio accurately.
Because the nebulizer was difficult to use and because it required a carrier gas for atomization, the use of an ultrasonic nozzle was recommended [Evans] and the nebulizer was replaced with an ultrasonic nozzle. After optimization of the experimental variables, very good products were obtained when the reactor was operated co-currently. (Counter-current operation has not been studied yet.) A typical XRD pattern is shown in Figure 3. No lines characteristic of CuCl$_2$ or CuCl$_2\cdot$2H$_2$O were visible though the line for CuCl was.

The amount of CuCl was measured as 3-5 wt% using a wet chemistry method in most of the products obtained with the ultrasonic nozzle. (CuCl was determined by dissolving a 50 mg sample in 3 mL of ferric ammonium sulfate reagent (10 g salt in 100 mL of 20% HCl), adding 0.5 mL phosphoric acid, and 20 mL deaerated water, and titrating the ferrous iron produced from cuprous copper. The titrant was 0.05 M ceric sulfate in 1 N H$_2$SO$_4$; ferroin was used as indicator. The titrant was standardized with weighed samples of ferrous ammonium sulfate salt. The uncertainty of the obtained CuCl concentrations was ±3 wt %.)

The amount of Cu$_2$OCl$_2$ was assumed to be 95-97 wt% based on the absence of other phases in the XRD patterns. (Wet chemistry analysis of the three constituents was not possible because of funding limitations.) While XRD does not usually respond to phases present at 5 wt% or less, we do not believe that the products contained CuCl$_2$. The reason for this assertion is that solutions of CuCl$_2$ are intensely colored, a very pale blue for low concentrations and a deep green for high concentrations. When a small portion of the hydrolysis products was washed with water, an insoluble black material precipitated. The water remained clear. Upon standing, the precipitate turned blue/green, a characteristic of copper hydroxychloride, a decomposition product of Cu$_2$OCl$_2$ and water.
3. Tests at subatmospheric pressure (Magali Ferrandon, ferrandon@anl.gov and F. Alvarez)

Examination of the results from the hydrolysis reaction and consideration of Le Chatelier’s Principle suggests that the amount of water required for complete reaction could be reduced by removing the gaseous products or by reducing the operating pressure to drive the reaction to the right. Since HCl is a desired product, we are examining possible methods to run the reaction at reduced pressure. Figure 4 shows the results of a sensitivity study that show a reduction in pressure from 1 bar to 0.5 bar reduces the steam to CuCl$_2$ molar ratio from about 17 to 12 while maintaining the yield of Cu$_2$OCl$_2$ near 100%.

![Figure 4. Results of a sensitivity study showing the effect of pressure on Cu$_2$OCl$_2$ yield versus the steam to CuCl$_2$ ratio at 375°C](image-url)
Experiments to validate this prediction were conducted in the spray reactor/ultrasonic nozzle apparatus to which an aspirator pump was added at the exit of the bubbler. Further details of the apparatus that include the aspirator and the experimental method will be published later [Ferrandon-2]. Preliminary experiments at subatmospheric pressures indicate that it should be possible to reduce the H₂O/CuCl₂ ratio. For example, Figure 5 shows two XRD patterns for hydrolysis products, one prepared at atmospheric and the second at 0.4 bar. The steam to CuCl₂ ratio was 11 in (A) and 15 in (B), less than the ratio of 23 used in the experiments without the aspirator.

Figure 5. XRD patterns of products obtained with the spray reactor/ultrasonic nozzle at 1 and 0.4 bar. The steam to CuCl₂ ratio was 11 in (a) and 15 in (b). The identified peaks correspond to Cu₂OCl₂ (■), CuCl₂·2H₂O (○), CuCl₂ (●), CuCl (▲), and Cu(OH)Cl (Δ).

One change in the procedure that impacted the results was the change in preheating/preflushing conditions. The preflushing consisted of passing 5 mL instead of
0.25 mL of liquid water through the ultrasonic nozzle for 60 minutes prior to starting the test. The higher liquid flowrate was the same as the CuCl$_2$ solution flowrate. This change was made to ensure that the steam to CuCl$_2$ ratio was constant throughout the experiment [Ferrandon-2]. However, there were two unexpected results. One was an increase in the amount of unreacted CuCl$_2$ and the formation of CuOHCl in the hydrolysis products as shown in Figure 6 and also as shown in the tests completed at atmospheric pressure in Figure 5. We believe that the presence of the CuCl$_2$ and CuOHCl peaks indicates that the operating conditions were not sufficiently optimized. Higher furnace temperatures or different flow rates may be needed to further promote the hydrolysis.

![Figure 6. XRD patterns of solid products with two preflushing methods](image)

The identified peaks correspond to Cu$_2$OCl$_2$ (■), CuCl$_2$·2H$_2$O (○), CuCl$_2$ (●), CuCl (▲) and Cu(OH)Cl (Δ). Conditions: CuCl$_2$ solution (5.62 m) = 5 mL/h; H$_2$O=0.5 mL/h; furnace: 370ºC, SHS line: 450ºC. Without pre-flushing: no water through the nozzle; with pre-flushing: 5 ml/hr water through the nozzle for 60 min prior to the introduction of CuCl$_2$ solution.)

All of the solid products from the hydrolysis reaction contained CuCl. The peak for CuCl is identified in Figures 5 and 6 by the closed triangle. Comparison of the XRD data indicated that the hydrolysis products obtained at reduced pressure had less intense peaks for CuCl reflecting a lower concentration then the products obtained at atmospheric pressure. This result was the second unexpected result. Recognizing that this XRD comparison is qualitative, the CuCl concentrations were measured quantitatively using the wet chemistry method, described above. The more quantitative analyses confirmed the qualitative ones. The effect of the different hydrolysis reactor pressures was significant in some cases. For example, the CuCl concentrations in the products prepared at 1 bar and 0.4 bar were 10 and 2 wt%, respectively, when the steam to CuCl$_2$ molar ratio was 15. The amount of CuCl measured in all of the products is shown in Figure 7 by the curves near the bottom of the figure.
Figure 7. Concentrations of CuCl and Cu₂OCl₂ as a function of H₂O/CuCl₂ molar ratio at 1, 0.7, and 0.4 bar (The amount of Cu₂OCl₂ was back calculated using the amount of O₂ released during heating.)

4. CuCl formation
CuCl is ubiquitous in the XRD patterns. There are two modes for CuCl formation.

One is the thermal decomposition of CuCl₂,

\[
2\text{CuCl}_2 \leftrightarrow 2\text{CuCl} + \text{Cl}_2
\]

and the second is the thermal decomposition of Cu₂OCl₂

\[
\text{Cu}_2\text{OCl}_2 \leftrightarrow 2\text{CuCl} + \frac{1}{2}\text{O}_2.
\]

The reaction 5 represents a parasitic reaction in that the decomposed CuCl₂ is not available for hydrolysis. The more important effect is that chlorine is formed and released into the effluent gas stream from the hydrolysis reactor. According to the conceptual model, described below, the effluent will be condensed prior to being sent to the cathode feed tank. Any dissolved Cl₂ and its dissolution products in water, HOCI and chloride ion, would be contained in the cathode feed and could adversely affect the performance of the electrolyzer. For this reason, either the Cl₂ must be removed in a separation step or not allowed to form, preferably the latter. Reaction 6 is somewhat less problematic. The decomposition of Cu₂OCl₂ is not a parasitic reaction because it occurs as the next step in the cycle. The major effect would be the release of O₂ into the gaseous effluent from the hydrolysis reactor. While O₂ is only slightly soluble in water
and presumably in HCl solutions, a separation step to remove the O₂ represents an additional capital cost if it is shown to be necessary.

The data at the top of Figure 7 above show the results of monitoring the oxygen evolution from the products of the hydrolysis reaction. The experiment consisted of heating the samples with a continuous flow of 50 ml/min Ar at a heating rate of 5°C/min from room temperature to 700°C and using mass spectrometry to analyze the effluent gases. (Zeton Altamira, Model AMI-100, equipped with a Dycor Dymaxion quadrupole mass spectrometer). The amount of O₂ was calibrated using a known amount of Cu to form CuO in presence of 5% O₂/He. The amount of O₂ from each sample was back calculated using the calibration data and the peak area of the O₂ curve. Samples with the highest amount of oxygen recovered were obtained from the subatmospheric experiments, which also contained the lowest concentration of CuCl. No chlorine or any other gaseous product was observed other than the oxygen. These data suggest that the CuCl observed in the product may be the result of Cu₂OCl₂ decomposition. Other data, discussed below, support this suggestion.

5. Spectroscopic and conductivity measurements at CEA (D. Doizi, [denis.doizi@cea.fr])

Several types of experiments have been completed to determine which of the reactions for CuCl formation is the most important. Conductivity, pH and UV-VIS spectroscopy measurements were used by Doizi et al. at the Commissariat à l'Energie Atomique (CEA). Their experiments are described in detail elsewhere [Ferrandon-2, Croizé]. In their experiments, CuCl₂ particles were contacted with steam from 190 to 540°C, with a hold period of 30 minutes at 390°C. The integrated conductivity of the condensed effluent increased with time as shown in Figure 8a corresponding to the sorption of the generated HCl. Doizi noted that the concentration of chloride ion was calculated from the conductivity measurements as 0.0115 mol/L while the pH measurement indicated a hydronium ion concentration of 0.01116 mol/L. The gaseous effluent was analyzed in real time by UV-VIS spectrometry. Chlorine has an absorption band between 300 and 400 nm. No chlorine was observed spectroscopically until the temperature reached 400°C and above, as shown in Figure 8b. These data suggest that the thermal decomposition of CuCl₂ to CuCl and Cl₂ does not occur until 400°C.
Figure 8a. Integrated conductivity of the condensed effluent from the hydrolysis reaction vs. temperature (Note the 30 min hold time at 390C.)

Figure 8b. Detection of Cl₂ gas during the hydrolysis reaction using UV-VIS spectroscopy. Note the hold time at 390C. The dotted line represents the point at which the temperature was raised from 390 to 400C.

Thermogravimetry and mass spectrometry experiments were conducted at Argonne National Laboratory to further study the thermal stability of CuCl₂ • 2H₂O and Cu₂OCl₂ in the presence and absence of steam. Details of the experiments are given elsewhere [Ferrandon-2]. The data in Figure 10 show the mass loss experienced by the two materials. The temperature profile consists of a heating rate of 2°C/min from room temperature to 150°C with a 30 min hold period at 150°C followed by a heating rate of
2C/min from 150C to 375 or 400C, where the hold time is 1 h. In flowing Ar, the initial weight loss of 22 wt% for CuCl$_2$ $\cdot$ 2H$_2$O represents the loss of the water of hydration and a small amount of sorbed water. A second smaller weight loss of 5.2 wt% starts at about 340C and continues to 375C. This loss includes chlorine released and sublimed CuCl. The weight losses for Cu$_2$OCl$_2$ in dry Ar were 0.5 wt 5% at 375 and 1.7% at 400C. In the presence of 8% steam and a maximum temperature of 375C, the weight loss increased to 4.0%. These data suggest that the decomposition of Cu$_2$OCl$_2$ may be enhanced by the presence of steam. Other experiments are being planned to confirm this hypothesis and, if it is confirmed, to find conditions to minimize the effect.

Figure 9. Thermogravimetric analysis of CuCl$_2$ decomposition in Ar (a) and Cu$_2$OCl$_2$ in Ar (b,c) and Ar/steam (d). Conditions: ~ 100 mg CuCl$_2$ $\cdot$ 2H$_2$O or Cu$_2$OCl$_2$, 50 mL/min Ar, from 25 to 150ºC, 150ºC (30 min), 150 to maximum temperature @ 2ºC/min, maximum temperature (60 min). Maximum temperature: 375ºC (a, b and d), 400ºC (c).

B. Copper oxychloride decomposition

1. Thermogravimetric analyses (M. Ferrandon, Ferrandon anl.gov)
   The decomposition of Cu$_2$OCl$_2$, Cu$_2$OCl$_2$(s) $\rightarrow$ $\frac{1}{2}$ O$_2$(g) + 2CuCl(s) is a relatively simple thermal decomposition reaction. The result of the initial study at Gas Research Institute was that Cu$_2$OCl$_2$ decomposed to produce molten CuCl; O$_2$ production was not confirmed [Carty]. Several more recent experiments have now been run to verify that O$_2$ is the only gaseous product and that the amount of oxygen corresponds to 100% of the theoretical amount [Serban, Ferrandon-1, -2]. The most recent work involved heating a product from the hydrolysis reactor from room temperature to 700C and following the evolution of the gaseous products with a mass spectrometry. The mass spectrum for O$_2$
is shown in Figure 10. The peak area was determined and using a calibration curve, it was determined that the area corresponded to 100% of the theoretical amount if the sample contained 95% Cu₂OCl₂, which is consistent with the presence of some CuCl. Note that evolution of O₂ starts at about 400°C and is essentially completed around 525°C.

Figure 10. A mass spectrum showing the evolution of O₂ from Cu₂OCl₂ produced during the hydrolysis reaction as a function of temperature in flowing Ar (50 mL/min)

2. Kinetics and mechanistic study
An early study that used a mass spectrometer to monitor gas production resulted in a proposed mechanism for the decomposition of Cu₂OCl₂ [Serban]. This study looked at the reaction between equimolar amounts of CuO and CuCl₂ and between CuO and Cl₂. The products of both of these reactions were molten CuCl and oxygen. The study showed that oxygen evolution in the former study started at 450°C, the same temperature at which pure CuCl₂ started to decompose to CuCl and chlorine in the latter study. Moreover, the reactions occurred in steps at various temperatures between 450 and 550°C. The mass spectrums showed that the temperature dependence for O₂ production and Cl₂ production had essentially the same structure. The kinetics of the reaction between CuO and Cl₂ was determined by measuring the reaction rate at four temperatures and monitoring the disappearance of Cl₂. Rate expressions were calculated and the energies of activation were determined. The apparent activation energy for CuCl₂ decomposition was 24.4 kcal/mol and appears to be the rate limiting step. The apparent activation energy for the reaction between CuO and Cl₂ was 12 kcal/mol. These activation energies are relatively low and suggest that no catalyst will be required for these reactions to occur. Based on these studies of the components of Cu₂OCl₂, a two-step mechanism was
proposed for its decomposition: (1) \( \text{CuCl}_2 \) decomposes to give chlorine and (2) the chlorine reacts very quickly with CuO to produce CuCl and oxygen.

C. The electrolysis reaction

1. Background
DOE-NE provided funds for the study of electrochemical technologies for hydrogen production using alternative thermochemical cycles production in the NERI-C program. Three universities, Pennsylvania State University (PSU), University of South Carolina (USC) and Tulane University participated. Below are highlights from their most recent results. Further details can be obtained from progress reports submitted under award number DE-FG07-07ID14886. The authors and contact information of the PI of each section are shown or from papers published by the authors.

The initial goal of the research was to obtain sufficient information about the proposed electrolysis to determine if target values for the cell voltage and current density could be met. A physical model of the electrolysis of CuCl and HCl was developed and the corresponding speciation was defined. Early results from AECL showed that copper crossover occurred with adverse effects. Copper crossover has the potential to be a showstopper because the copper poisons the membrane and causes instability of the cell voltage when copper deposits on the cathode. For this reason, further effort in the NERI-C program was focused on identifying methods and materials that would prevent copper crossover or mitigate its effects.

2. Development and testing of anion exchange membranes(PSU: Mike Chung, Wentian Lin, Elena Chalkova, and Serguei Lvov [lvov@psu.edu])

The main objective of this task was to develop new membrane materials with high Cl\(^-\) conductivity and low Cu permeability to ensure stable and efficient operation of the CuCl/HCl electrolyzer.

New membrane materials that had the potential to prevent copper crossover were designed, fabricated and tested. Suitable membranes had to have good Cl\(^-\) ion conductivity while preventing diffusion of cuprous and cupric ions through the membrane. Table 3 summarizes experimental results for two sets of promising membrane materials. These have very high ion exchange capacity (IEC) values and are stable towards both cuprous and cupric ions. The conductivity tests were carried out at ambient temperature in 2M HCl and 2M HCl + 0.2M CuCl solutions. The membrane samples were equilibrated for 24 hours before starting the conductivity measurements in the same solution.
Table 3. Summary of Cl\textsuperscript{-} Conductivity for anion exchange membranes developed at PSU

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC (mmol/g)</th>
<th>R, Ohm</th>
<th>σ, mS/cm</th>
<th>R, Ohm</th>
<th>σ, mS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-3a</td>
<td>4.0</td>
<td>0.5*</td>
<td>30.06</td>
<td>4.2</td>
<td>3.58</td>
</tr>
<tr>
<td>B-3b</td>
<td>3.1</td>
<td>0.474</td>
<td>106.09</td>
<td>0.8</td>
<td>62.86</td>
</tr>
<tr>
<td>B-3c</td>
<td>3.9</td>
<td>0.904</td>
<td>57.55</td>
<td>1.1</td>
<td>47.29</td>
</tr>
<tr>
<td>C-4a</td>
<td>3.1</td>
<td>4.8</td>
<td>12.04</td>
<td>10.48</td>
<td>5.52</td>
</tr>
<tr>
<td>C-4b</td>
<td>2.9</td>
<td>0.29</td>
<td>119.59</td>
<td>0.44</td>
<td>78.82</td>
</tr>
<tr>
<td>C-4c</td>
<td>2.6</td>
<td>0.98</td>
<td>27.72</td>
<td>1.29</td>
<td>21.06</td>
</tr>
</tbody>
</table>

Note: The conductivity values presented in the table were obtained after equilibration of a membrane in the conductivity cell for 20 minutes

The ionic conductivity appeared to be very high, especially, for membranes B3b and C3b. Two membrane sets (B set without cross-linking and C set with cross-linking) are compared to understand the cross-linking effect to the Cl\textsuperscript{-} conductivity. All of the membranes except B-3a did not show visible Cu precipitation and the usual increase in the membrane resistance after conductivity measurement in HCl-CuCl. This work is considered proprietary at this time.

Commercially available membranes were also tested at PSU. Comparison in Table 4 shows that the recently invented anion exchange membranes offer superior performance to the commercially available ones. However, Nafion, a cation exchange membrane, has higher conductivity than all of the anion exchange membranes. Future work is therefore concerned with both anion and cation exchange membranes.

Table 4. Properties of membranes tested in the electrolyzer

<table>
<thead>
<tr>
<th>Membrane type\textsuperscript{*}</th>
<th>Membrane thickness, Mm</th>
<th>IEC, meq/g</th>
<th>Water uptake, %</th>
<th>Conductivity, mS/cm in 2M HCl</th>
<th>Conductivity, mS/cm in 2M HCl + 0.2 M CuCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHA\textsuperscript{a}</td>
<td>205</td>
<td>2.0</td>
<td>22</td>
<td>12.61</td>
<td>0.66</td>
</tr>
<tr>
<td>AMX\textsuperscript{a}</td>
<td>140</td>
<td>1.4-1.7</td>
<td>25-30</td>
<td>7.65</td>
<td>2.06</td>
</tr>
<tr>
<td>ACS\textsuperscript{a}</td>
<td>110</td>
<td>1.7</td>
<td>25</td>
<td>5.30</td>
<td>0.22</td>
</tr>
<tr>
<td>ACM\textsuperscript{a}</td>
<td>100</td>
<td>1.0</td>
<td>7.5</td>
<td>4.59</td>
<td>0.005</td>
</tr>
<tr>
<td>AM-3\textsuperscript{a}</td>
<td>150</td>
<td>1.3-2.0</td>
<td>15-25</td>
<td>4.45</td>
<td>0.25</td>
</tr>
<tr>
<td>AHT\textsuperscript{b}</td>
<td>350</td>
<td>1.8</td>
<td>10.3</td>
<td>4.82</td>
<td>0.11</td>
</tr>
<tr>
<td>Nafion\textsuperscript{c}</td>
<td>125</td>
<td>0.9</td>
<td>30</td>
<td>90</td>
<td>14.4</td>
</tr>
</tbody>
</table>

Membrane manufacturers: \textsuperscript{a}Tokuyama Soda, \textsuperscript{b}Asahi Glass, and \textsuperscript{c}du Pont de Nemours & Co.
3. Electrolysis model development (Yanming Gong, Elena Chalkova, Victor Balashov, Nikolai Akinfiev, Mark Fedkin,Yaw Yeboah, and Serguei Lvov [lvov@psu.edu])

A thermodynamic model for the Cu(I,II)-HCl-H$_2$O system was developed on the basis of the representative data on CuCl(s) solubility in aqueous solutions of HCl in the concentration interval 1–6 mol kg$^{-1}$ HCl. The model is based on a number of aqueous Cu(I) species [Cu$^+$, CuOH$^+$, Cu(OH)$_2$$^-$$^-$, CuCl$^0$, CuCl$_2$$^-$$^-$, HCuCl$_2$$^0$], aqueous Cu(II) species [Cu$^{2+}$, CuOH$^+$, CuO$^0$, HCuO$_2$$^-$$^-$, CuO$_2$$^{2-}$, CuCl$^+$, CuCl$_2$$^0$, CuCl$_3$$^-$, CuCl$_4$$^{2-}$] and a mixed Cu(I)/Cu(II) chloride aqueous complex, Cu$_2$Cl$_3$$^0$. The thermodynamic approach used a modelling approach based on (1) the standard thermodynamic properties of the listed above species, (2) a model for the activity coefficients, and (3) use of HCh software.

The results of our thermodynamic calculations show that the theoretical OCP for both solutions are close to the experimentally observed values, which are 0.421 and 0.466 V for solutions (a) and (b) respectively. These calculations take into account the influence of a small amount of atmospheric oxygen which is normally dissolved in water. Note that based on our calculations the virtually complete conversion of Cu(I) to Cu(II) takes place at ~ 0.7 V.

Thermodynamic analysis was performed to determine the calculated distribution of the main Cu(I) and Cu(II) species versus redox potential ($E_h$) during the equilibrium electrolysis for solutions (a) and (b) in aqueous HCl solution. The results are shown in Figure 11. These data are important for the estimation of the voltage efficiency of the electrolyzer and for understanding the phase equilibria in the anolyte over the experimental ranges of temperature and applied potential. The conditions for the results in Figure 13a are 0.2 M CuCl + 2 M HCl(aq), nominal and in Figure 13b, 1.0 M CuCl + 6M HCl, nominal.

Figure 11a. Speciation diagrams for the Cu(I) $\rightarrow$ Cu(II) conversion in equilibrium electrolysis in 0.2 M CuCl + 2 M HCl(aq)
The main Cu(I) species for the 0.2099 mol kg\(^{-1}\) CuCl(aq) solution in 2.099 mol kg\(^{-1}\) HCl are H\(\text{CuCl}_2\)\(^{\circ}\) and \(\text{CuCl}_2\)\(^{-}\) while the main Cu(II) species are \(\text{Cu}^{2+}\) and \(\text{CuCl}^{+}\). In the more concentrated anolyte solution (b) (1.172 mol kg\(^{-1}\) CuCl in 7.031 mol kg\(^{-1}\) HCl), there are the same Cu(I) species, but the speciation of Cu(II) becomes more versatile with the input of \(\text{CuCl}_2\)\(^{\circ}\), \(\text{CuCl}_3\)\(^{-}\), and \(\text{CuCl}_4\)\(^{2-}\).

Linear sweep voltammetry (LSV) measurements with a scanning range from 0.3 to 0.9 V were also completed at 24, 45, and 65 °C in the cell with the AHA anion-exchange membrane. The results showed are shown in Figure 12. These data suggest that the electrolysis processes were promoted by the temperature increase. A similar effect was observed with the Nafion-115 membrane (Not shown). The apparent enhancement of the electrolytic performance with increasing temperature is likely due to an increase in the transfer coefficient and higher exchange current density. These results are in agreement with those reported by AECL in their half-cell tests. These data suggest that higher operating temperatures will result in reduced cell voltages.
The anode is carbon powder on gas diffusion layer (GDL), cathode is carbon supported Pt on the gas diffusion layer (GDL) with Pt loading of 0.5 mg/cm², anolyte is 0.2 M CuCl + 2 M HCl(aq), and catholyte is 2 M HCl(aq).

4. Further development of the electrolyzer system (PSU: Victor Balashov, Rich Schatz, Elena Chalkova, Mark Fedkin, and Serguei Lvov (lvov@psu.edu))

In the most recent work at PSU, new experimental data on the CuCl-HCl electrolysis was obtained using HYDRion cation-exchange membranes. Reference data on pure H₂O electrolysis were also collected in the same electrolyzer system for comparison. The estimated current and voltage efficiencies for the electrolytic process clearly demonstrate the advantages of the CuCl-HCl system with respect to the amount of electrochemical work required for this part of the Cu-Cl cycle.

The electrolyzer system consisted of a 5-cm² PEM fuel cell hardware (Electrochem Inc.) and associated feed tanks as shown in Figure 13. Currently, the electrolyzer system was upgraded to allow two alternative modes of operation: circulation mode and flow-through mode. In all cases, special precautions were introduced for anolyte preparation to avoid oxidation of the Cu(I) with atmospheric gases and diminishing its reactivity. In all experiments, CuCl + HCl solutions were prepared in an Ar bag, and all solution tanks were purged with Ar gas. To perform electrolysis, the aqueous solution of CuCl (0.2 M) mixed with aqueous HCl (2 M) was supplied to the anode, and the aqueous HCl solution (2 M) or pure water were supplied to the cathode. Further an external voltage (range 0.35–0.9 V) was applied to trigger the hydrogen producing reaction. The H₂ produced in the electrochemical reaction was collected from the cathode side in a gas collector.
The hydrogen produced in the electrochemical reaction $2\text{H}^+(\text{aq}) + e^- = \text{H}_2(\text{g})$ on the cathode was recycled back to tank T-1. The additional pressure was fed to tank T-2 where, by siphon, distilled water was transferred to Tank T-3. The mass of T-3 was measured at constant, 30 second intervals, to determine the production rate and total hydrogen production. The temperatures of the experiment, cathode recirculation tank T-1 and anode supply tank T-5 were monitored by Omega Engineering type K thermocouples. The experimental temperature in all runs was 26 °C. The catholyte solution was normally recycled during the operation. Since the CuCl(aq) was sensitive to oxidation, ultra high purity argon gas was passed through tank T-Ar, the waste and supply tanks, T-4 and T-5 respectively, were connected to T-Ar which maintained a continuous argon environment during the experiment to prevent their contact with air. The experimental variables were electrolyte flow rate and temperature.

The electrolysis in the CuCl-HCl / H$_2$O system was conducted in the flow-through regime four times with the same portion (1.1 kg) of CuCl-HCl aqueous solution at 26 °C during two hours. The experiment was performed at two flow rates of the anolyte: 30 cm$^3$ min$^{-1}$ and 68 cm$^3$ min$^{-1}$. The LSV measurements for the electrolysis performed with HYDRion-1 membrane sample are shown in Figure 14. Obviously, the observed current densities depend on the reagent flow rate, especially in the high current region, where the process kinetics is largely controlled by mass transfer at the electrodes.
Figure 14. Polarization curves for CuCl electrolysis obtained with HYDRion Nafion-based MEAs at two anolyte flow rates at 30°C. Anolyte composition: 0.2 mol kg\(^{-1}\) CuCl in 2 mol kg\(^{-1}\) HCl(aq). The electrode active surface area of 5 cm\(^2\) was used to calculate current density.

The current efficiency, \(\eta_c\), of the CuCl-HCl electrolyzer system can be estimated from the comparison of the experimentally produced amount of hydrogen, \(H_2(\text{exp})\), per unit of time to the theoretical rate of hydrogen gas generation at a particular current density, \(H_2(\text{theor})\), as calculated from the Faraday’s law:

\[
\eta_c = \left[\frac{H_2(\text{exp})}{H_2(\text{theor})}\right] \times 100\%
\]

(7)

Based on the relatively small deviation of the actual process from the Faradaic electrolysis line (Figure 16), the average current efficiency calculated for all experimental points in CuCl-HCl/H_2O system was found to be around 98%. This essentially means that the hydrogen production reaction \(2H^+(aq) + 2e^- \rightarrow H_2(g)\) was the main process consuming applied current, and no side reactions were apparent during the time of the experiment.

The voltage efficiency, \(\eta_v\), was estimated in this study as the percent ratio of the experimentally obtained open circle potential, \(E_{\text{OCP}}(\text{exp})\), to the applied voltage, \(E_{\text{app}}\):

\[
\eta_v = \left[\frac{E_{\text{OCP}}(\text{exp})}{E_{\text{app}}}\right] \times 100\%
\]

(8)

Based on this formulation, it is obvious that the voltage efficiency will be dependent on the current density. The voltage efficiency calculated via Equation (8) for different compositions of anolyte and catholyte using OCP values are shown in Figure 15.
With the current electrolyzer design, the voltage efficiency of 50% is reachable at current density of 0.5 A/cm² in case of relatively concentrated reagents.

The total system efficiency can be estimated as a product of the current efficiency and voltage efficiency and would be close to 50% at the optimal operating current density of 0.5 A/cm².

5. Summary of AECL results  (S. Suppiah [suppiahs@aecl.ca])
Results of early work with a half cell are summarized below. These results have been confirmed by other researchers are PSU and USC.

1. A Pt catalyst at the anode was not necessary. In fact, the current density was higher for a catalyst-free graphite plate electrode than for a Pt/C electrode. At room temperature and 0.9 V, the maximum current density obtained was 429 mA/cm² in a single cell experiment. (The catholyte was 6M HCl while the anolyte was 1 M CuCl in 6 M HCl)
2. The limiting current density increased with temperature under static conditions. At 0.8 V in a static Cu(I) half cell, the limiting current density increased from about 100 to 300 mA/cm² as the temperature was increased from 25 to 80°C for a solution of 1.5 M CuCl in 6 M HCl.

3. The limiting current density increased with stirring, which indicates a mass transfer limited reaction. Under the same conditions as in #2 above, stirring and increasing the temperature from 25 to 80°C, the current density increased from about 320 to 700 mA/cm².

4. At 0.8 V, the limiting current density increased linearly with Cu(I) concentration in the Cu(I) half cell reaction in 6 M HCl solutions.

5. The cell emf was not stable with respect to time as shown in Figure 16, which later work showed to be due to copper crossover.

![Figure 16. The increase in cell voltage with time due to copper crossover](image)

A schematic of AECL’s single cell experimental set-up with recycle is shown in Figure 17. A flow rate of about 1 L/min is typical and both the spent anolyte and catholyte are recycled. Note that the spent anolyte passes through a beaker containing copper metal coils while the spent catholyte passes through two columns prior to recycle. The purpose of the copper metal is to reduce the Cu(II) in the spent anolyte to Cu(I) while the purpose of the anion exchange resin and the chelating IX resin is to remove any copper ion from the spent catholyte. A Nafion membrane and a standard PEM fuel-cell type electrolyzer were used in the initial experiments:
Thus, one of the challenges associated with the electrolyzer’s development is determining the best method to minimize or, preferably eliminate, copper crossover. AECL’s approach has been to change the design of their cell and to replace the Nafion membrane to a cation exchange membrane with a coating selective to monovalent ions relative to divalent ions. Results shown in Figure 18 demonstrate the progress that has been made. Relatively stable voltages have now been achieved for several days instead of the 0.5 to 3 hours shown in past work. The current density in the experiments in Figure 18 was 100 mA/cm². Higher current densities for a given voltage are expected when the cell is operated at higher temperatures.
D. Separations

1. Background
The reactions in Table 1 describing the CuCl cycle are simplistic. They are meant to give an overview of the chemistry. They do not include separations or process steps that show how the reactions are driven to the right and what the effect of non-stoichiometric amounts of reagents is.

2. HCl Handling
For example, the hydrolysis reaction would be written more correctly as \(2\text{CuCl}_2 + 34\text{H}_2\text{O} \rightarrow \text{Cu}_2\text{OCl}_2 + 2\text{HCl} + 33\text{H}_2\text{O}\) on the basis of a steam to CuCl\(_2\) ratio of 17 at atmospheric pressure. What isn’t explicitly addressed is how the HCl and H\(_2\)O effluent would be handled. Since a relatively high concentration (2-6 N HCl) of hydrochloric acid is needed in the electrolyzer, the conceptual process design has focused on reducing the number of moles of steam per mol CuCl\(_2\). The advantages of this approach are a reduction in the energy costs to heat and vaporize the larger amounts of water and in the capital costs that are associated with a large number of large reactors. In addition, it might be possible to transfer the condensed effluent from the hydrolysis reactor directly to the cathode feed tank. For example, if the H\(_2\)O to HCl molar ratio is around 8, the molarity of the condensed hydrochloric acid is near 6N. An optimum steam to CuCl\(_2\) ratio for the hydrolysis reactor would be about 8.
2. Crystallization or handling of ‘spent’ anolyte

A more complex separation is expected to be needed for handling the spent anolyte. According to the Aspen flowsheet, the spent anolyte will contain unreacted CuCl, HCl and the desired CuCl₂. HCl, if carried into the hydrolysis reactor, will inhibit the hydrolysis reaction because it is a product of the hydrolysis reaction, thereby driving the reaction to the left. Sensitivity studies confirm this effect. Unreacted CuCl in the hydrolysis reactor should be inert according to thermodynamics. However, carrying CuCl into the reactor increases its size and provides no benefit.

The conceptual process design specifies a crystallization process for precipitating the CuCl₂ into a slurry with minimal HCl and CuCl. This is based on a model for the crystallization process prepared by P. Mathias [Mathias]. It is based on literature data at 10°C [Novikov]. A temperature dependence for these data was estimated. Before a separation process can be determined and optimized, the solubilities of CuCl and CuCl₂ in aqueous HCl solutions must be measured at the expected operating temperature of the electrolyzer down to about 55°C.

The objective of the crystallizer is to convert the ‘spent anolyte’ into a CuCl₂ slurry for the hydrolysis feed. Separating the CuCl₂ from the other components in the spent anolyte is therefore desirable. The electrolysis experiments (described above) indicate that running the electrolyzer at higher temperatures will reduce the cell voltage requirements and for this reason, we propose to run the electrolyzer near 100°C, will be sufficient to separate the CuCl₂ from the bulk of the HCl and in fact the concentrations of CuCl₂, CuCl and HCl in the spent anolyte are only placeholders at this time. There is literature that shows that the maximum solubility of CuCl₂ and CuCl in HCl solution are 3 and 1 M, respectively. These solutions are quite dense, about 1.5 – 1.5 g/mL.

III. RESULTS AND DISCUSSION-MODELING ACTIVITIES

The modeling effort consists of developing a conceptual process design/Aspen flowsheet, optimizing heat recovery, and minimizing capital costs. Commercially practiced operations were incorporated into the process design wherever possible. Hydrogen production costs were estimated using the H2A methodology.

A. Flowsheet development

AspenPlus was used to simulate the process design. The initial work was done at the University of Chicago-Illinois (UIC) [Nankani]. A simplified version of the Aspen flowsheet is given in Figure 19. This is the flowsheet for which the current values for efficiency are based. This flowsheet is currently undergoing revision and further optimization. Details of the optimization will be presented at a later time.
AspenPlus was used to develop mass and energy balances for a process based on the conceptual process design. The Aspen simulation provided stream flows and properties as well as heat exchanger duties and work requirements for pumps. Heat usage was optimized with pinch analysis and a heat exchanger network. The results are discussed below.

B. Conceptual process design The conceptual design includes four unit operations:
1. The hydrolysis/oxychloride decomposition reactors
2. Direct heat exchanger
3. The electrolyzer
4. The crystallizer

1. Hydrolysis/Oxychloride Decomposition Reactors (Dave Tatterson [tatter@corecomm.net])
The hydrolysis/oxychloride decomposition reactor system consists of two reactor systems—the hydrolysis reactor and the oxychloride decomposition reactor as shown in Figure 20. The feed of the oxychloride decomposition reactor is the product of the hydrolysis reactor. Thermal energy from the nuclear or solar source is used to decompose the Cu₂OCl₂ in the oxychloride decomposition reactor. The reactors are sized using residence times observed in the laboratory. The effluent from the oxychloride decomposition reactor is a molten salt. The heat is recovered in a direct heat exchanger.
In the hydrolysis reactor, the hot, pressurized (24 bar) CuCl$_2$ slurry is sprayed into a superheated (400°C) steam environment at 0.25 bar where it forms a free jet. As the jet expands it aspirates the superheated steam into the jet resulting in high mass and heat transfer between the CuCl$_2$ in the jet and the steam. The CuCl$_2$ is converted to Cu$_2$OCl$_2$ and HCl. The HCl and unreacted steam exit the hydrolysis reactor, are cooled in feed pre-heaters and then fed to the cathode of the electrolyzer via the cathode feed tank. A steam ejector and the volume contraction of the hydrolysis stream as it condenses pulls the vacuum on the hydrolysis reactor. Dry, free flowing solid Cu$_2$OCl$_2$ accumulates at the bottom of the hydrolysis reactor. The solid copper oxychloride flows by gravity through an L valve to the oxychloride decomposition reactor. The hydrolysis reactor is elevated relative to the oxychloride decomposition reactor. The static head of the solids in L valve provide the pressure to move the solids from the hydrolysis reactor to the oxychloride reactor. The stand pipe below the hydrolysis reactor can be fluidized with steam if necessary to assure smooth flow.

The hydrolysis reactor is very similar to a spray roaster used in the steel industry to recover HCl from FeCl$_2$ generated by the steel pickling process [Wikipedia]. The flow of solid Cu$_2$OCl$_2$ from the hydrolysis reactor to the oxychloride decomposition reactor is similar to the flow of cracking catalyst in a fluid bed catalytic reactor in a refinery.

In the oxychloride decomposition reactor, the Cu$_2$OCl$_2$ is heated up to 550C. Between 450 and 550C, the Cu$_2$OCl$_2$ decomposes to oxygen and molten CuCl. The oxygen leaves the oxychloride decomposition reactor as a gas and the molten CuCl spills over the weir. The stand pipe below the oxychloride decomposition reactor can be fluidized with air if required to assure smooth flow into the oxychloride decomposition reactor. Air may be aspirated into the oxygen stream using a venturi valve to cool and dilute the oxygen.
2. Direct heat exchanger  
(Dave Tatterson [tatter@corecomm.net])
The heat in the molten CuCl stream is recovered in a heat exchanger followed by a direct heat exchanger as shown schematically in Figure 21. The molten CuCl enters the direct heat exchanger and is atomized by a spinning disc. As the molten CuCl cools it heats the (acid-poor) vapor stream from the cathode flash. The vapor stream is then feed to the hydrolysis reactor. During the cooling the CuCl is granulated. The granulated CuCl is fed back to the anode feed tank via a screw feeder or via gravity flow. The direct heat exchanger is very similar to the Bateman Granulation system which is used to make granulated steel or slag.
We have assumed that the electrolyzer will operate near 100°C at 24 bar in order to produce hydrogen at 300 psi. A conceptual design for the electrolyzer has been developed and is discussed below.

3. Electrolyzer (Alan Zdune, zdunek@iit.edu)

Figure 22 is a schematic of the electrolyzer as a component of the overall process. More details of the proposed electrolyzer configuration are shown in Figures 23 and 24. It consists of individual electrolyzer cells consisting of a membrane and anodic/cathodic compartments using a modular design of stacks and modules to attain the necessary hydrogen production throughput. The ion-exchange membrane is located in the middle of the cell and is sandwiched between the two electrodes, the anode and the cathode. Both the anode and cathode are porous, carbon/carbon-felt electrodes typically used in PEM fuel cell design. In the CuCl electrolyzer, the cathode has an electrocatalyst layer to promote the hydrogen generation reaction whereas the anode does not need this layer. Moving outwards from the electrode is the bipolar plate, also called a flowplate, which acts as a channel for gas and electrolyte flow into and out of the anodic and cathodic compartments.
In the proposed modular electrolyzer design, multiple cells are combined to make an electrolyzer stack. The stacks are then arranged into core modules of 2 or more stacks each in order to optimize the reactant/product flow, power, and operational and maintenance requirements. For the CuCl hybrid thermal process, three electrolyte flow trains have been proposed. Thus, the electrolyzer stacks should be grouped in such a way to make three core modules with a single input and output stream each for the anode and cathode electrolyte flows and with the proper amount of stacks per module to generate the hydrogen throughput. For a single cell area of 3 m², 300 cells/stack and 10 stacks/module, 6 modules (2 per process train) are required to achieve the 27,000 m² to produce 125,000kg of hydrogen/day. The 6 modules are contained in 9 pressure vessels as shown in Figures 23 and 24.
Figure 23. Schematic of PEM electrolyzer cell, single-cell and double-cell.

Figure 24. Electrolyzer configuration: Individual cells combined in a stack; multiple stacks combined in a module; 3-modules for 3 electrolyte trains

4. Anode and Crystallizer Subsection (Dave Tatterson [tatter@corecomm.net])

Figure 25 shows a schematic of the anode and crystallizer. The inlet streams to the anode feed tank are feed water, recycled granulated CuCl, any make up HCl and crystallizer recycle. The solution containing dissolved CuCl, HCl and residual CuCl₂ is then pressurized to 24 bar and transferred to the anode section of the electrolyzer. At the anode the CuCl is oxidized to form CuCl₂. The conversion of CuCl to CuCl₂ is expected to be about 80-90% for a liquid electrolyzer. The spent anolyte is transferred to a crystallizer. This cooler could be similar to the scrapped surface crystallizer manufactured by Armstrong Engineering. After exiting the cooler, the solid CuCl₂ is
collected in the bottom of a hydroclone. The product CuCl₂ is the feed to the hydrolysis reactor. The overflow of the hydroclone is recycled back to the anode feed tank through a pressure let down valve.

![Schematic of the proposed crystallizer](image)

**Figure 25. Schematic of the proposed crystallizer**

5. **Cathode and Hydrogen Generation Section (Dave Tatterson [tatter@corecomm.net])**

   In the current conceptual design, aqueous HCl is pumped (24 bar) from the cathode feed tank to the cathode. At the cathode the H⁺ ion is reduced to H₂. The chloride ion migrates across the electrolyzer membrane as described above. Water and unreacted HCl are then heated to 106°C and flashed to atmospheric pressure. The vapor from the flash (which contains less than 1mole % HCl) is then sent to the direct heat exchanger and superheated to 400°C. It is then sent to the hydrolysis reactor. The liquid stream from the flash is recycled back to the cathode feed tank. However, based on the results of the most recent tests from AECL and PSU, this part of the conceptual design is undergoing revision.
6. Efficiency and cost of H₂ production (Dave Tatterson [tatter@corecomm.net])

Aspen Plus was used to develop mass and energy balances for a process based on the conceptual process design [Nankani]. The heat and energy demands for the chemical plant, the solar plant and the intermediate heat exchanger were determined for a CuCl cycle plant producing 125 MT H₂/day as 191 MW of thermal energy and 100.5 MW of electrical energy [Kolb]. The energy efficiency of the process is defined as energy out divided by energy in. This calculation assumes a 40% factor for converting heat to electricity. Based on the low heating value for hydrogen, the efficiency of this process was estimated as:

\[
\text{Efficiency} = \frac{\text{Mol. of H}_2 \text{ Produced} \times \text{LHV}}{\text{(Shaft work + Electrochemical work + Pinch Heat)}}
\]

Efficiency = 125,000 x 33.3/ (24(3000/0.4 + 97,500/0.4 + 191,000) = 39%(LHV) \quad (9)

This efficiency value is subject to change as more is learned about the chemistry within the cycle. For example, the operability of the crystallizer has not been demonstrated. In the crystallizer the spent anolyte is processed into a CuCl₂ slurry suitable for the feed for the hydrolysis reactor. The current Aspen flowsheet assumes a crystallization process in which the CuCl₂ partially precipitates and forms a slurry as the temperature is dropped from >80°C to 55°C. The crystallization process is based upon published solubility data at 10°C and an estimated temperature dependence. The experiments completed to date on the electrolyzer constitute proof-of-concept and suggest that it should be possible to meet the current and voltage targets within the efficiency estimate. For the electrolyzer, the cell operating parameters are assumed to be 0.7 V and 500 mA/cm² for 2015. Technical improvements are assumed for membranes, electrocatalysts, and electrode materials such that a reduction in cell emf to 0.63 V at a current density of 500 mA/cm² for 2025 is possible. Other assumptions are given in Table 5. The current AspenPlus® flowsheet is being revised to include new data.
Table 5. Assumptions in the efficiency/cost estimate for H₂ production

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyzer operates at a current density of 500mA/cm² at 0.7 V (2015) and 0.63V (2025).</td>
<td>Recently 0.7 volts and 100mA/cm² has been obtained at room temperature for 3-4 days. Improvement is expected by operating at 60-100C. A 10% efficiency improvement is assumed between 2015 and 2025.</td>
</tr>
<tr>
<td>Copper does not migrate across the electrolysis membrane</td>
<td>Promising results at AECL and at PSU indicate membranes/methods can prevent copper crossover.</td>
</tr>
<tr>
<td>Electrolysis cell area is 1.5 m² (2015) and 3m² in (2025)</td>
<td>Current state-of-the art, large-scale electrolysers can have electrode sizes of up to 1-1.5 m². Improvements in the multi-stack design, optimized electrolyte flow patterns, increased uniformity of the current/potential distribution in each single cell, as well as solving structural issues inherent in a larger electrode area should allow an increase in size to 3m².</td>
</tr>
<tr>
<td>Corrosion issues can be solved by coating with porcelain coating at a cost of 6% above carbon steel.</td>
<td>Private communication with Steven Pew and Pat Walsh of Porcelain Industries, Inc. of Dickson, TN, suggest that porcelain coated carbon steel is one of the most corrosion resistant materials. The coating costs are in the $1 to $4/sq ft range. Porcelain Industries routinely coat complex pieces of equipment.</td>
</tr>
<tr>
<td>Resident times in the hydrolysis reactor are 5 sec. (2015) and 2.5 sec (2025)</td>
<td>Laboratory results at Argonne and NREL show these residence times to be reasonable and that hydrolysis of CuCl₂ to Cu₂OCl₂ occurs extremely rapidly in high and mass transfer situations.</td>
</tr>
<tr>
<td>Crystallizer operates as a cooler followed by a hydroclone at 55C</td>
<td>Experimental verification is required.</td>
</tr>
<tr>
<td>Bulk HCl cost is $241/metric ton. Bulk CuCl cost is $7200/metric ton.</td>
<td>These values were obtained from the internet. (2007)</td>
</tr>
<tr>
<td>Cost of heliostat field can be reduced from $127/m² in 2015 to $90/m² in 2025.</td>
<td>Sandia National Laboratory provided these estimates [Kolb].</td>
</tr>
</tbody>
</table>

The cost of hydrogen production was estimated using the H2A methodology. The results of the H2A analysis are summarized in Table 6 [DOE-H2A Analysis]. These results have been reviewed and approved by TIAX but are subject to the same limitations as the efficiency estimate above. Within the sensitivity range, the envisioned CuCl
thermal/chemical hybrid process has the potential to meet DOE’s goal of $3/gge at the plant gate. These results are based on the use of solar power tower as the heat source.

### Table 6. Results of efficiency and H2A cost analysis for H2 production

<table>
<thead>
<tr>
<th>Case</th>
<th>Capital Investment, $MM, Solar/Chemical</th>
<th>Cell EMF, V</th>
<th>Electrical Cost, $/kw</th>
<th>$/kg of H2</th>
<th>Sensitivity Range, $/kg</th>
<th>Efficiency, % (LHV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar 2015</td>
<td>208.3/138</td>
<td>0.7</td>
<td>0.068</td>
<td>4.53</td>
<td>3.78-5.31</td>
<td>39</td>
</tr>
<tr>
<td>Solar 2025</td>
<td>168.5/110.6</td>
<td>0.63</td>
<td>0.048</td>
<td>3.48</td>
<td>2.91-4.11</td>
<td>41</td>
</tr>
</tbody>
</table>

7. **Modeling activities within the NERI-C program (Dr. T. Stanford, stanford@cec.sc.edu)**

Modeling activities were also supported in the NERI-C program. Dr. T. Stanford at USC has been involved in exploring other separation processes and the effect they have on efficiency. This work is ongoing. The work involved simulating several variations of the initial conceptual design using AspenPlus®. The efficiency of the Cu-Cl cycle is primarily dependent on the management of the effluent HCl-steam mixture from the hydrolysis reactor and consequently work was focused on investigating and optimizing methods for separating/recycling this stream.

Alternative methods for the separation of the HCl-water mixture, including electrodialysis (ED) and distillation, have been considered. While ED (or an alternative separation) is less energy intensive than distillation, little improvement in cycle efficiency is achieved because condensation of the hydrolysis reactor product gas and vaporization of the water recycled to the hydrolysis reactor are required in these schemes.

Current work has focused on improvement in cycle efficiency by (a) eliminating the HCl-water separation and (b) minimizing the amount of energy required for condensation and vaporization of process streams. Several simulations have been completed that require mixing of various amounts of catholyte from the electrolyzer with condensed product vapor from the hydrolyzer. Because these schemes involve recycle of some HCl and water to the hydrolysis reactor, the temperature of the hydrolysis reaction needs to be increased by 5 to 15°C. Removal of the HCl-water separation step from the design not only eliminates this energy load from the cycle, but also makes it possible to reduce the amount of process fluid condensed and vaporized. These design improvements have resulted in improved cycle efficiency.

To eliminate the need for condensation of the hydrolysis reactor product gas, a simulation was completed in which a semipermeable membrane is used to remove light gases from it. Only that portion of this stream not required for recycle to the hydrolysis reactor is condensed. Further, this simulation assumes that the electrolyzer employs a cation exchange membrane (all previous schemes had assumed that the electrolyzer employed
an anion exchange membrane) and requires no liquid catholyte. This greatly simplifies the design and further reduces the energy load for the cycle. This scheme has the highest cycle efficiency of all the conceptual designs studied to date.

The change in the electrolyzer design to one that does not use a liquid catholyte feed was proposed by Dr. J. Weidner, also at USC. Besides possible improvements in cycle efficiency calculated in the simulation, another advantage of such a design, according to Dr. Weidner, is that copper crossover should be completely eliminated.

IV. CONCLUSIONS

Significant progress has been made in our understanding of the hydrolysis reaction. Our recent experimental work has shown that using subatmospheric pressures in the hydrolysis reactor will permit reduction in steam usage. Steam to copper chloride molar ratios for experiments run at subatmospheric pressures were reduced by about a factor of 2, compared to those run at atmospheric pressure. In addition, the amount of CuCl measured in the products obtained at 0.4 bar was significantly less in those obtained at 1 bar. Moreover, various spectroscopic and thermogravimetric studies indicate that the formation of CuCl during the hydrolysis reaction is not primarily caused by CuCl₂ decomposition to CuCl and Cl₂ but by Cu₂OCl₂ decomposition to CuCl and O₂. The latter reaction appears to be catalyzed in a steam environment.

Progress has also been made with the electrolysis reaction by our INERI and NERI-C partners. AECL has run their electrolyzer for 2-3 days at stable voltages, 0.6 to 0.7 V, at room temperature, suggesting that copper crossover, if it occurred, did not have an adverse effect on the electrolyzer’s performance. The improvement is credited to an modifications in the electrolysis cell design. It is important to note that the target for the electrolysis cell’s voltage is 0.7 V for 2015 and 0.63 V for 2025 with a current density of 500 mA/cm². While the cell voltages obtained by AECL are near the targets, the current density was lower at 100 mA/cm². Further improvement is expected because other tests at both AECL and PSU showed that current density increased with operating temperature for a given voltage. A unique anion exchange membrane has been developed at PSU that prevents copper crossover for up to 2 hours.

Modeling activities are ongoing. Using the current conceptual process design, the efficiency was calculated using an AspenPlus® flowsheet/heat exchanger network and a cost analysis was completed using the H2A methodology. This work shows that the Cu-Cl cycle has the potential to meet DOE’s targets. Work is ongoing to investigate other methods for handling the HCl and steam/water mixture, which has been recognized as the primary driver for the heat load and much of the cost of the chemical plant.
V. FUTURE WORK

Future work consists of optimizing the operation of the hydrolysis reactor at subatmospheric pressure and then designing larger scale equipment. Kinetic and mechanistic studies are planned to assist in the optimization. A materials testing program will also be part of this task because this reaction involves the most corrosive materials—liquid CuCl₂ at the entrance, steam and HCl near 400°C at the exit.

All of the steps in the cycle have been demonstrated either in the lab or modeled except the crystallization process. An energy efficient method to separate most of the CuCl₂ from an aqueous hydrochloric acid solution of CuCl and CuCl₂ must be developed. The current flowsheet uses literature data to estimate the solubility of CuCl₂ in an aqueous solution containing CuCl₂, CuCl and HCl. These data were obtained at 10°C and a temperature dependence was estimated. Measured data are required for future work. We are therefore planning to measure solubility of CuCl and CuCl₂ in the 4 component system at higher temperatures, from 55 to near 100°C and with various HCl concentrations. These measured data will be added to the model. Experiments will then be conducted to demonstrate the crystallization process as proposed in the current flowsheet. Alternate separation processes, such as evaporative cooling may also be investigated. This type of crystallizer promotes supersaturation by removing the solvent, thereby increasing solute concentration.

As funds permit, Argonne National Laboratory will start an experimental program to investigate various electrolyzer cell designs (narrow gap-wide gap) and to optimize operating conditions, e.g., anolyte and catholyte feed compositions, temperature, flow rate, etc.

REFERENCES

[Beghi]

[Carty]

Brown

[DOE]

[Doizi]

[Dokiya]

[Evans]
R. Evans, personal communication, Argonne National Laboratory, 2008.

[Ferrandon-1]

[Ferrandon-2]

[Ferrandon-3]

[Kolb]
G. Kolb, Personal communication, Argonne National Laboratory, 2008.

[Lewis-1]

[Lewis-2]

[Lewis-3]
[Nankani]

[Parry]
T. Parry, I. Thermodynamics and Magnetism of Cu₂OCl₂ and II. Repairs to Microcalorimeter, A Thesis submitted to the faculty of Brigham Young University, December, 2008.

[Mathias]

[Novikov]

[Serban]

Wikipedia
[http://en.wikipedia.org/wiki/Hydrochloric_acid_regeneration]
ATTACHMENT F

University of Colorado

Development of a Solar Thermal $Z_nO/Z_n$ Water Splitting Thermochemical Cycle

(19 Pages)
Development of a Solar-thermal ZnO/Zn Water-splitting Thermochemical Cycle

Final Report (DE-PS36-03GO93007 - Subcontract RF-05-SHGR-006)

Alan W. Weimer (PI), Christopher Perkins, Paul Lichty, Hans Funke, Jeremy Zartman, and David Hirsch
Department of Chemical and Biological Engineering
University of Colorado
Boulder, CO 80309-0424

Carl Bingham and Allan Lewandowski
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401-3393

Sophia Haussener and Aldo Steinfeld
Department of Mechanical and Process Engineering
ETH Zurich
8092 Zurich, Switzerland

April 1, 2009

Contact: Professor Alan W. Weimer, (303)-492-3759; alan.weimer@colorado.edu
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/m^2; 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/m^2. 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.

\[
\begin{align*}
\text{ZnO} & \rightarrow \text{Zn} + \frac{1}{2}\text{O}_2 \\
\text{Zn} + \text{H}_2\text{O} & \rightarrow \text{ZnO} + \text{H}_2 \\
\hline \\
\text{H}_2\text{O} & \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2
\end{align*}
\]

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 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:


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):


**Aerosol Dissociation of ZnO**

![Figure 2]

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);


**Figure 3**
Production of hydrogen from Zn/H₂O

![Diagram of reacted particle with passivating ZnO film and nano-size conversion data](Figure 3)

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 MWth
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 MWth each field
Secondary Concentrators: 90.8% efficiency; 106.8 m² surface area each CPC; 7414 suns concentration; of the 40.9 MWth to CPC from one field, 37.2 MWth is delivered to the receiver from one field; 112 MWth 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); ∆T = 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 MWth
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 MWth from each field
Secondary Concentrators: 90.8% efficiency; 106.8 m² each CPC; 7414 suns concentration;
of the 40.9 MWth to CPC from one field, 37.2 MWth is delivered to the receiver from one field;
112 MWth 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); ∆= 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)

\[
\text{ZnO + 3 Ar} \rightarrow \text{Zn} + \frac{1}{2} \text{O}_2 + 3 \text{Ar}
\]

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

\[
\text{Zn} + \text{H}_2\text{O} \rightarrow \text{ZnO} + \text{H}_2
\]

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

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

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

Determine Q reactor for 85% conversion

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

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

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

**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:

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

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

For the 85% conversion case:

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

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

The Zn recovery is the same for both cases:

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

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

70% Conversion:
\[(7.37 \times 10^{11} + 3.70 \times 10^{12} + 1.42 \times 10^{12})(\text{J/day})(1 \text{ hour/3600s})(1 \text{ W/1J/s}) (1 \text{ GW/10^9 W})= 1.6269 \text{ GWhr/day}\]

85% Conversion:
\[(2.95 \times 10^{11} + 3.068 \times 10^{12} + 1.42 \times 10^{12})(\text{J/day})(1 \text{ hour/3600s})(1 \text{ W/1J/s}) (1 \text{ GW/10^9 W})= 1.3286 \text{ GWhr/day}\]

Examining the 70% conversion case:
\[(7.37 \times 10^{11} + 3.70 \times 10^{12} + 1.42 \times 10^{12})/(5.812 \times 10^6 \text{ kg ZnO})(1 \text{ mol/0.08137 kg ZnO})(40.3 \text{ J/mol-K})(5.812 \times 10^6 \text{ kg ZnO})(3 \text{ mol Ar/mol ZnO})(20.786 \text{ J/mol-K}) = 799 \text{ K}\]

Examining the 85% conversion case:
\[(2.95 \times 10^{11} + 3.07 \times 10^{12} + 1.42 \times 10^{12})/(4.7865 \times 10^6 \text{ kg ZnO})(1 \text{ mol/0.08137 kg ZnO})(40.3 \text{ J/mol-K})(4.7865 \times 10^6 \text{ kg ZnO})(3 \text{ mol Ar/mol ZnO})(20.786 \text{ J/mol-K}) = 792 \text{ K}\]
Using this amount of heat for preheat is feasible because the resulting temperature increases in the feedstocks do not exceed 1180-298 = 882 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 m² of heliostat and we have 3 fields per reactor, then each reactor requires 167,813 m² of heliostat (each 156 m²); this requires 15 receivers

Thus, the entire plant requires 2.517 x 10⁶ m² of heliostat. Total land area is 1620 acres. Total CPC area is 4800 m². Each CPC (3 per receiver) is 106.8 m².

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)**

<table>
<thead>
<tr>
<th>Field</th>
<th>West</th>
<th>North</th>
<th>East</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field</td>
<td>.531</td>
<td>.563</td>
<td>.531</td>
</tr>
<tr>
<td>Receiver</td>
<td>.796</td>
<td>.815</td>
<td>.796</td>
</tr>
<tr>
<td>Net</td>
<td>.437</td>
<td>.469</td>
<td>.437</td>
</tr>
</tbody>
</table>

Annual Weighted \(\bar{E}\) = 0.449 (TMY)

Yearly Delivered Daggett (45%), 1252 kWh/m²

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

167,814 m² 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 MWthermal

Figure 5
**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 $2.349 \times 10^6$ 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, $(2.517 \times 10^6$ m²/total system)($126.5/m^2) = $318.4 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 x $126.53/m² = $1,265/m²), purchased, we have $(1,265/m²)(4,800 m²/total system) = $6.07 M purchased
For the 2025 case, we have 4480 m² of CPC at 10 x $90/m² = $900/m²,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 $[600,000 + 17.72 (m)^{2.392}]*1.41$ 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/linear inch)(16)^{0.6} = $72.20/linear inch = $2842/linear m

**2015 Case**
For 70% conversion, 1.74 s residence time is required, requiring 8.49 m 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:
\[(420 \text{ tubes})(\$42,346/\text{tube}) = \$17.79 \text{ M}\]

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/m² 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/m² from Sargent and Lundy) $ 7.55 M
Zinc oxide (45.7 kg ZnO/kg H₂; assuming
  Need for 13 hr inventory; inventory is 2.48 \times 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
<table>
<thead>
<tr>
<th>Item</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Recovery Turbines</td>
<td>$1.56 M purchased</td>
</tr>
<tr>
<td>Zn/H2O Reactor</td>
<td>$0.655 M purchased</td>
</tr>
<tr>
<td>Pumps/Motors</td>
<td>$3.09 M purchased</td>
</tr>
<tr>
<td>VSA (3 stage)</td>
<td>$16.51 M purchased vendor quote</td>
</tr>
<tr>
<td>VSA Screw Compressors (3 stage)</td>
<td>$5.84 M purchased</td>
</tr>
<tr>
<td>Hydrogen compression components</td>
<td>$25.00 M installed from compressor</td>
</tr>
</tbody>
</table>

**2025 Case**
Single Tube Siliconized Graphite Reactors; 85% conversion; single stage VSA; 2nd step at pressure; $90/m² heliostats

**First Step**
- Heliostats ($90/m² 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/m² from Sargent and Lundy) $7.05 M
- Zinc oxide (45.7 kg ZnO/kg H₂; assuming need for 13 hr inventory; inventory is 2.48 x 10⁶ 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/H2O Reactor (2 X for 300 psig) $1.20 M purchased
- Pumps/Motors $0.54 M purchased
- Power Recovery Turbine: $1.56 M purchased vendor quote
- VSA (1 stage) $5.53 M purchased vendor quote
- VSA Screw Compressors (1 stage) $1.96 M purchased vendor quote

**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-h/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 5.00x10⁷ mol/day. The heat of reaction is -105 kJ/mol, so this gives an output of 5.25x10¹² 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 x 10⁷ 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 x 10⁷ mol water/day] (46,330 J/mol) = 2.63 x 10¹² 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 x 10¹² J – 2.63 x 10¹² J = 2.62 x 10¹² J/day remaining for electricity generation. For an 38% efficient power recovery turbine, (.38) (2.62 x 10¹² J/day) (2.778 x 10⁻⁷ kW-h/J/day) = 2.72940 x 10⁵ kW-h/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 x 10¹¹ J/day)(1 day/24 hr)(1 hr/3600 s)(1.342 x 10⁻³ hp/J/s) = 15,262 hp.

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 (kJ/kg)(100,000 kg/day) = 1.2 x 10¹³ J/day

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

141,600 (kJ/kg)(100,000 kg/day) = 1.416 x 10¹³ J/day
In the second reaction step, $2.62 \times 10^{12}$ J/day is recovered for electricity generation at 80%, leaving $2.096 \times 10^{12}$ J/day recovered energy as electricity.

For the 2015 case, 7.5 kW-h/kg H$_2$ is required for separation and various plant electricity usage. This is $2.7 \times 10^{12}$ J/day of energy; this will be taken from the generated electricity. For the 2025 case, $9.00 \times 10^{11}$ J/day of energy are required for these costs.

2015 case:

For this case, the heat input is:

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

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 H$_2$ production is $(0.449)(0.382) = 17.2\%$ efficient. For the 2025 case, overall efficiency from sun to LHV H$_2$ 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 $762$M 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 $719$M. For the 2025 case, 89% of the capital is solar related.

The base cost of H$_2$ for the 2015 case is $5.58$/kg H$_2$, while $4.14$/kg H$_2$ for the 2025 case. Tornado charts in Figures 8 and 9 show the sensitivity of selling price as a function of various cost inputs.
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.
**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:


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

ATTACHMENT G

General Atomics

High Efficiency Generation of Hydrogen Fuels using Solar Thermochemical Splitting of Water

(122 Pages)
January 13, 2011

Dr. Robert Perret, Ph.D.
UNLV Research Foundation
Box 452036
Las Vegas, NV 89154-2036


Dear Dr. Perret:

Enclosed for your use and information is one copy of the paper/report for the reference subcontract:

<table>
<thead>
<tr>
<th>GA REPORT</th>
<th>TITLE</th>
</tr>
</thead>
</table>

If you have any questions or comments, please do not hesitate to contact me by telephone at 858.455.4214, at FAX 858.455.3545 or by E-mail at Troy.Gilson@gat.com.

Sincerely,

Troy Gilson
Contracts Administrator

Enclosure: As Stated

No. of Copies: See Subcontract, Appendix C

Cc: Loni.Benard@unlv.edu
HIGH EFFICIENCY GENERATION OF HYDROGEN FUELS USING SOLAR THERMOCHEMICAL SPLITTING OF WATER

Task — Solar Hydrogen Generation Research Final Report

by

L.C. BROWN and B. WONG

Prepared under Subcontract No. RF-05-SHGR-007 for the University of Las Vegas, Nevada Research Foundation under US Department of Energy Grant DE-FG36-03GO13062

DATE PUBLISHED: JANUARY 2011
HIGH EFFICIENCY GENERATION OF HYDROGEN FUELS USING SOLAR THERMOCHEMICAL SPLITTING OF WATER

Task — Solar Hydrogen Generation Research
Final Report

by
L.C. BROWN and B. WONG

Prepared under
Subcontract No. RF-05-SHGR-007
for the University of Las Vegas, Nevada Research Foundation
under US Department of Energy Grant DE-FG36-03GO13062

GENERAL ATOMICS PROJECT 30232
DATE PUBLISHED: JANUARY 2011
EXECUTIVE SUMMARY

The present work is part of the Solar Hydrogen Generation Research (SHGR) project that is funded by the United States Department of Energy. The goal of the project is to explore and develop thermochemical hydrogen cycles that have high thermal efficiency and have the potential to provide low cost hydrogen. The project was divided into three phases. In Phase I, a survey was carried out to identify in the literature published water splitting thermochemical cycles (TCs) that can be adapted to a solar source. A set of criteria to screen these TCs were established and used to determine the applicability of all TCs to a solar driven device. A total of 360 cycles had been screened and 50 of the top scoring cycles were selected for further analysis in Phase II. In this phase, in depth thermodynamics and process flowsheet studies on the 50 top cycles were carried out in order to determine the feasibility of the reaction steps within each cycle and to calculate the cycle’s thermal efficiency. At the end of Phase II, 14 TCs with the highest thermal efficiency were selected for laboratory feasibility studies in Phase III. The goal is to use the experimental data to further reduce the selected cycles down to a set of two to three for eventual on sun demonstrations.

GA in collaboration with UNLV carried out laboratory studies on the sulfate and the cadmium based cycles among the 14 selected ones. Experiments were conducted to explore the conditions that enhance the reaction kinetics of the low temperature hydrogen generation step for both the manganese sulfate and the molybdenum barium sulfate cycles. Even though the hydrogen reaction was thermodynamically possible, it was found that other more energetically favorable reaction paths existed. Hence, these reactions would have been only possible if their kinetics were fast. Experimental results using a flow through reactor did not show any significant production of hydrogen from the hydrogen generation reactions within these two cycles. Furthermore, characterization of the solid reaction products showed the reactions were dominated by undesirable non hydrogen generating reactions. It was thus concluded that sulfate based TCs are not viable candidates for hydrogen generation using a pure thermochemical approach.

Laboratory work was also conducted to determine the feasibility of the cadmium oxide cycle. The cycle consists of three process steps. First, cadmium oxide is decomposed at elevated temperatures. The decomposed cadmium vapor is then quenched to arrest any cadmium oxygen recombination in the second step. The third step reacts the freshly generated cadmium with water or steam at lower temperatures to generate hydrogen and cadmium oxide. Hence, the feasibility studies were divided into three areas: i) cadmium oxide decomposition, ii) cadmium-oxygen vapor reaction and iii) cadmium hydrolysis.

The effect of carrier gas on the decomposition process was investigated. It was found that decomposition kinetics depend strongly on the diffusion of oxygen gas away from the solid-gas interface.
In addition, presence of oxygen in the carrier gas was also found to promote cadmium-oxygen recombination and thus hindered the forward decomposition. By using a combination of low heating rate and helium as carrier gas, it was shown that decomposition could be completed as low as 1150°C. This could translate to a lower solar field cost and the possibility of using a non-solar heat source. With the generated data, a preliminary cadmium oxide decomposer design concept was made. The design utilized a fluidized bed inside the solar cavity. The circulating motion of the particles provides enhanced mass and heat transfer, which had been shown to be critical for cadmium oxide decomposition.

The reaction rates between cadmium and oxygen vapors were measured at elevated temperatures. This was accomplished by using a novel experimental setup that was designed to work on a TGA. Preliminary measured reaction rates showed that less than 2% of the cadmium vapor had reacted per second. Hence, the quenching of cadmium vapor from the decomposition temperature to a molten state will need to be accomplished in a few seconds to obtain a desirable yield of cadmium for hydrolysis. The complete set of results will provide a more comprehensive picture on the quench rate requirement. This data, along with future quench modeling studies results, will form the basis of the quench process design.

The project also investigated the various pathways to generate hydrogen using both solid and molten cadmium. It was found that carbon dioxide addition and shear deformation of cadmium were both required in order to attain fast hydrogen generation when using solid cadmium. The carbon dioxide helped to break up the protective cadmium hydroxide surface layer and the shearing motion made available fresh cadmium surfaces for reaction. The drawback to this approach is the requirement to separate carbon dioxide gas from the hydrogen that has been generated. Experimental work had also successfully demonstrated the use of molten cadmium to carry out the hydrolysis step. The optimal temperature for fast hydrogen generation was determined to be between 460 – 480°C. It was found that enhanced surface contact between steam and molten cadmium was essential to high steam to hydrogen conversion. A rotary kiln design was used to successfully demonstrate an approach to realize this. Furthermore, it was shown that the addition of inert pellets in the rotary kiln helped enhance the conversion by spreading out the molten cadmium during rotation. Based on the results obtained, a concept for a high pressure rotary kiln to carry out the hydrolysis step on a larger scale was established.

The results from the feasibility studies were used to modify and improve the existing flowsheet for a solar cadmium cycle that generates 100,000kg of hydrogen per day. The cycle was broken down into day time and 24 hours operations. Cadmium oxide and post decomposition vapor quenching were carried out during sunlight hours. Molten cadmium hydrolysis and electricity generation were designed to take place around the clock. This design lessens the dependence on the grid for electricity inputs. Overall thermal efficiency of this flowsheet was calculated to be at 58% (LHV).
In order to prepare the cadmium oxide cycle for an on sun demonstration, the project recommends that cadmium quenching modeling studies be carried out. The results will help design the quench process. In addition, prototypes based on the design concepts for the cadmium oxide decomposer and the cadmium hydrolyzer should be fabricated and tested in order to affirm their validity.
STATEMENT OF OBJECTIVES

1. To survey existing literature and development a database to catalog all thermochemical cycles capable of hydrogen production.

2. Develop a matrix to evaluate all thermochemical cycles that have been identified. Select the most promising cycles for experimental evaluation.

3. Determine the feasibility of sulfate based thermochemical cycles.

4. Determine the feasibility of cadmium based cycles.
DELIVERABLES:

<table>
<thead>
<tr>
<th>Task</th>
<th>Deliverables</th>
<th>Completion (Date)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Literature Survey, Database Establishment and Management</td>
<td>100% (12/2005)</td>
</tr>
<tr>
<td>2</td>
<td>Thermochemical cycles evaluation based on cycle characteristics and thermodynamic data</td>
<td>100% (8/2006)</td>
</tr>
<tr>
<td>3</td>
<td>Laboratory studies on the feasibilities of sulfate based thermochemical hydrogen cycle</td>
<td>100% (1/2007)</td>
</tr>
<tr>
<td>4</td>
<td>Feasibilities studies on cadmium based hydrogen thermochemical cycles</td>
<td>85%</td>
</tr>
</tbody>
</table>

COST SHARE

General Atomics had contributed $486,636 as cost share to this project. This amounts to 23.2% of the total project layout. The cost share effort was used towards process flow sheet design and system engineering for the cadmium cycle, including the solar decomposer and solar field design.
FINANCIAL REPORT

<table>
<thead>
<tr>
<th></th>
<th>Estimated Federal Outlay</th>
<th>Actual Federal Outlay ($)</th>
<th>Estimated Recipient Outlay</th>
<th>Actual Recipient Outlay ($)</th>
<th>Cumulative Federal ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITD Dec 04</td>
<td>80497</td>
<td>20124</td>
<td>80497</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD Mar 05</td>
<td>114014</td>
<td>28503</td>
<td>194511</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD Jun 05</td>
<td>167258</td>
<td>41815</td>
<td>361769</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD Sep 05</td>
<td>120485</td>
<td>30121</td>
<td>482254</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD Dec 05</td>
<td>167148</td>
<td>41787</td>
<td>649401</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD Mar 06</td>
<td>144583</td>
<td>36146</td>
<td>793984</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD Jun 06</td>
<td>143255</td>
<td>35814</td>
<td>937239</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD Sep 06</td>
<td>89175</td>
<td>22294</td>
<td>1026415</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD Dec 06</td>
<td>79426</td>
<td>19856</td>
<td>1105840</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD Mar 07</td>
<td>73846</td>
<td>18462</td>
<td>1179687</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD June 07</td>
<td>104363</td>
<td>21690</td>
<td>1284050</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD Sept 07</td>
<td>122951</td>
<td>44457</td>
<td>1407001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD Dec 07</td>
<td>130397</td>
<td>72196</td>
<td>1537398</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITD May 08</td>
<td>69677</td>
<td>28900</td>
<td>1607075</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total Project</strong></td>
<td></td>
<td><strong>$486636</strong></td>
<td><strong>$1607075</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ACKNOWLEDGEMENTS

In addition to GA and UNLV team members, researchers from Sandia National Laboratory, National Renewal Energy Laboratory and University of Colorado also contributed to the thermochemical cycles survey and screening work (GA Report GA-A24972, May 2005) included in this final report.
# TABLE OF CONTENTS

1. Introduction .................................................................................................................. 1
1.1 Solar Thermochemical Hydrogen (STCH) .................................................................. 2
2. Phase I – TC survey and Preliminary Assessment ..................................................... 4
  2.1 Economic Considerations ......................................................................................... 5
  2.2 Solar Considerations ............................................................................................... 7
  2.3 Literature and Level of Previous Effort ...................................................................... 9
  2.4 Environmental and Safety Studies ........................................................................... 9
3. Phase II – Thermodynamic and Efficiency Evaluation of TC and Preliminary Feasibility Studies ................................................................. 16
4. Phase III – Validation of Sulfate Cycles ..................................................................... 23
  4.1 Experimental Set Up ............................................................................................... 24
  4.2 Manganese Sulfate Cycle Feasibility Studies (PID 131) .......................................... 25
  4.3 Feasibilities studies on Molybdenum Barium Sulfate (PID 149) ........................ 28
5. Cadmium Cycle Feasibility Studies ............................................................................ 34
  5.1 Hydrogen Generation Using Solid Cadmium ......................................................... 36
    5.1.1 Experimental Set Up ......................................................................................... 36
    5.1.2 Effect of Particle Size and Carbon Dioxide Chemical Addition ....................... 39
    5.1.3 Effect of Ammonia Bicarbonate, Mercury and Titanium ................................. 42
    5.1.4 Mechanical Means for Cadmium Size Reduction ............................................. 45
  5.2 Hydrolysis with Molten Liquid Cadmium .............................................................. 47
    5.2.1 Molten cadmium hydrolysis using a steam bubbler system ............................... 48
    5.2.2 Molten cadmium hydrolysis with a rotary kiln ................................................. 55
  5.3 High Temperature Cadmium – Oxygen Recombination Experiment .................... 59
    5.3.1 Cadmium – Oxygen Reaction Experimental Set Up ......................................... 59
    5.3.2 Cadmium – Oxygen Reaction Experiment Results ......................................... 62
  5.4 Cadmium Oxide (CdO) and Cadmium Carbonate (CdCO₃) Decomposition .......... 70
    5.4.1 Experimental Set Up for CdO and CdCO₃ Decomposition Experiments .......... 70
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.4.2</td>
<td>CdO and CdCO$_3$ Decomposition Experimental Results</td>
<td>71</td>
</tr>
<tr>
<td>6</td>
<td>Process Flowsheet Design and CdO Decomposer Design Concept</td>
<td>80</td>
</tr>
<tr>
<td>6.1</td>
<td>Solar Cadmium Hydrogen Process Flowsheet</td>
<td>80</td>
</tr>
<tr>
<td>6.2</td>
<td>Solar Reactor Design</td>
<td>86</td>
</tr>
<tr>
<td>7</td>
<td>Summary</td>
<td>89</td>
</tr>
<tr>
<td>8</td>
<td>Accomplishments</td>
<td>91</td>
</tr>
<tr>
<td>9</td>
<td>Issues and Recommendations</td>
<td>93</td>
</tr>
<tr>
<td>10</td>
<td>Publications and Presentations</td>
<td>94</td>
</tr>
<tr>
<td>11</td>
<td>References</td>
<td>95</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Basic process flow diagram to determine the number of separation steps in PID 131</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>The four solar devices use in Phase I screening. Their operating temperature range is shown with and their “sweet spot” being underlined</td>
<td>8</td>
</tr>
<tr>
<td>2.3</td>
<td>Example of the Phase I scoring results for PID 1-3.</td>
<td>11</td>
</tr>
<tr>
<td>2.4</td>
<td>Coweb plot of mean ranking of forty cycles to investigate the effect of varying weighting parameters.</td>
<td>12</td>
</tr>
<tr>
<td>3.1</td>
<td>Detailed process flowsheet for PID 131</td>
<td>17</td>
</tr>
<tr>
<td>3.2</td>
<td>One of the equilibrium and heat and mass balance reaction calculations used to determine the efficiency of PID 131</td>
<td>18</td>
</tr>
<tr>
<td>4.1</td>
<td>A schematic of the flow through system for experimental studies of the hydrogen generation reaction within the sulfate cycles.</td>
<td>25</td>
</tr>
<tr>
<td>4.2</td>
<td>RGA spectrum from the manganese sulfate cycle hydrogen generation experiment.</td>
<td>26</td>
</tr>
<tr>
<td>4.3</td>
<td>X-ray diffraction spectrum of post experiment residue inside the reaction flask. The diffraction angle for MnSO₃ are marks by the red dots.</td>
<td>27</td>
</tr>
<tr>
<td>4.4</td>
<td>X-ray diffraction spectrum of post experiment residue inside the reaction flask. The diffraction peaks for MnSO₃ are marks by the red dots.</td>
<td>28</td>
</tr>
<tr>
<td>4.5</td>
<td>X-ray diffraction spectrum of post experiment residue inside the flask for the reaction between BaO, SO₂ and H₂O at 100°C.</td>
<td>31</td>
</tr>
<tr>
<td>4.6</td>
<td>The residual gas analyzer data shows the relative vapor pressures of several gases coming off the reaction between BaMoO₄ and sulfurous acid. Note: O₂ and H₂S signals are believed to be artifacts arising from cracking of SO₂ to sulfur (S₃₂ ~ O₂ and S₃₄ ~ H₂S).</td>
<td>32</td>
</tr>
<tr>
<td>4.7</td>
<td>At 2000 seconds, the pressure vessel was opened to vent gases to the residual gas analyzer. No increased H₂ is seen, but plenty of excess SO₂ and water.</td>
<td>33</td>
</tr>
<tr>
<td>4.8</td>
<td>X-ray diffraction spectrum of post experiment residue inside the flask for the reaction between BaO, SO₂ and H₂O at 230°C.</td>
<td>34</td>
</tr>
<tr>
<td>5.1</td>
<td>The process steps in a cadmium oxide thermochemical hydrogen cycle.</td>
<td>36</td>
</tr>
<tr>
<td>5.2</td>
<td>(a) Hepa air handling system for the fume hood. (b) The protective air curtain around the experimental set up</td>
<td>37</td>
</tr>
<tr>
<td>5.3</td>
<td>(a) The bomb that was used for hydrogen generation experiments with solid cadmium. (b) A schematic of the set up with the use of tungsten carbide grinding media.</td>
<td>39</td>
</tr>
</tbody>
</table>
5.4 The bubbling of carbon dioxide helps break up the surface Cd(OH)$_2$ by forming CdCO$_3$.

5.5 SEM micrograph of the cadmium pellet surface (a) before and (b) after reactor with carbon dioxide in a water bath. Cadmium carbonate crystals form on the particle surface as a result of the reaction.

5.6 Temperature and pressure curves of within the pressure vessel resulting from the use of different chemical additions: (a) baseline with no addition, (b) ammonia bicarbonate, (c) ammonia bicarbonate and ammonia hydroxide and (d) titanium powder and ammonia bicarbonate.

5.7 (a) Cadmium pellets before grinding & (b) after 8 minutes in a blender.

5.8 Cadmium-ammonia bicarbonate mixture after 30min in a blender. Cadmium bicarbonate formed as a result of the hydrogen generation reaction.

5.9 SEM micrographs of cadmium pellets that have shear deformed in a blender (a) & (c) without and (b) & (d) without cadmium carbonate addition.

5.10 The effect of temperature on H$_2$ concentration in the process stream for the molten cadmium hydrolysis process.

5.11 A flow through system using water vapor saturated carrier gas for molten cadmium hydrolysis.

5.12 Hydrogen generation rate using a vapor saturated carrier gas flow through system.

5.13 A flow through system using steam for molten cadmium hydrolysis.

5.14 (a) A schematic of the glass capsule for the hydrogen generation reaction using molten cadmium. (b) The actual glass capsule.

5.15 (a) RGA spectrum showing hydrogen generated from the hydrolysis reaction. The MFC output flow rate is constant at 10sccm. (b) The same output stream as measured by the H2 scan.

5.16 Steam to hydrogen conversion in molten cadmium hydrolysis.

5.17 Effect of steam flow rate on the steam to hydrogen conversion ratio for molten cadmium hydrolysis using a bubbler.

5.18 (a) The re-solidified cadmium piece with brown cadmium oxide on the surface. (b) cubic cadmium oxide particles.

5.19 SEM micrograph of CdO particles from hydrolysis reaction at a two set temperatures of 350 and 438C.

5.20 (a) A schematic and (b) the actual rotary kiln-furnace laboratory set up for cadmium hydrolysis. (c) the single ended glass kiln with a cavity for reaction.

5.21 RGA spectrum for a molten zinc hydrolysis run with a rotary kiln.
5.22 RGA spectrum for a molten cadmium hydrolysis run with a rotary kiln. 58

5.23 (a). A schematic of the Cd-O\textsubscript{2} recombination experimental set up for use with a TGA. (b) The actual Cd-O\textsubscript{2} recombination experimental set up (TC: thermocouple) 60

5.24 The effect of spacer height on the TGA crucible temperature 61

5.25 (a) An enclosure with a HEPA filter blower that covers the TGA. This prevents any dust from releasing into the room. (b) A helium quenching gas cutoff setup that stops the He gas flow whenever an overpressure due to a leak is detected inside the TGA 62

5.26 TGA furnace temperature profile: (a) normal set up and (b) with quench tube. 63

5.27 TGA plot from a cadmium-oxygen reaction experiment. (a) temperature and TGA crucible weight profile and (b) temperature and oxygen profile. 64

5.28 Zinc-oxygen vapor reaction rate as a function of oxygen flow rate and TGA furnace set temperature. 66

5.29 Cadmium-oxygen vapor reaction rate for various oxygen flow rate at 1035°C. 67

5.30 Typical TGA CdO decomposition curve 71

5.31 Cadmium carbonate decomposition curves under different gas flow. 72

5.32 Figure 5.32. Effect of carrier gas on the start and end decomposition temperature for cadmium oxide. 73

5.33 CdO decomposition rate in helium a function of temperature 74

5.34 CdO decomposition rate in air a function of temperature 74

5.35 CdO decomposition rate in pure oxygen a function of temperature 75

5.36 The effect of heating rate on CdO decomposition completion temperature in helium 75

5.37 Arrhenius plot and data fitting for CdO non-isothermal decomposition 77

5.38 Effect of carrier gas environment on E\textsubscript{a} and k* for CdO decomposition. 78

5.39 Effect of heating rate on k* and E\textsubscript{a}. 79

6.1 A simplified block diagram of the cadmium cycle flow sheet. 81

6.2 The detail flowsheet for a cadmium hydrogen cycle created with Aspen Plus 82

6.3 The detail flowsheet for a cadmium hydrogen cycle with integrated heat flow and power generation circuit 83

6.4 A block diagram of a 24 cadmium hydrogen flowsheet that takes into account the diurnal nature of the solar heat source 84
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>The detail flowsheet for a cadmium hydrogen cycle that takes into account the diurnal nature of the solar heat source</td>
</tr>
<tr>
<td>6.6</td>
<td>A multi-concentrator cadmium decomposer design which incorporates molten cadmium quenching</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>2.1</td>
<td>The scoring assignment for each individual criterion use in Phase I evaluation</td>
</tr>
<tr>
<td>2.2</td>
<td>Raw weighing factor generated based operation issues and selection criteria</td>
</tr>
<tr>
<td>2.3</td>
<td>Weighing factor for each criterion for the different solar devices</td>
</tr>
<tr>
<td>3.1</td>
<td>Thermal efficiencies for the TC assessed in Phase II of the program.</td>
</tr>
<tr>
<td>3.2</td>
<td>TCs that have been selected for laboratory feasibility demonstration</td>
</tr>
<tr>
<td>4.1</td>
<td>Metal Sulfate Cycles that were chosen for feasibility studies by the GA-UNLV team</td>
</tr>
<tr>
<td>5.1</td>
<td>Cadmium based thermochemical hydrogen cycles</td>
</tr>
<tr>
<td>5.2</td>
<td>Effect of cadmium particle size and carbon dioxide addition on hydrogen generation</td>
</tr>
<tr>
<td>5.3</td>
<td>Summary of the results from runs under different aqueous environments</td>
</tr>
<tr>
<td>5.4</td>
<td>Mohs hardness of various materials</td>
</tr>
<tr>
<td>5.5</td>
<td>Set up parameters and preliminary molten cadmium hydrolysis results in a rotary kiln.</td>
</tr>
<tr>
<td>5.6</td>
<td>Measurement results from zinc-oxygen reaction at various TGA furnace set temperatures and oxygen concentrations.</td>
</tr>
<tr>
<td>5.7</td>
<td>Measurement results from cadmium-oxygen reaction at various TGA furnace set temperatures and oxygen concentrations.</td>
</tr>
<tr>
<td>5.8</td>
<td>Experimental set up conditions for all the cadmium oxide decomposition experiment.</td>
</tr>
<tr>
<td>5.9</td>
<td>Diffusivity of oxygen in various gases at ambient conditions</td>
</tr>
<tr>
<td>5.10</td>
<td>Calculated apparent activation energy for CdO decomposition in various gas environments</td>
</tr>
<tr>
<td>5.11</td>
<td>Effect of loading geometry on cadmium oxide decomposition kinetics</td>
</tr>
</tbody>
</table>
1. Introduction

Solar energy is unique among various renewable energies because of its ability to generate high temperature heat through concentrated solar power (CSP) technologies. The use of CSP to produce a reaction environment of 1500°C or higher has been readily demonstrated. This high temperature heat enables the application of many water-splitting thermochemical cycles (TCs) to produce hydrogen (H₂) that would not have otherwise been possible. A thermochemical water-splitting H₂ cycle usually consists of a series of chemical reactions that sum to a net effect of converting water into H₂ and oxygen (O₂).

Among the reactions, the high temperature endothermic dissociation step that reduces the oxidation state of a chemical, i.e. dissociation of metal oxide into pure metal and O₂, is normally the key. This reaction couples with one or more low temperature exothermic reactions that re-oxidizes the chemical, i.e. increase the oxidation state, via a reaction with water and spontaneously generates H₂. An example of such a TC is given below:

Dissociation: \[ \text{ZnO(s)} \rightarrow \text{Zn(g)} + 1/2 \text{O}_2(g) \] \[2000^\circ\text{C} \] \[ \text{1.1} \]

H₂ generation: \[ \text{H}_2\text{O(g)} + \text{Zn(s)} \rightarrow \text{ZnO(s)} + \text{H}_2(g) \] \[500^\circ\text{C} \] \[ \text{1.2} \]

Net reaction: \[ \text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2 \text{O}_2 \]

There is another class of TC that employs a thermochemical reaction only for the high temperature chemical dissociation step. H₂ is produced via a lower temperature electrolysis step instead of a chemical reaction. This is because for this class of TCs, there is no temperature at which the thermochemical generation of H₂ is spontaneous and it will only proceed if an electrical potential is applied. Such a cycle in which part of the cycle is carried out in an electrochemical cell is termed a hybrid cycle. An example of a hybrid TC is the Westinghouse cycle:

Dissociation: \[ \text{2H}_2\text{SO}_4(g) \rightarrow 2\text{H}_2\text{O(g)} + 2\text{SO}_2(g) + \text{O}_2(g) \] \[~850^\circ\text{C} \] \[ \text{1.3} \]

H₂ generation: \[ \text{2H}_2\text{O(l)} + \text{SO}_2(g) + \text{I}_2(g) \rightarrow \text{H}_2\text{SO}_4(l_1) + 2 \text{HI}(l_2) \] \[120^\circ\text{C} \] \[ \text{1.6} \]

As a general rule, the lower the maximum temperature of the cycle, the more likely that the cycle will require an electrochemical step. A way to avoid this and have a pure TC cycle with a lower peak temperature is to employ multiple reaction steps. An example can be found in the General Atomics sulfur-iodine (S-I) cycle:

Dissociation: \[ \text{H}_2\text{SO}_4(g) \rightarrow \text{H}_2\text{O(g)} + \text{SO}_2(g) + 1/2 \text{O}_2(g) \] \[~850^\circ\text{C} \] \[ \text{1.5} \]

Intermediate: \[ \text{2H}_2\text{O(l)} + \text{SO}_2(g) + \text{I}_2(g) \rightarrow \text{H}_2\text{SO}_4(l_1) + 2 \text{HI}(l_2) \] \[120^\circ\text{C} \] \[ \text{1.6} \]
H₂ generation: \( 2 \text{HI} \rightarrow \text{I}_2 + \text{H}_2 \) ~350°C ——— 1.7

Net reaction: \( \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \) ——— 1.8

TCs are unique because they produce no effluents as all the chemicals are recycled. Heat energy and water are the sole inputs required for hydrogen generation thus making these cycles environmentally attractive and sound. In addition, a TC can be thought of as a chemical heat engine. Just as a mechanical heat engine that converts heat to mechanical energy, a TC converts heat into chemical energy. Also, like a mechanical heat engine, the maximum theoretical efficiency of a thermochemical cycle varies with the source (hot - \( T_h \)) and the sink (cold- \( T_c \)) temperatures in the manner given by Carnot.

\[ \eta \sim (1 - T_c/T_h) \] ——— 1.9

Thus, solar TCs have the capability to achieve much higher efficiencies than conventional hydrogen production methods. Many TCs have been estimated to have efficiencies between 40 to 50% based on the lower heating value of \( \text{H}_2 \). This can be compared to other solar driven \( \text{H}_2 \) generation processes such as electrolysis and photoelectrochemical, which have efficiencies of 22% and 12% respectively. This illustrates both the advantage and potential of producing \( \text{H}_2 \) via a solar driven TC.

### 1.1 Solar Thermochemical Hydrogen (STCH)

The Solar Thermochemical Hydrogen (STCH) program was established in 2003 by the US Department of Energy to conduct research and development into the feasibility of producing \( \text{H}_2 \) via TC using concentrated solar power. (The program was renamed Solar Hydrogen Generation Research (SHGR) in 2004). The program had two main goals: first was to select two to three viable solar TCs for bench scale demonstration and the second was to develop solar tower technology that drives these TCs. It is a collaboration between the University of Nevada Las Vegas (UNLV), the University of Colorado (CU), the National Renewal Energy Laboratory (NREL), Sandia National Laboratories (SNL), the University of Hawaii (HU) and General Atomics (GA). The project was directed by the University of Nevada Las Vegas Research Foundation (UNLV-RF).

The project to select viable TCs for demonstration is divided into three Phases:

1. In Phase I, a survey was carried out to identify all published data for TC-\( \text{H}_2 \) water splitting processes that can be adapted to a solar source. A set of criteria to screen these TCs was established to determine their practicality when used in a solar driven device. A total of 356 cycles have been screened and 50 of the top scoring cycles were selected for studies in Phase II.

2. In Phase II, in depth thermodynamics and flowsheet analysis into each of the 50 top cycles were carried out to determine their thermal efficiency. They were then further down selected to a manageable numbers so that experimental work could be carried out to demonstrate their
feasibilities. Information from Phase I and II were put into a publically accessible database managed by UNLV

3. In the final Phase of the project, feasibility experiments to demonstrate the chemical steps in the 14 selected TCs were conducted. Once a TC was determined to be viable, further experiments were carried out to explore the operating conditions for optimal reaction kinetics and thermal efficiency. In parallel, process modeling and design work were also conducted to set up the TC in a solar plant. This provides preliminary assessments on the economics of the TC. GA, in partnership with UNLV, has carried out feasibilities studies on the sulfate and cadmium based cycles. Process design work was carried out for the cadmium oxide cycle.
2. Phase I – TC survey and Preliminary Assessment

   The first charter of SHGR was to establish a database that includes all the published water splitting TCs along with the relevant technical information. The database is open to researchers and the public who are interested in solar hydrogen. Since many TCs have been proposed over the last 40 years, the survey began with a literature search, performed at UNLV, to identify all published cycles. They were added to an existing database that has been compiled for the purpose of locating cycles suitable for nuclear hydrogen production (Brown 2003). Additional submissions were contributed by other researchers, particularly Claude Royèr (private communications) who had independently added additional cycles to the nuclear cycle database. A smaller scale survey was carried out by the scientists at CEA (Abanades 2006). In the present survey supported by SHGR, more than 350 distinct cycles have been identified and new ones are being added when ascertained. Each cycle is assigned an identification number (PID) in addition to a process name. Furthermore, cycles are also categorized based on elements and chemicals for search purpose.

   The Phase I screening process was designed to restrict the number of TCs that qualified for detailed evaluation. The purpose then was not to select the best processes, but rather to eliminate from consideration those processes that likely would not be worth the effort of a detailed evaluation. The basic methodology for the cycle screening process is based on that used by an earlier study which sought to identify thermochemical water-splitting cycles suitable for nuclear energy (Brown 2003). The basic technique was to establish screening criteria that would discriminate against the less promising processes. The methodology was to choose a set of objective criteria and for each criterion, define a metric that would generate a numerical score in the range of 0 to 10. A weighted average of the scores of the individual criterion would generate a composite score for the cycle.

   Once all the cycles were assembled, we sought to eliminate duplicate cycles. These were often not obvious, for a variety of reasons. As a simple example, one cycle may have 4 steps, one of which is

   \[ \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \quad (2.1) \]

   A similar cycle may have this single step written as 2 reactions, and thus giving a cycle total of 5 steps

   \[ \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_3 \quad (2.2) \]

   \[ \text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2} \text{O}_2 \quad (2.3) \]

   So the latter cycle is a 5 step process, while the former cycle is a 4 step cycle. These two cycles would be classified as duplicate and were merged into one cycle. The compiled database thus resulted in a final total of about 180 distinct cycles.
Sixteen measurable criteria were devised for use in measuring the feasibility of a cycle. The criteria, along with an indication of the metric are given in Table 2.1. For each criterion, a metric was defined and a score of between 0 and 10 was given for each TC. Every attempt was made to make the criteria objective, which was possible in most cases. For example, toxicity rankings were taken from EPA and NIOSH publications. When a chemical was not listed in these compilations, a ranking for the chemical was assigned by an experienced chemist. This ranking was then used for the chemical for any cycle in which it was present. Whenever there was not a published ranking for a criterion, one was established based on the experience and expertise of the contributing members. For example, the corrosiveness ranking stems from the rate of chemical attack on common engineering materials used in chemical plant construction. The criteria used to screen the feasibility of a TC can be broken down into four different general categories: i) economic considerations, ii) applicability to solar power system, iii) level of previous effort and iv) environmental and safety issues. The following sections provide a more detailed description of the criterion in each of these categories.

### 2.1. Economic Considerations

**Criterion 1. Number of chemical reactions**

A two step cycle would in general be less complex than a 5 step cycle: fewer movements of materials, fewer separations and fewer chemicals. Determining the number of chemical reactions in a cycle has been a question in the past. For example, the decomposition of sulfuric acid can be stated as a single chemical reaction or as a pair of sequential reactions:

\[
\text{either } \quad \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \quad ——— 2.4
\]

\[
\text{or, } \quad \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_3 \quad ——— 2.5
\]

followed by

\[
\text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2} \text{O}_2 \quad ——— 2.6
\]

In cases like this, where the reactions could in practice be combined and intermediate chemical separations were not required, the lesser number of reactions was assumed. This actually resulted in a decrease in the number of cycles in the data base as some same basic cycles were often found to have been expressed in multiple ways.

**Criterion 2. Number of separation steps**

A much abbreviated flow diagram was constructed for each cycle in order to determine the number of “difficult” separations needed. It is based solely on the fundamental reaction equations of each cycle. The following types of separations were classified as difficult:
• solid-solid separations, where the products are two solids
• solid-liquid separations, where a filtration or other means would be needed
• liquid-liquid separations, where two liquids (miscible or immiscible) were found.
• gas-gas separations, such as separating O₂ from HCl.
• aqueous/non-aqueous, such as dehydrating aqueous H₂SO₄ to make anhydrous H₂SO₄

Gas-liquid and gas-solid separations were considered “easy” and were not included in the tally for the total separation steps within each cycle. Figure 2.1 shows an example of the process flow diagram used to determine the number of separation steps for PID 131 (Manganese sulfate cycle).

Two other assumptions were made in this evaluation. First, the details of the separation such as the actual operation were not considered. However, provisions were made to include certain straightforward procedures that could be implemented to reduce the number of separation steps. For example, if by cooling the products 100°C, a difficult gas-gas separation could become an easy gas-liquid separation, the processing step would be included in the flow diagram. The second assumption concerns the recycling of chemicals. Since many reactions are at equilibrium and do not proceed to completion, recycle of all liquid and gas reactants from the product stream are required. A significant number of the difficult separations stemmed from recycle of gas or liquid reactants. On the other hand, it was assumed that reactions involving solids will proceed to completion turning all reactants into products and no recycling would be required.
**Criterion 3. Number of chemical elements**

The number of chemicals in a TC indirectly reflects the complexity of the process as a greater number of species have to be dealt with. This normally resulted in a more complex process.

**Criterion 4. Abundance of chemical elements**

The favorable TCs are those that employ common chemicals and elements as they would be less expensive and are readily available in large quantities. This criterion gauges at the abundance of the scarcest element in the cycle, and assigns points based on that limiting abundance.

**Criterion 5. Corrosiveness of chemicals**

Corrosive chemicals require the use of more expensive corrosion resistant equipment. Chemicals were classified from least to most corrosive, based on their corrosiveness on common metallic materials of construction.

**Criterion 6. Degree of solids flow**

This criterion determines the extent to which solids movement and batch processing are required. The movement of solids within a process is often difficult and costly whereas liquids and gases could be transported easily. Hence, TCs with only continuous flow are easy whereas batch processes are difficult. Points were assigned to each cycle based on the most difficult handling step, which have been categorized as follows: (1) continuous flow of gases and liquid, (2) batch flow of gasses and liquid through fixed beds of solids, (3) continuous flow of solids, and (4) batch flow of solids. A cycle which requires multiple handling steps was ranked based on its least desirable chemical transportation step.

### 2.2. Solar Considerations

**Criterion 7. Use of radiant heat transfer to solids**

The transfer of heat to solids is more favored at higher temperatures, so TCs which use very high temperature solids have an advantage in this regard. This criterion sets a sliding scale based on temperature ranges from below 900°C to above 1800°C.
**Criterion 8. Temperature of high temperature endothermic step**

The highest temperature of a cycle was compared to the optimal temperature range for a given solar device. If this temperature was near the “sweet spot”, then a high point score was assigned to the cycle when paired with this device. The further away the temperature was from the “sweet spot”, the lower the point score. Our screening analysis considered the applicability of four solar devices illustrated in Figure 2.2.

For the purpose of rating cycles, cycles which were not well matched to a solar device, and received 0 points on this particular criterion, were excluded from further assessment even though they had high scores from the other criteria.

**Figure 2.2** The four solar devices uses in Phase I screening. Their operating temperature range is shown with the “sweet spot” being underlined.

**Criterion 9. Compatible with thermal transients and/or diurnal storage**

High temperature solar devices shown in Figure 2.2 utilize light concentrated by mirrors to generate high heat. Their effectiveness are greatly reduced when an interruption, such as a passing cloud, occurs between the sun and the mirror field. In addition, they can provide direct heat for only about 8–10 hours per day. The original intension of this criterion was to determine the applicability of a TC to
such start/stop cycles in the heat supply. However, this factor was found to be very difficult to quantify and it was determined that the cycle will be scored based on $O_2$ generation at the high temperature reaction step. A cycle with this characteristic is compatible with direct solar energy input to solids in a windowless receiver.

2.3. Literature and Level of Previous Effort

**Criterion 10. Number of literature papers**

If a TC had been extensively studied, it is a measure of its proficiency and viability. Thus, a higher number of papers published on the cycle would indicate that it will have a better chance to succeed and problems associated with it would have already been addressed.

**Criterion 11. Scale of test**

A given TC can be studied via theoretical calculations, or their feasibility can be demonstrated in a small scale apparatus. Favorable cycles that have been studied would attract support for larger scale efforts: such as bench scale, followed by pilot plant, etc. These TCs probably have a better chance of commercial success.

**Criterion 12. Energy efficiency and Cost**

This criterion sought in the literature where the energy efficiency or cost of a TC has been evaluated from a flow sheet analysis. Cycles that have had such studies are more viable candidates than those which have not been studied.

2.4. Environmental and Safety Studies

**Criterion 13. Acute toxicity to humans**

Chemicals used in a production plant should not be an immediate hazard for injury and death. This criterion looked at “the most dangerous chemical” in a cycle, as determined for acute human exposure. Points were assigned to the IDLH (Immediate Dangerous to Life and Health) values found in the NIOSH (National Institute of Occupational Safety and Health) Pocket Guide to Chemical Hazards.
**Criterion 14. Long term toxicity to humans**

A chemical may be safe for short term human exposure but can be dangerous over long term at low exposure level. This criterion considered “the most dangerous chemical” in a cycle, as determined by chronic long term human exposure. Points were assigned based on the REL (Recommended Exposure Limits) values taken from the NIOSH Pocket Guide to Chemical Hazards.

**Criterion 15. Environmental toxicity**

A chemical may be safe for human exposure but can be deemed damaging to the environment. This criterion examined “the most dangerous chemical” in a cycle, as determined for environmental exposure, from EPA categories of reportable quantities discharged to the environment. These values were found in 40 CFR1, table 302.4 and Appendix A of part 355, and points were assigned accordingly.

**Criterion 16. Reactivity with air or water**

A chemical may be inert in an enclosed setting but may become very hazardous with an accidental exposure to air or water. This criterion took the sum of the NFPA (National Fire Protection Association) hazard ratings for flammability and reactivity with air & water, for each chemical in a cycle, and assigned points based on the highest sum.

The scoring scheme of each criterion, other than those derived from published rankings, was established after careful deliberation among the group members based on their technical expertise and practical experience. All the identified TCs received a base score for all criteria as shown in Table 2.1. However, depending on the thermal solar device that is used to drive the TC, the importance of the individual criterion to the selection process will vary. For example, a trough will not be able to support a reaction that has an endothermic step above 1000°C or a tower is more adaptable to solid flow than a dish. Hence, a **weighting factor** is required when scoring the feasibility of each TC to the various solar thermal devices.

This weighting factor was arrived in two steps using a six-sigma methodology. First, the importance of each of the 16 criteria in relation to the operation of a solar hydrogen production system was determined. Team members from GA, SNL, UNLV and CU identified 5 factors which were essential
in the development and operation of a solar thermal hydrogen production plant and they are i) capital cost, ii) operation and management, iii) development risk, iv) diurnal cycle and v) environmental risk respectively. A multiplication factor (mp) between 1-5 is assigned to each of them based on their importance to the overall selection process. Next, the relevance of each criterion with respect to the 5 operational factors was determined. A relevance value of 0, 1, 3 or 9 is assigned to each criterion according to its significance to the factor (see Table 2.2). A preliminary set of raw weighting factors for each criterion is obtained by totaling the sum of products of the multiplication factor and the relevance value.

The next step was to arrive at a set of weighting factors which are specific to the individual solar devices. Based on the raw weighting factors and the expertise of the team members, weighting factors between 1-10 were generated and assigned to each criterion per solar device (Table 2.3).

The scoring of each cycle was completed by multiplying criteria score with the weighing factor for each individual solar device and then normalized by a score multiplier to make the maximum score 100 points. An example of the scoring result for PID 1-3 is shown in Figure 2.3 (McQuillan 2005). Based on this method, 360 cycles were evaluated and 67 TCs with the highest scores were selected for Phase II studies (see Table 3.1).

<table>
<thead>
<tr>
<th>PID#</th>
<th>name</th>
<th>T (C) Multiplier</th>
<th>Reactions</th>
<th>trough</th>
<th>lower</th>
<th>dish</th>
<th>adv</th>
<th>lower</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfur-iodine</td>
<td>850</td>
<td>2H2SO4(g) = 2SC2(g) + 2H2O(g) + O2(g)</td>
<td>41.92</td>
<td>41.02</td>
<td>53.46</td>
<td>61.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>2H2(g) = 2(g) + H2(g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>2O2(a) + 3SO2(a) + 2H2O = 2H2(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H2SO4(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Nickel-Manganese Ferrite</td>
<td>800</td>
<td>0.50</td>
<td>NiMnFe4O6 + 2H2O = NiMnFe4O8 + 2H2(g)</td>
<td>50.19</td>
<td>50.19</td>
<td>60.42</td>
<td>67.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>NiMnFe4O8 + NiMnFe4O8 + O2(g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Mercury-Calcium Bromide-1</td>
<td>200</td>
<td>1.00</td>
<td>2HBr(g) + Hg(l) = HgBr2 + H2(g)</td>
<td>6.92</td>
<td>6.92</td>
<td>12.69</td>
<td>26.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>2HgO(g) = 2Hg(g) + O2(g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>750</td>
<td>CaBr2(l) + H2O = CaO + 2HBr(g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>CaO + HgBr2 = CaBr2 + HgO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.3 Example of the Phase I scoring results for PID 1-3.

One question that must be addressed was how well does this type of process eliminates from the study those cycles with a low probability of success. Stepwise regression and rank correlation methods were employed by SNL to answer this question. Figure 2.4 shows a coweb plot from this study. The results of this study are that (1) results indicate the selected cycles were not highly dependant on criteria weights, (2) the screening process was robust and (3) it was generally accurate in determining most promising cycles for further analysis.
Figure 2.4. Coweb plot of mean ranking of forty cycles to investigate the effect of varying weighting parameters.
### Table 2.1. The scoring assignment for each individual criterion used in Phase I evaluation.

<table>
<thead>
<tr>
<th>No.</th>
<th>Criteria</th>
<th>CRITERIA SCORE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Number of chemical reactions</td>
<td>&gt;4</td>
</tr>
<tr>
<td>2</td>
<td>Number of separation step</td>
<td>&gt;4</td>
</tr>
<tr>
<td>3</td>
<td>Number of chemical elements</td>
<td>&gt;4</td>
</tr>
<tr>
<td>4</td>
<td>Abundance of chemical elements</td>
<td>fr</td>
</tr>
<tr>
<td>5</td>
<td>Corrosiveness of chemicals</td>
<td>Oxidizing and complexing acid system (H[II], HCl/HNO3)</td>
</tr>
<tr>
<td></td>
<td>Hydrogen halides [HCl, HBr, HI]</td>
<td>Anhydrides of strong acids (H3PO4, HNO3)</td>
</tr>
<tr>
<td></td>
<td>Transition metal salts [CoCl2]</td>
<td>Alkaline and hydrides [NaOH, LiOH]</td>
</tr>
<tr>
<td>6</td>
<td>Degree of solids flow</td>
<td>Batch flow of solids</td>
</tr>
<tr>
<td>7</td>
<td>Use of radiant heat transfer to solids</td>
<td>No high temp heating</td>
</tr>
<tr>
<td>8a</td>
<td>Temperature of high temperature endothermic step</td>
<td>Less than 300°C or Greater than 650°C</td>
</tr>
<tr>
<td>8b</td>
<td>Temperature of high temperature endothermic step</td>
<td>Less than 500°C or Greater than 2200°C</td>
</tr>
<tr>
<td>8c</td>
<td>Temperature of high temperature endothermic step</td>
<td>Less than 400°C or Greater than 700°C</td>
</tr>
<tr>
<td>8d</td>
<td>Temperature of high temperature endothermic step</td>
<td>Less than 500°C or Greater than 2000°C</td>
</tr>
<tr>
<td>9</td>
<td>Compatible with thermal transients and/or dural storage*</td>
<td>O2 release from high temp. oxide</td>
</tr>
<tr>
<td>10</td>
<td>Number of Papers</td>
<td>1, 2-3, 4-6, 7-10, 11-15, 16-21, 22-28, 29-36, 37-45, 46-55, 56+</td>
</tr>
<tr>
<td>11</td>
<td>Scale of test</td>
<td>No lab. work, Test tube, Bench scale, Pilot scale</td>
</tr>
<tr>
<td>12</td>
<td>Efficiency and/or cost figures</td>
<td>No calculated efficiency, Calculated efficiency based on elementary reactions, Estimated efficiency with rough spreadsheet, Calculated efficiency with detailed spreadsheet, Detailed calculated cost</td>
</tr>
<tr>
<td>13</td>
<td>Chemical toxicity to human</td>
<td>IDEL &gt;= 1 ppm U, Hg, As</td>
</tr>
<tr>
<td>14</td>
<td>Long term toxicity to human</td>
<td>REL &gt;= 0.001 ppm As, Be, Cd</td>
</tr>
<tr>
<td>15</td>
<td>Environmental chemical toxicity</td>
<td>Category X (1 lb. reportable), Category A (10 lb. reportable), Category B (100 lb. reportable), Category C (1000 lb. reportable), Category D (10000 lb. reportable)</td>
</tr>
<tr>
<td>16</td>
<td>Reactivity with air and water</td>
<td>&gt;6</td>
</tr>
</tbody>
</table>
Table 2.2. Raw weighting factors generated based on operation issues and selection criteria

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Few reactions</td>
<td>9</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>63</td>
</tr>
<tr>
<td>Fewer steps</td>
<td>9</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>63</td>
</tr>
<tr>
<td>Fewer chemical elements</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>Abundance of elements</td>
<td>9</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>49</td>
</tr>
<tr>
<td>Minimize corrosive chemicals</td>
<td>9</td>
<td>3</td>
<td>9</td>
<td>0</td>
<td>3</td>
<td>81</td>
</tr>
<tr>
<td>Minimize solids flow</td>
<td>3</td>
<td>9</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>57</td>
</tr>
<tr>
<td>Use of radiant heat transfer to solids</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>9</td>
<td>0</td>
<td>45</td>
</tr>
<tr>
<td>Temperature compatible to solar source</td>
<td>9</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>51</td>
</tr>
<tr>
<td>Oxygen release from high temperature step*</td>
<td>9</td>
<td>3</td>
<td>1</td>
<td>9</td>
<td>1</td>
<td>106</td>
</tr>
<tr>
<td>Many Papers</td>
<td>0</td>
<td>0</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Extensive testing</td>
<td>0</td>
<td>1</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td>Basis for economic justification</td>
<td>0</td>
<td>0</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>NIOSH IDL</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>99</td>
</tr>
<tr>
<td>NIOSH REL/TWA t</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>33</td>
</tr>
<tr>
<td>EPA release/report limit</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>9</td>
<td>51</td>
</tr>
<tr>
<td>Not flammable/water reactive</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>23</td>
</tr>
</tbody>
</table>
Table 2.3. Weighting factors for each criterion for the different solar devices

<table>
<thead>
<tr>
<th></th>
<th>Raw Weighing Factor</th>
<th>Weighing Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trough</td>
<td>Low Temp Tower</td>
</tr>
<tr>
<td>1</td>
<td>Number of chemical reactions</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
<td>Number of separation step</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>Number of chemical elements</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>Abundance of chemical elements</td>
<td>49</td>
</tr>
<tr>
<td>5</td>
<td>Corrosiveness of chemicals</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>Degree of solids flow</td>
<td>57</td>
</tr>
<tr>
<td>7</td>
<td>Use of radiant heat transfer to solids</td>
<td>45</td>
</tr>
<tr>
<td>8</td>
<td>Temperature of high temp. endothermic step</td>
<td>51</td>
</tr>
<tr>
<td>9</td>
<td>Compatible with thermal transients and/or diurnal storage</td>
<td>106</td>
</tr>
<tr>
<td>10</td>
<td>Number of Papers</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>Scale of test</td>
<td>22</td>
</tr>
<tr>
<td>12</td>
<td>Efficiency and/or cost figures</td>
<td>18</td>
</tr>
<tr>
<td>13</td>
<td>Chemical toxicity to human</td>
<td>99</td>
</tr>
<tr>
<td>14</td>
<td>Long term toxicity to human</td>
<td>33</td>
</tr>
<tr>
<td>15</td>
<td>Environmental chemical toxicity</td>
<td>51</td>
</tr>
<tr>
<td>16</td>
<td>Reactivity with air and water</td>
<td>23</td>
</tr>
</tbody>
</table>

Maximum raw score: 520 490 620 650
Score multiplier: 0.192 0.204 0.161 0.154
Maximum Score: 100 100 100 100
Cut-off: 33 35 51 55
3. Phase II – Thermodynamic and Efficiency Evaluation of TC and Preliminary Feasibility Studies

The 67 highest ranked cycles from the Phase I screening were evaluated for their potential thermal efficiency. This process required the development of a plausible overall hydrogen plant design employing the TC. A detailed flowsheet for each TC was developed which included a mass and energy balance of all the reactions steps and reasonable heat recuperation. Based on this, the overall hydrogen production efficiency was calculated. The efficiency took into account all forms of heat and work used in the process. The calculations were done primarily using HSC Chemistry Software Database and ASPEN® modeling software was used when necessary. The efficiency was calculated by the relation

\[
\eta = \frac{-\Delta H^\circ_{25C}(H_2O(\ell))}{[Q_{solar} + (W_s + \Delta G^\circ_T + RT \ln(\Pi a_p/\Pi a_r) + nFE_{ov})/\eta_e]} \quad 3.1
\]

where
- \(\eta\) is the calculated efficiency,
- \(\Delta H^\circ_{25C}(H_2O(\ell))\) is the standard enthalpy of formation of liquid water,
- \(Q_{solar}\) is the net solar heat determined from the mass and energy balance,
- \(W_s\) is the amount of shaft work required, primarily compression work,
- \(\Delta G^\circ_T\) is the standard free energy of any electrochemical step,
- \(R\) is the universal gas constant,
- \(T\) is the temperature of the electrochemical step,
- \(a_p\) are the activities of the products of the electrochemical step,
- \(n_p\) are the stoichiometric coefficients of the electrochemical products,
- \(a_r\) are the activities of the reactants of the electrochemical step,
- \(n_p\) are the stoichiometric coefficients of the electrochemical reactants,
- \(n\) is the number of charges transferred in the electrochemical step,
- \(F\) is Faraday’s constant,
- \(E_{ov}\) is the over-voltage of the electrochemical step, taken as 0.2 volts if no membrane is required and 0.4 volts if a membrane is needed,
- \(\eta_e\) is the efficiency of electrical generation, optimistically taken as 0.5.

The only terms difficult to estimate were the activities of the participants of electrochemical reactions and based on past experience they tend to have a negligible affect on the calculated efficiency.
Figures 3.1 and 3.2 show an example of this process using PID 131. First, a detailed process flowsheet was set up (Figure 3.1) which could be compared to the simplified block diagram in Figure 2.1. Based on this, the heat and mass balance, and phase equilibrium for the various reactions were determined using HSC (Figure 3.2). The thermodynamic efficiency was then calculated from the flowsheet. A few TCs have previously been analyzed for efficiency to a much greater depth than our analysis. In these cases the published values were used. Table 3.1 lists the 67 cycles that have been evaluated in Phase II, with their assessed energy efficiency. The detailed flowsheet for each of the 67 cycles can be found in a project report (McQuillan 2005). Processes which have efficiency of 0.0 means that one or more of the reaction steps within the TC is thermodynamically impossible.

![Figure 3.1 Detailed process flowsheet for PID 131.](image-url)
The objective criteria for retaining a cycle for further study was that the cycle efficiency should be significantly (~3-5%) greater than can be realized by conversion of solar heat into electricity followed by conventional low temperature electrolysis (21%). The 14 cycles listed in Table 3.2 have sufficient potential that they were retained for consideration in Phase III of the SHGR program. In this phase, laboratory investigations to validate the feasibility and scale-up issues of the selected cycles were conducted. The majority of the selected TCs fell into four groups: sulfuric acid cycles, sulfate cycles, volatile metal oxide cycles and non-volatile metal oxide cycles. These TCs generally require temperatures in the range provided by advanced towers or dishes. A hybrid copper chloride cycle was also included in the phase III evaluation. This cycle required a reaction temperature up to around 700°C and could be powered by a trough.

All the information gathered and generated in Phase I and II have been placed in a database maintained at UNLV. The SHGR database (http://shgr.unlv.edu/) is a living document that will continue to be updated by the project team. It is open for public use and access is granted by registering on the website.
Table 3.1. Thermal efficiencies for the TCs assessed in Phase II of the program.

<table>
<thead>
<tr>
<th>PID</th>
<th>Cycle Name</th>
<th>Efficiency LHV (0.846*HHV)</th>
<th>Efficiency HHV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfur-Iodine</td>
<td>38.1</td>
<td>45a</td>
</tr>
<tr>
<td>2</td>
<td>Nickel-Manganese Ferrite</td>
<td>44.0</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>Iron Chloride-1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>Hybrid Cadmium</td>
<td>45.1</td>
<td>53.3</td>
</tr>
<tr>
<td>6</td>
<td>Zinc-Zinc Oxide</td>
<td>45.0</td>
<td>53.2</td>
</tr>
<tr>
<td>7</td>
<td>Iron oxide</td>
<td>42.3</td>
<td>50.0</td>
</tr>
<tr>
<td>9</td>
<td>Manganese-Carbon 0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>14</td>
<td>Sodium-Manganese-1 0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>16</td>
<td>Vanadium Oxychloride-1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>22</td>
<td>Iron Chloride-4</td>
<td>31.0</td>
<td>36.6</td>
</tr>
<tr>
<td>23</td>
<td>Manganese Chloride-1</td>
<td>26.6</td>
<td>31.4</td>
</tr>
<tr>
<td>24</td>
<td>Hybrid Lithium Nitrate</td>
<td>32.8</td>
<td>38.8</td>
</tr>
<tr>
<td>25</td>
<td>Cesium Hydroxide</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>26</td>
<td>Copper Magnesium Chloride</td>
<td>17.4</td>
<td>20.6</td>
</tr>
<tr>
<td>36</td>
<td>Cesium Amalgam-1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>49</td>
<td>Uranium Carbonate-1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>50</td>
<td>Lithium Manganese</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>51</td>
<td>Potassium Peroxide</td>
<td>&lt;23.5</td>
<td>&lt;27.8</td>
</tr>
<tr>
<td>53</td>
<td>Hybrid Chlorine</td>
<td>21.6</td>
<td>25.5</td>
</tr>
<tr>
<td>56</td>
<td>Copper Chloride</td>
<td>29.2</td>
<td>34.5</td>
</tr>
<tr>
<td>61</td>
<td>Sodium-Iron</td>
<td>22.8</td>
<td>27.0</td>
</tr>
<tr>
<td>62</td>
<td>Iron Bromide</td>
<td>&lt;27.7</td>
<td>&lt;32.8</td>
</tr>
<tr>
<td>63</td>
<td>Iron-Carbon Monoxide-2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>67</td>
<td>Hybrid Sulfur</td>
<td>43.1</td>
<td>50.9a</td>
</tr>
<tr>
<td>68</td>
<td>Arsenic-Ammonium Iodide</td>
<td>6.7</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>----------</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>70</td>
<td>Hybrid Sulfur-Bromine</td>
<td>33.4</td>
<td>39.5</td>
</tr>
<tr>
<td>72</td>
<td>Calcium-Iron Bromide-2</td>
<td>33.8</td>
<td>40.0</td>
</tr>
<tr>
<td>82</td>
<td>Manganese-Magnesium Iodide-1</td>
<td>&lt;</td>
<td>32.2</td>
</tr>
<tr>
<td>91</td>
<td>Carbon-Scandium Bromide</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>93</td>
<td>Tungsten-Aluminum Bromide</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>103</td>
<td>Cerium Chloride</td>
<td>18.0</td>
<td>21.3</td>
</tr>
<tr>
<td>104</td>
<td>Magnesium-Cerium Chloride</td>
<td>15.1</td>
<td>17.9</td>
</tr>
<tr>
<td>105</td>
<td>Manganese-Ethane-Ethylene</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>106</td>
<td>High temperature electrolysis</td>
<td>49.1</td>
<td>58.0</td>
</tr>
<tr>
<td>110</td>
<td>Sodium Manganese-3</td>
<td>50.0</td>
<td>59.1</td>
</tr>
<tr>
<td>111</td>
<td>Sodium-Manganese Ferrite-1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>112</td>
<td>Iron Chloride-9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>114</td>
<td>Hybrid Nitrogen-Iodine</td>
<td>&lt;28.2</td>
<td>&lt;33.3</td>
</tr>
<tr>
<td>124</td>
<td>Copper Sulfate-1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>126</td>
<td>Cesium Amalgum-2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>129</td>
<td>Magnesium Sulfate</td>
<td>5.1</td>
<td>6°</td>
</tr>
<tr>
<td>131</td>
<td>Manganese Sulfate</td>
<td>35.4</td>
<td>41.8°</td>
</tr>
<tr>
<td>132</td>
<td>Ferrous Sulfate-3</td>
<td>14.4</td>
<td>17°</td>
</tr>
<tr>
<td>133</td>
<td>Ferrous Sulfate-4</td>
<td>0.0</td>
<td>0°</td>
</tr>
<tr>
<td>134</td>
<td>Cobalt Sulfate</td>
<td>29.9</td>
<td>35.3°</td>
</tr>
<tr>
<td>147</td>
<td>Cadmium Sulfate</td>
<td>46.5</td>
<td>55°</td>
</tr>
<tr>
<td>149</td>
<td>Barium-Molybdenum Sulfate</td>
<td>39.5</td>
<td>46.7°</td>
</tr>
<tr>
<td>151</td>
<td>Carbon-Sulfur</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Component</td>
<td>Efficiency 1</td>
<td>Efficiency 2</td>
</tr>
<tr>
<td>---</td>
<td>----------------------------------</td>
<td>--------------</td>
<td>--------------</td>
</tr>
<tr>
<td>152</td>
<td>Iron-Zinc &lt;</td>
<td>&lt;19.9</td>
<td>&lt;23.5</td>
</tr>
<tr>
<td>153</td>
<td>Sodium-Manganese Ferrite-2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>154</td>
<td>Sodium Ferrite</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>160</td>
<td>Arsenic-Iodine &lt;</td>
<td>&lt;21.2</td>
<td>&lt;25</td>
</tr>
<tr>
<td>162</td>
<td>Uranium Carbonate-2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>163</td>
<td>Manganese Carbonate</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>177</td>
<td>Lead Chloride</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>182</td>
<td>Cadmium Carbonate</td>
<td>44.3</td>
<td>52.4</td>
</tr>
<tr>
<td>184</td>
<td>Hybrid Antimony-Bromine</td>
<td>30.6</td>
<td>36.2</td>
</tr>
<tr>
<td>185</td>
<td>Hybrid Cobalt Bromide-2</td>
<td>21.7</td>
<td>25.6</td>
</tr>
<tr>
<td>191</td>
<td>Hybrid Copper</td>
<td>41.6</td>
<td>49.2</td>
</tr>
<tr>
<td>193</td>
<td>Multivalent sulfur-3</td>
<td>35.5</td>
<td>42.2</td>
</tr>
<tr>
<td>194</td>
<td>Zinc-Manganese Ferrite</td>
<td>44.0</td>
<td>52&lt;sup&gt;b,d&lt;/sup&gt;</td>
</tr>
<tr>
<td>196</td>
<td>Sodium Carbonate-Iodate</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>198</td>
<td>Calcium Bromide</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>199</td>
<td>Iron Chloride-11</td>
<td>&lt;16.9</td>
<td>&lt;20&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>200</td>
<td>Iron Chloride-12</td>
<td>16.9</td>
<td>20&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>201</td>
<td>Carbon Oxides</td>
<td>31.4</td>
<td>37.1</td>
</tr>
<tr>
<td>202</td>
<td>Methanol-Formaldehyde</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

-<sup>a</sup> efficiency calculated from previous studies
-<sup>b</sup> efficiency estimated, limited thermodynamic data
-<sup>c</sup> efficiency calculated presuming cycle is not a hybrid
-<sup>d</sup> assumed same as PID 2
-na not assessable
### Table 3.2. TCs that have been selected for laboratory feasibility demonstration.

<table>
<thead>
<tr>
<th>TC Type</th>
<th>Efficiency</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sulfuric Acid Cycles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hybrid Sulfur</td>
<td>51%</td>
<td>900</td>
</tr>
<tr>
<td>Sulfur Iodine</td>
<td>45%</td>
<td>900</td>
</tr>
<tr>
<td>Multivalent sulfur</td>
<td>42%</td>
<td>1570</td>
</tr>
<tr>
<td><strong>Metal Sulfate Cycles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium sulfate</td>
<td>55%</td>
<td>1200</td>
</tr>
<tr>
<td>Barium sulfate</td>
<td>47%</td>
<td>1200</td>
</tr>
<tr>
<td>Manganese sulfate</td>
<td>42%</td>
<td>1200</td>
</tr>
<tr>
<td><strong>Volatile Metal Oxide Cycles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>53.2%</td>
<td>2200</td>
</tr>
<tr>
<td>Hybrid Cadmium</td>
<td>53%</td>
<td>1600</td>
</tr>
<tr>
<td>Cadmium Carbonate</td>
<td>52%</td>
<td>1600</td>
</tr>
<tr>
<td><strong>Non-volatile Metal Oxide Cycles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>50%</td>
<td>2200</td>
</tr>
<tr>
<td>Sodium Manganese</td>
<td>59.1%</td>
<td>1560</td>
</tr>
<tr>
<td>Nickel Manganese Ferrite</td>
<td>52%</td>
<td>1800</td>
</tr>
<tr>
<td>Zinc Manganese Ferrite</td>
<td>52%</td>
<td>1800</td>
</tr>
<tr>
<td><strong>Other</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hybrid Copper Chloride</td>
<td>49%</td>
<td>550</td>
</tr>
</tbody>
</table>
4. Phase III – Validation of Sulfate Cycles

The results of the Phase II thermal efficiency calculations determined that 14 different TCs from five different chemical classes have high thermal efficiency (See Table 3.2) and their associated reactions are thermodynamically possible. However, the chemical reactions within some of these TCs have never been experimentally demonstrated. As part of the SGHE program, laboratory experiments were set up to investigate some of the reaction steps within the 14 selected TCs. For those TCs that had previously been proven to be feasible, the effort was focused on further developing the TC for a possible on sun demonstration. Among the 14 TCs, sulfur-iodine and hybrid sulfur are the most prominent and most studied. They were further developed under the support of the DOE Nuclear Hydrogen Initiative (NHI) so they were not considered in the experimental scope of this project. As for the other 12 TCs, continued development of the zinc-zinc oxide and feasibility studies of the sodium manganese oxide TCs were undertaken by CU and NREL. SNL concentrated their effort to develop the nickel manganese and zinc manganese ferrite TCs. GA and UNLV, under the support of this contract, investigated the feasibility of the various reaction steps within the families of sulfate and cadmium based cycles. The results from the sulfates cycle experiments are discussed in this chapter whereas those pertaining to the cadmium cycles are presented in the next chapter.

Table 4.1 lists the two sulfate cycles that were chosen as representatives for experimental studies. Both these cycles have high calculated thermal efficiencies and the high temperature endothermic step was calculated to be at between 1100-1200°C. The immediate goal was to determine whether hydrogen generation using sulfate based cycles were practical.

<table>
<thead>
<tr>
<th>PID</th>
<th>Cycle</th>
<th>Thermal Efficiency (LHV)</th>
<th>Experimental Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>131</td>
<td>Manganese sulfate</td>
<td>42%</td>
<td>Low temp H₂ evolution</td>
</tr>
<tr>
<td>149</td>
<td>Molybdenum barium sulfate</td>
<td>47%</td>
<td>Low temp H₂ evolution</td>
</tr>
</tbody>
</table>

All the associated reaction steps for the two sulfate cycles listed in Table 4.1 are shown below.

**Manganese Sulfate Cycle**

\[
\begin{align*}
\text{MnSO}_4 & \rightarrow \text{MnO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 & \text{(1200°C)} & \text{——— 4.1} \\
\text{MnO} + \text{SO}_2 + \text{H}_2\text{O} & \rightarrow \text{MnSO}_4 + \text{H}_2 & \text{(100°C)} & \text{——— 4.2}
\end{align*}
\]
Molybdenum Barium Sulfate Cycle

\[
\text{BaSO}_4 + \text{MoO}_3 \rightarrow \text{BaMoO}_4 + \text{SO}_2 + \frac{1}{2} \text{O}_2 \quad (1200^\circ\text{C}) \quad ——— 4.3 \\
\text{BaMoO}_4 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{BaSO}_4 + \text{MoO}_3 + \text{H}_2 \quad (200^\circ\text{C}) \quad ——— 4.4
\]

For the sulfate TCs to be viable, all the reactions steps must proceed as written above. The laboratory studies focused on experiments which explored whether the low temperature hydrogen generation step could be carried out as a pure thermochemical reaction and without the aid of electrolysis. The literature was ambiguous on the optimal and achievable reaction pathways. The high thermal efficiencies associated with the sulfate TCs were based on the assumption that no electrolysis is required. Even though thermodynamic calculations showed that hydrogen could be spontaneously evolved without electrolysis, they also revealed that other side reactions that do not result in hydrogen generation are thermodynamically more favorable. Thus, hydrogen generation within the sulfate cycle hinges on kinetic effects and will only be probable if the hydrolysis step has a comparably fast reaction time.

4.1 Experimental Set Up

Experiments for the two selected sulfate TCs were carried out at atmospheric pressure in a flow through system that was constructed using standard lab glassware. A schematic of the set up is shown in Figure 4.1. Two sets of reaction conditions that replicate those for the hydrogen generation steps (eq. 4.2 and 4.4) were employed:

1. Aqueous sulphur dioxide (sulfurous acid) was added to the respective metal oxides in a reactor flask and the set up was stirred at 25°C or 100°C. A nitrogen purge gas was used to maintain a flow through the system.

2. Aqueous sulphur dioxide was added to the metal oxides and the mixture was stirred at 25°C or 100°C. A flow of SO₂ gas was bubbled through the reaction mixture to try to maintain a high H₂SO₃ concentration within the liquid.

The flow rate of both nitrogen and sulfur dioxide was controlled by mass flow controller (MFC). A sodium hydroxide bath was used to scrub the SO₂ gas from the flowing stream after the reactor. The vent after the scrubber was swept into a RGA (residual gas analyzer) to identify and quantify the gases that had been produced by the reactions. Each experiment lasted between 2 to 6 hours. At the end of each run, the solids which remained inside the reactor flask was extracted, dried and characterized using powder x-ray diffraction.
4.2 Manganese Sulfate Cycle Feasibility Studies (PID 131)

The experiments were run in the following manner. First green MnO powder was added to the reactor flask followed by aqueous SO$_2$. The set up was then quickly heated to 100°C and kept at that temperature. A reaction was observed to proceed rapidly and within ten minutes, a significant quantity of white powder had precipitated within the flask. At the end of each run, the flask usually contained a mixture of the green and white powders. For all the experimental runs that had been conducted, the RGA never recorded a hydrogen signal that was significantly above that of the background of the instrument. An example of the RGA output spectrum from one of the experiments is shown in Figure 4.2. Aqueous SO$_2$ was added to the reaction flask at the ten minute mark and the set up was then heated to 100°C. Consequently, the measured SO$_2$ and O$_2$ RGA partial pressure signal jumped. The nitrogen purge gas (upper blue curve) was kept constant at a rate of 27 cc/minute. At the 6.6 hour mark, the nitrogen flow was replaced with a hydrogen flow (lower magenta curve) to verify the RGA sensor response to H$_2$. For the duration of the experiment, the measured partial pressure of H$_2$ was about 1/1000 the pressure of the N$_2$, indicating that the flow of H$_2$ was no more than 1/1000 of the N$_2$ flow to a first order approximation. Hence, the hydrogen generation rate was less than 0.027 cc/minute and remained essentially constant over the test period of 5-6 hours. If the reaction had gone to completion in 6 hours, the estimated an average hydrogen evolution rate would be 3.18 cc/minute.
The hydrogen generation reaction for this manganese sulfate cycle was expected to be as written in eq. 4.2 with MnSO₄ as a finish product. A search of the published database showed that there are other reactions between manganese oxide and sulfuric dioxide that are thermodynamically feasible and they are listed below. However, none of these reactions favored the formation of hydrogen:

\[ \text{MnO} + \text{SO}_2 \rightarrow \text{MnSO}_3 \]  
\[ 4\text{MnO} + 4\text{SO}_2 \rightarrow 3\text{MnSO}_4 + \text{MnS} \]  
\[ 2\text{MnO} + 3\text{SO}_2 \rightarrow 2\text{MnSO}_4 + \text{S} \]  
\[ 2\text{MnO} + 2\text{SO}_2 + \text{H}_2\text{O} \rightarrow 2\text{MnSO}_4 + \text{H}_2\text{S} \]

The diffraction peaks from the x-ray powder diffraction spectrum of the residual powder matched those of MnSO₃ (Figure 4.3). This confirms the nature of the white powder that remained inside the flaks at the end of the experiment. Thus, MnSO₃ formed rapidly in the present reaction instead of MnSO₄ as the hydrogen generation reaction had suggested. After the formation of MnSO₃, hydrogen generation becomes difficult because the chemical reaction to accomplish this:

\[ \text{MnSO}_3(s) + \text{H}_2\text{O}(l) \rightarrow \text{MnSO}_4(s) + \text{H}_2(g) \]
is thermodynamically uphill below 100°C. Hence, no hydrogen was expected under the experimental conditions that were used. Due to lack of thermodynamic data on MnSO₃, it was not straightforward to determine whether hydrogen can be made with MnSO₃ as an intermediate product within a pure thermochemical cycle. On the other hand, one can find out if the formation of reduced sulfur species will be favored over hydrogen. For the hydrogen generation reaction to take place and this cycle to be valid, hydrogen must be a thermodynamically favorable product and kinetically, it must be favored over the reduced sulfur species.

Figure 4.3 X-ray diffraction spectrum of post experiment residue inside the reaction flask. The diffraction angle for MnSO₃ are marks led by the red dots.

Literature data (Henning 1989) suggested that MnSO₃ would not be stable in aqueous solutions at temperature above 100°C. The experiment was repeated at elevated temperature in an effort to determine whether the hydrogen generation reaction would be more favorable given the apparent instability of MnSO₃. Instead of using the atmospheric flow through system, the reaction was carried out in a pressure vessel at 250°C in order to minimize steam formation. The results obtained were similar to those from the low temperature runs as no hydrogen production was detected by the RGA. The x-ray powder diffraction spectrum from the residue once again reveals the presence of a large amount of
MnSO₃ (Figure 4.4). The diffraction peaks within the spectrum can be matched with those from MnSO₃ or MnSO₃·3H₂O and no peak representing any reduced sulfur species such as MnS, S, or H₂S could be observed. Contrary to the literature, it seems that MnSO₃ is thermodynamic stable even at elevated temperatures and thus no reduced sulfur species were formed. In conclusion, the manganese sulfate cycle cannot be used as a pure thermochemical cycle and will most likely require the aid of electrolysis to achieve hydrogen generation.

Figure 4.4 X-ray diffraction spectrum of post experiment residue inside the reaction flask. The diffraction peaks for MnSO₃ are marks by the red dots.

4.3 Feasibilities studies on Molybdenum Barium Sulfate (PID 149)

The hydrogen generation step of the barium molybdenum sulfate cycle (eq. 4.10) is an adaptation from that of the barium oxide cycle (eq. 4.11).

\[
\text{BaMoO}_4 + \text{H}_2\text{SO}_3 \rightarrow \text{BaSO}_4 + \text{MoO}_3 + \text{H}_2 \quad \text{4.10}
\]
Based on calculations using HSC chemistry, it was found that there are the alternative barium oxide-sulfur dioxide reactions which are more thermodynamically favorable when compared to the hydrogen production reaction, similar to what was discovered in the manganese sulfate cycle. These chemical reactions are listed below:

\[
\begin{align*}
4\text{BaO} + 4\text{SO}_2 &= 3\text{BaSO}_4 + \text{BaS} \\
2\text{BaO} + 3\text{SO}_2 &= 2\text{BaSO}_4 + \text{S} \\
2\text{BaO} + 2\text{SO}_2 + \text{H}_2\text{O} &= 2\text{BaSO}_4 + \text{H}_2\text{S}
\end{align*}
\]

Experiments were conducted using procedures similar to those for MnO with the intention of determining whether the kinetics of the hydrogen generation step could be fast to result in hydrogen production. This set of experiments was carried out using a lower nitrogen flow rate, which helped to increase the sensitivity for hydrogen detection. Three different starting oxides were used and they were \textit{i)} \text{BaO}, \textit{ii)} \text{BaMoO}_4 and \textit{iii)} \text{BaO} + \text{MoO}_3 respectively.

In flow through experiments with all the barium based oxides, no significant hydrogen formation could be observed from the RGA output spectra. In the BaO experiment, which spanned a total of three hours, the theoretical steady state hydrogen evolution rate was estimated to be 3.2 cc/minute assuming full conversion into BaSO\(_4\). However, a hydrogen flow rate of less than 0.01 cc/minute were deduced from the RGA results. In tests using aqueous solutions at both 25 and 100°C, BaSO\(_3\) formed as a result of the reaction between BaO and SO\(_2\) and neither hydrogen nor reduced sulfur species was produced. Powder x-ray diffraction spectrum of the residue product only contained BaSO\(_3\) peaks (Figure 4.5). In the second series of experiments which used BaMoO\(_4\) as starting material, no significant production of hydrogen was detected by the RGA at the reaction temperatures of 25°C or 100°C. The RGA hydrogen signal was 3 orders of magnitude below atmospheric pressure, and showed no increase even when SO\(_2\) was added to the system at about 200 seconds (Figure 4.6). For the third starting composition using mixed oxide, the reaction between BaO + MoO\(_3\) revealed an interesting side reaction which indicates an energy efficiency lower than the originally calculated value. According to the proposed cycle, hydrogen evolution occurs in the presence of molybdenum that is in the +6 oxidation state. During the experiment, formation of a blue solution was observed which indicates the molybdenum ions were in the +5 oxidation state. To the extent that the oxidation state of molybdenum was reduced, the hydrogen formation reaction will not take place. Further literature research indicates that MoO\(_3\) can be reduced to a lower oxidation state by sulfurous...
acid. The production of MoO$_3$ in this PID, and the formation of lower oxidation state molybdenum in the presence of sulfurous acid, will decrease the potential energy efficiency of the proposed cycle.

For the barium oxide-sulfur dioxide based hydrogen generation experiments that were carried out at elevated temperature and pressure, no hydrogen could be observed similar to the manganese sulfate cycle. In the test conducted with BaO inside a pressure vessel (250°C and 47 atm) with excess SO$_2$ and H$_2$O, neither H$_2$S nor H$_2$ gases were detected by the RGA (Figure 4.7). On the other hand, at the end of the experiment, solids of BaSO$_4$ and elemental sulfur were found inside the pressure vessel. The combination of BaSO$_4$ and elemental sulfur are the thermodynamically most stable products. Given that the driving force for making hydrogen is higher for BaO than for BaMoO$_4$, it is unlikely that hydrogen can be made using either BaO or BaMoO$_4$. Thus, it was concluded that if the Molybdenum Barium Sulfate cycle was to be pursued any further, it would have to be carried out as a hybrid cycle using electrolysis in the hydrogen generation step.

In conclusion, the sulfate cycles were not able to generate any hydrogen in the low temperature hydrolysis step with a thermochemical approach. Thus, they will most likely require the application of electrolysis in order to make hydrogen. Such a step would lead to reduced thermal efficiency. Henceforth, metal sulfate cycles are not viable candidates for a pure thermochemical hydrogen production cycle.
Figure 4.5. X-ray diffraction spectrum of post experiment residue inside the flask for the reaction between BaO, SO₂ and H₂O at 100°C.
Figure 4.6. The residual gas analyzer data shows the relative vapor pressures of several gases coming off the reaction between BaMoO$_4$ and sulfurous acid. Note: O$_2$ and H$_2$S signals are believed to be artifacts arising from cracking of SO$_2$ to sulfur (S$^{32} \sim$ O$_2$ and S$^{34} \sim$ H$_2$S).

Figure 4.7. At 2000 seconds, the pressure vessel was opened to vent gases to the residual gas analyzer. No increased H$_2$ is seen, but plenty of excess SO$_2$ and water.
Figure 4.8. X-ray diffraction spectrum of post experiment residue inside the flask for the reaction between BaO, SO₂ and H₂O at 230°C.
5. Cadmium Cycle Feasibility Studies

Cadmium based cycles have been shown by preliminary flow sheet calculations to have the highest thermal efficiencies among all thermochemical hydrogen cycles. This is due to the fact that the temperature required for cadmium oxide decomposition is lower than most other oxide based cycles and the process heat can be recovered efficiently during the process. There are two cadmium based TCs that can be employed to generate hydrogen. First is the cadmium carbonate cycle which was calculated to have a thermal efficiency of 52% (LHV). The reaction steps of this cycle have been investigated previously (Pangborn 1975, Mason 1979, 1980). The other cadmium based cycle is the simplified cycle consisting of just cadmium and oxygen. This cycle had been shown to have an even higher thermal efficiency at 59% (see Table 5.1). These high thermal efficiencies from flowsheet evaluation show that cadmium based solar thermochemical hydrogen generating cycles have the potential to supply low cost hydrogen if the process are demonstrated to be practical and feasible. In addition to these cycles, Whaley et al had studied the hybrid cadmium cycle utilizing electrolysis to carry out the hydrolysis step (Whaley 1983). That approach was not considered in the present studies as the project aimed to study the feasibility of a pure thermochemical cadmium hydrogen cycle.

<table>
<thead>
<tr>
<th>PID</th>
<th>Cycle</th>
<th>Thermal Efficiency (LHV)</th>
<th>Experimental Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>181</td>
<td>Cadmium carbonate</td>
<td>52%</td>
<td>Low temp H₂ evolution</td>
</tr>
<tr>
<td></td>
<td>Cadmium oxide</td>
<td>59%</td>
<td>i) Low temp H₂ evolution</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ii) CdO decomposition</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>iii) Cd+O₂ recombination</td>
</tr>
</tbody>
</table>

The cadmium carbonate cycle has three reaction steps whereas the cadmium oxide cycle consists of only two. The high temperature cadmium dissociation step is the same for both cycles and their variance comes in the low temperature process steps. In the carbonate cycle, carbon dioxide is used in the hydrogen generation step resulting in the formation of cadmium carbonate (eq. 5.2). The cadmium carbonate dissociated spontaneously at around 300°C during ramp up in the decomposition reaction. This carbon dioxide gas needs to be captured and reused. On the other hand, the oxide cycle conducts the hydrolysis step with only water. In this case, the cadmium can either be in solid or molten form (eq. 5.5).
Cadmium Carbonate Cycle

\[
\begin{align*}
    \text{CdO(s)} & \rightarrow \text{Cd(g)} + \frac{1}{2} \text{O}_2(g) \quad (1450^\circ \text{C}) \quad \text{———} \quad 5.1 \\
    \text{Cd(s)} + \text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{CdCO}_3(s) + \text{H}_2(g) \quad (25^\circ \text{C}) \quad \text{———} \quad 5.2 \\
    \text{CdCO}_3 (s) & \rightarrow \text{CdO} + \text{CO}_2(g) \quad (300^\circ \text{C}) \quad \text{———} \quad 5.3
\end{align*}
\]

Cadmium Oxide Cycle

\[
\begin{align*}
    \text{CdO(s)} & \rightarrow \text{Cd(g)} + \frac{1}{2} \text{O}_2(g) \quad (1450^\circ \text{C}) \quad \text{———} \quad 5.4 \\
    \text{Cd(l,s)} + \text{H}_2\text{O} & \rightarrow \text{CdO(s)} + \text{H}_2(g) \quad (25-450^\circ \text{C}) \quad \text{———} \quad 5.5
\end{align*}
\]

A simplified cycle flow diagram based on the cadmium oxide cycle is shown in Figure 5.1. To make either one of the cadmium based cycle into a practical thermochemical cycle, a decomposed vapor quench step must be included in the overall process design. The purpose of this process step is to arrest the reaction between the post decomposition cadmium vapor and oxygen gas that are present in the process stream while the gases are cooling down. Since hydrogen yield is directly proportional to the amount of cadmium available for hydrolysis, this recombination/back reaction will need to be minimized by rapidly quenching to ensure a high post decomposition cadmium yield.

Based on the required process steps of the two cadmium cycles, laboratory feasibility studies of the cadmium based cycles were divided into three different parts. First the reaction kinetics of the low temperature hydrolysis step was studied. Special attention was paid to determine whether the use of carbon dioxide was essential to hydrogen generation and to understand the underlying mechanism behind the reaction. Both hydrogen generation using solid and molten cadmium were studied. Results were used to define a preliminary design concept for the hydrolysis step. The second part of the feasibility studies involved the decomposition of cadmium oxide and cadmium carbonate. Factors which affected the decomposition temperature, rate and kinetics were studied and the data were used for a conceptual decomposer design. The third and final part of the study involved measuring the reaction rate between cadmium vapor and oxygen at various temperatures and oxygen concentrations. The data was used to construct a model to describe the recombination process so that it could be used as inputs in designing the cadmium quench step.
5.1. Hydrogen Generation Using Solid Cadmium

Cadmium is a well known corrosion resistant material. It was widely employed as a surface coating on other metallic materials in order to prevent corrosion, especially in aqueous applications. Thus it is very resistant to oxidation in an aqueous environment. Its corrosion resistance stems from the fact that when it reacts with water, a impervious nanometer thick cadmium hydroxide Cd(OH)$_2$ layer is formed on the surface of the cadmium metal. Hydrogen is also generated as a consequence of this oxidation reaction:

$$
Cd(s) + 2H_2O \rightarrow Cd(OH)_2(s) + H_2(g) \quad 5.6
$$

This surface layer of cadmium hydroxide had been shown to be continuous (Gauer 1970, Ciampi 1991) and its formation on the cadmium metal surface stops the oxidation reaction from proceeding any further (Heusler 1990). In order to generate hydrogen continuously using this reaction, fresh cadmium surfaces must be exposed via the removal or break up of this surface oxide through either mechanical or chemical means (Breiter 1967). For the experiments in this project, both these options to remove the surface oxide had been explored in an attempt to arrive at the optimal hydrogen production route.

5.1.1 Experimental Set Up

A dedicated fume hood was retrofitted at General Atomics for the low temperature hydrogen generation experiments using cadmium. The exhaust of the hood was connected directly to a Hepa filter to trap any airborne particles (Figure 5.2a). An air curtain surrounding the fume hood has also been
installed which helped to contain particles that had escaped from the hood. The enclosed area was lined with sticky floor mats which acted to secure any loose particles (Figure 5.2b). The inside of the fume hood was lined with paper. All these precautions were taken to ensure that cadmium particles did not escape from inside the fume hood as they pose a health risk when inhaled. In addition, personal protective equipment was issued for all operators who were handling cadmium based materials. Routine chemical swipes were conducted to ensure no cd contamination occurred.

![HEPA air handling system for the fume hood.](a)
Experiments to explore the conditions for evolution of hydrogen from solid cadmium metal were carried out mostly in a batch manner inside a pressure vessel (Figure 5.3a). The vessel has a magnetically coupled rotary drive that can be used to institute a stirring or grinding action within the bomb at elevated temperature and pressure. Tungsten carbide (WC) grinding media were mixed in with the cadmium pellets inside the pressure vessel. All the solid particles were submerged in water. The size of the WC pellets was about 3mm in diameter and the cadmium size ranges from 20 to 300 mesh (48-480µm). Chemicals such as ammonia bicarbonate were added to the pressure vessel to study their effect on the reaction kinetics. Mason et al had found the use of ammonium chloride (NH₄Cl) help increase the reaction kinetics (Mason 1980). However, they also observed the formation of multiple cadmium based compounds such as CdCO₃, Cd(NH₃)₂Cl₂ and CdCl₂. The presence of multiple compounds made the process significantly more complicated so the use of ammonium chloride was not considered.

A schematic of the experimental set up is shown in Figure 5.3b. After the desired chemicals, along with cadmium and WC pellets, had been added to the water bath, the temperature of the sealed pressure vessel was slowly raised to 120°C over a 2-3 hours time span. When the set temperature was reached, the stirring rod was then set to rotate at 300 rpm and began the stirring/grinding motion. The circular motion kept the contents of the bomb in motion for the entire test duration between 12-36 hours.
This movement enabled the hard tungsten carbide particles to impinge and deform the soft cadmium particles. As a result, the surface Cd(OH)\textsubscript{2} layer was broken up and new cadmium surface areas were exposed for reaction. The pressure of the set up was monitored during the experiment to detect the generation of gases. As hydrogen was generated by the reaction, the pressure inside the bomb increased. At the end of the experiment, the contents inside the bomb were vented in a controlled manner through a MFC into a RGA for analysis. The amount of hydrogen generated was quantified from the resulting pressure increase and the RGA spectrum.

Figure 5.3 (a) The bomb that was used for hydrogen generation experiments with solid cadmium. (b) A schematic of the set up with the use of tungsten carbide grinding media.

5.1.2 Effect of Particle Size and Carbon Dioxide Chemical Addition

The effect of initial cadmium particle size and carbon dioxide on the hydrogen generation was studied as previously work had suggested that CO\textsubscript{2} is an integral part of the carbonate cycle (Mason 1979, 1980). The temperature of the test system was kept constant at 120°C and 20g of cadmium was used for all the experiments. The results are shown in Table 5.2 and they indicated that the use of CO\textsubscript{2} to pressurize the vessel did not result in any increase in hydrogen yield, which was in contrast to the expectation that CO\textsubscript{2} pressure would increase the H\textsubscript{2} evolution rate. In addition, Cd particle size (total surface area) did not seem to have any significant impact on the total hydrogen yield and the rate of conversion. In going from 20 mesh to 100 mesh to 325 mesh (average grain size of 0.841 to 0.149 to
0.044mm), the surface area per unit weight increased by factors of 1 to 25 to 264. However, the average reaction rates (with no CO\textsubscript{2} present) changed by only a factor of 4 and the rates did not change monotonically with this area ratio. It was postulated that if the reaction rate to produce H\textsubscript{2} is very rapid in early times, the buildup of products must have slowed the reaction rate. Since we could only measure the average yield rate at the end of the experiment, the average reaction rate per hour would become progressively smaller as the reaction time increased. The fact that the total hydrogen yield in these experiments was within a factor of 2 indicates that the reaction had most likely attained equilibrium inside the pressure vessel. In conclusion, grain size and carbon dioxide are only of secondary importance in controlling the reaction rate of this process.

Table 5.2. Effect of cadmium particle size and carbon dioxide addition on hydrogen generation

<table>
<thead>
<tr>
<th>Test Conditions</th>
<th>(Average) Yield H\textsubscript{2} % per hour</th>
<th>Total time of measurement</th>
<th>Total yield% (1\textsuperscript{st} vent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No CO\textsubscript{2} (5-20 mesh* Cd)</td>
<td>0.82%</td>
<td>22.3 hours</td>
<td>18.3%</td>
</tr>
<tr>
<td>No CO\textsubscript{2} (100 mesh** Cd)</td>
<td>1.50%</td>
<td>16.6 hours</td>
<td>24.8</td>
</tr>
<tr>
<td>No CO\textsubscript{2} added (325 mesh** Cd)</td>
<td>0.45%</td>
<td>21.5 hours</td>
<td>9.8%</td>
</tr>
<tr>
<td>750 psi CO\textsubscript{2} added (325 mesh Cd)</td>
<td>0.26%</td>
<td>66.5 hours</td>
<td>17.0%</td>
</tr>
</tbody>
</table>

*5-20 mesh cadmium was from Alfa Aesar 99.95% Lot D27129
** 100 and 325 mesh cadmium powder was from Sigma-Aldrich 99.5% mixed lot
These cadmium samples were used for all other subsequent experiments.

In order to attain insight into the role of carbon dioxide on the hydrogen generation process, a small flow through system was set up (Figure 5.4). Cadmium pellets were simply submerged in a water bath inside a glass tube reactor and carbon dioxide was bubbled through the reactor at a rate of 50 sccm. The bubbling action of the flowing gas created a stirring motion and helped to agitate the pellets. After about 30 minutes of carbon dioxide flowing, the water becomes milky due to a suspension of the white cadmium carbonate particles. Scanning Electron Microscopy (SEM) examination of the cadmium pellets showed that the post reaction surface was decorated with cadmium carbonate particles (Figure 5.5). The carbon dioxide reacts with the cadmium hydroxide that had formed on the cadmium surface as a result of the hydrogen generation equation in eq. 5.6.

\[
\text{Cd(OH)}_2 + \text{CO}_2 \rightarrow \text{CdCO}_3 + \text{H}_2\text{O} \quad \quad \text{5.7}
\]

This reaction transformed the cadmium hydroxide layer into a cadmium carbonate layer. In contrast to the cadmium hydroxide layer, the cadmium carbonate layer was discontinuous and consisted of small crystals. This breakup of the cadmium hydroxide layer helped to expose fresh cadmium surface for further reaction with water. As the cadmium carbonate layer grows, the crystallites broke off the surface and
formed a suspension in water. Hence, the use of carbon dioxide can help to promote the hydrogen generation by helping to break up the surface protective layer and reveal fresh cadmium surface for reaction. A high concentration of carbon dioxide constantly flowing through the system was required in order for the reaction to proceed at a measurable rate which can possibly explain why the reaction was not observed in the batch experiment with the vessel pressurized with carbon dioxide. Even though the use of carbon dioxide provides an avenue for solid cadmium hydrolysis, this approach requires separation of the hydrogen that has been produced from the flowing carbon dioxide stream. A balance of the optimal approach will need to be defined by a flowsheet.

![Figure 5.4](image.jpg)

**Figure 5.4.** The bubbling of carbon dioxide helps break up the surface Cd(OH)₂ by forming CdCO₃.

![Figure 5.5](image.jpg)

**Figure 5.5.** SEM micrograph of the cadmium pellet surface (a) before and (b) after reactor with carbon dioxide in a water bath. Cadmium carbonate crystals form on the particle surface as a result of the reaction.
5.1.3 Effect of Ammonia Bicarbonate, Mercury and Titanium

The effect of chemical additions on the hydrogen generation was studied next. Ammonia bicarbonate (NH₄HCO₃), ammonia hydroxide (NH₄OH), titanium powder and mercury were added separately to the water bath that contained cadmium pellets inside the pressure vessel. All the additives were selected as potential options to help break up the protective cadmium hydroxide surface layer and enhance hydrogen generation. The two ammonia compounds were chosen based on previous data that ammonia chloride helped to enhance the solid cadmium hydrolysis production rate. These ammonia compounds are not expected to generate multiple cadmium based products as was in the case of ammonia chloride. The logic behind adding the individual chemicals was as follow:

- Ammonia bicarbonate is readily soluble in water and its addition increases the amount of dissolved carbon dioxide in the water bath. This helps to turn the cadmium hydroxide surface layer into cadmium carbonate as described in the previous section. The use of soluble bicarbonate reduces the need to separate carbon dioxide and hydrogen after the reaction.

- Ammonia hydroxide increases the pH of the water bath which in theory will help to accelerate the oxidation reaction between cadmium and water (Breiter 1967, Juzeliunas 1992, Ristic 2004)

- Titanium, when in contact with cadmium, can induce a galvanic effect that can lead to enhanced cadmium oxidation (Tomlinson 1975, Heusler 1990, Zerbino 1990)

- Mercury can act as a catalyst to break up the surface hydroxide layer on the amalgamated cadmium surface and enable fresh cadmium surfaces to undergo reaction

Table 5.3 shows a summary of the experimental results with different chemical additions. The highest hydrogen yield of 5.9%/hr was obtained with the addition of ammonia bicarbonate alone. The data implies that carbonate is necessary for rapid hydrogen generation. Figure 5.3a shows a plot of the pressure within the bomb for a case with only cadmium pellets, water and tungsten carbide grinding media. The pressure continued to rise when the experiment was stopped after forty hours. This shows that the reaction was not complete and not all the cadmium had been oxidized. The calculated average hydrogen reaction rate yield was about 1.9%/hour. This can be compared to the experiment in which ammonia bicarbonate was used (Figure 5.3b). The reaction went to a completion after about 22 hours at the reaction temperature. This approach fit well with a 24 hours process cycle. The hydrogen yield with only ammonia bicarbonate additions varies from 1.3 to 5.9%. The reason for the variation will need to be further explored if this hydrogen generation approach is employed in the future. There are a couple drawbacks in using ammonia bicarbonate. First being that ammonia gas is produced during the hydrogen generation process and a separation between hydrogen and ammonia will be required. In addition, the
carbon dioxide from the dissociation step will also need to be separated from the decomposed oxygen so that it can be used to reform ammonia bicarbonate.

There is a stark contrast in the hydrogen generation rate between the addition of ammonia bicarbonate and ammonia hydroxide. With only ammonia hydroxide addition, the solution has the highest pH (~12) but the reaction proceeded at an extremely slow rate with the average conversion of about 0.1% per hour. When ammonia bicarbonate was added to reduce the pH (9-11), the rate increased to between 1-1.6% per hour (Figure 5.3c).

### Table 5.3. Summary of the results from runs with various chemical additions

<table>
<thead>
<tr>
<th>Chemical Addition*</th>
<th>(Average)Yield H$_2$ % per hour</th>
<th>Total time of measurement</th>
<th>Total yield% (1$^{st}$ vent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water and cadmium only</td>
<td>1.9%</td>
<td>40.2 hours</td>
<td>76%</td>
</tr>
<tr>
<td>NH$_4$HCO$_3$ &amp; NH$_4$OH (more basic)</td>
<td>1.2 %</td>
<td>22.0 hours</td>
<td>33%</td>
</tr>
<tr>
<td>NH$_4$OH</td>
<td>0.1 %</td>
<td>18.5 hours</td>
<td>2.1%</td>
</tr>
<tr>
<td>NH$_4$HCO$_3$</td>
<td>1.3%</td>
<td>19.25 hours</td>
<td>24.4%</td>
</tr>
<tr>
<td>NH$_4$HCO$_3$ + Hg</td>
<td>0.9%</td>
<td>20 hours</td>
<td>17.8%</td>
</tr>
<tr>
<td>NH$_4$HCO$_3$</td>
<td>5.9%</td>
<td>16.9 hours</td>
<td>100%</td>
</tr>
<tr>
<td>NH$_4$HCO$_3$ + Ti</td>
<td>0.8%</td>
<td>19 hours</td>
<td>14.8%</td>
</tr>
</tbody>
</table>

*5-20 mesh cadmium pellets was used for the experiment.

The use of titanium powder did not result in any increase in hydrogen production thus the galvanic effect is not effective in enhancing hydrogen generation. The effect of a small addition of mercury was also tested. When it was added to an ammonia bicarbonate solution, a hydrogen yield of 0.9% per hour was obtained which was no improvement compared to the baseline case using ammonia bicarbonate. In a second experiment, mercury was added directly to the cadmium – water bath without ammonia bicarbonate. Gaseous carbon dioxide was used instead to pressurize the vessel to function as a carbonate former. No hydrogen was observed in this case.
Figure 5.6. Temperature and pressure curves of within the pressure vessel resulting from the use of different chemical additions: (a) baseline with no addition, (b) ammonia bicarbonate, (c) ammonia bicarbonate and ammonia hydroxide and (d) titanium powder and ammonia bicarbonate.
5.1.4 Mechanical Means for Cadmium Size Reduction

Physical deformation and size reduction of cadmium particles is an important element in using solid cadmium for hydrogen generation. The deformation helps to generate new surfaces for cadmium to undergo reaction with water. Hence, alternatives to the mechanical grinding used in the pressure vessel experiments were explored to find other options to speed up the size reduction process. Table 5.4 lists the hardness of cadmium compared to some other common materials. Cadmium is a relatively soft material and can thus be broken up relatively easily in theory.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mohs Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>2.0</td>
</tr>
<tr>
<td>Lead</td>
<td>1.5</td>
</tr>
<tr>
<td>Gold</td>
<td>2.5 – 3</td>
</tr>
<tr>
<td>SiC</td>
<td>9 - 10</td>
</tr>
</tbody>
</table>

In light of the softness of cadmium, we explored the use of shear deformation for size reduction. This was accomplished with the aid of a commercial blender. Figure 5.7 shows the cadmium pellets for both before and after 8 minutes of operation inside a blender in the presence of water. A rapid size reduction of more than 50% was obtained. A similar test was carried out with the addition of ammonia bicarbonate. After 30min of blending action, a white suspension was formed. The mixture was separated into a solid and liquid fraction. The solid fraction contained a slush of cadmium that had been broken down (Figure 5.8a). The size reduction was significant as no particles larger than 0.5mm could be observed. In the liquid fraction, a layer of cadmium carbonate particles could be found settled on the bottom of the extracted liquid. The carbonate formed as a result of hydrogen generation within the blender. Figure 5.9 shows the SEM micrographs of the cadmium pellets that have been blended for 10 minutes with only water and with ammonia bicarbonate added. The size reduction appears to be more effective with the presence of carbonate but more qualitative studies will need to be carried out. On the cadmium particles that were broken up in the presence of dissolved ammonia bicarbonate, small hexagonal cadmium carbonate crystals could be observed on the surface which was a consequence of the hydrogen generation reaction.
Figure 5.7 (a) Cadmium pellets before grinding & (b) after 8 minutes in a blender.

Figure 5.8. Cadmium-ammonia bicarbonate mixture after 30 min in a blender. Cadmium bicarbonate formed as a result of the hydrogen generation reaction.
These findings help formulate an efficient hydrolysis process using solid cadmium. However, the process will inevitably include mechanical work to reduce the size of cadmium particles and this will lower the overall thermal efficiency of the process. On the other hand, if the quench step dictates that solid cadmium will need to be used, these results showed a pathway forward. The main emphasis on hydrolysis going forward will be on molten cadmium.

5.2 Hydrolysis with Molten Liquid Cadmium

Another pathway to generate hydrogen in a cadmium-based cycle is to react molten cadmium with hot steam (eq. 5.5). A similar approach has been applied previously for molten zinc hydrolysis (Berman 2000, Vishnevetsky 2007). This approach eliminates the requirement to employ carbon dioxide to help
break up the protective cadmium hydroxide layer on the metal surface and the need for gas separation. Furthermore, energy will no longer be necessary to breakdown solid cadmium mechanically. Cadmium metal melts at 321°C and thermodynamic calculations have shown the hydrogen concentration \((H_2/(H_2+H_2O))\) for the hydrolysis reaction (eq. 5.5) to be at around 5% at this temperature. This means that equilibrium is reached when 5% of the steam in contact with molten cadmium has reacted to form hydrogen and the reaction will not proceed any further until the hydrogen concentration is reduced. Figure 5.10 shows a plot on the effect of temperature on \(H_2\) concentration in the flowing steam for the molten cadmium hydrolysis process. As the molten cadmium temperature increases, the equilibrium \(H_2\) concentration decreases. On the other hand, reaction kinetics will increase at higher temperatures and enhance the reaction rate. Thus, the optimal temperature with respect to hydrogen yield and reaction rate will need to be determined.

![Figure 5.10. The effect of temperature on \(H_2\) concentration in the process stream for the molten cadmium hydrolysis process](image)

**Figure 5.10.** The effect of temperature on \(H_2\) concentration in the process stream for the molten cadmium hydrolysis process

### 5.2.1. Molten cadmium hydrolysis using a steam bubbler system

To demonstrate the feasibility of using molten cadmium for hydrolysis, a steam bubbler system was constructed and a schematic of the system is shown in Figure 5.11. In this system, the carrier gas (helium, carbon dioxide or nitrogen) was saturated with water moisture as it bubbled through the water tank at just below the boiling point. The vapor saturated carrier gas was then bubbled through a column of molten cadmium to carry out the hydrogen generation reaction. The molten cadmium was housed in a
glass capsule with a thermal well for temperature monitoring. After the reactor, the process stream was cooled down so the steam condensed into a water trap and the remaining gases were sent to an RGA for analysis. Using the hydrogen to carrier gas ratio in the RGA spectrum, the amount and rate of hydrogen generation (normalized by reaction time) with respect to molten cadmium temperature could then be determined. A H2 sensor which directly measures the concentration of hydrogen in a gas stream was also installed in line to confirm the RGA measurement data. Results from these runs showed very low levels of hydrogen production and little cadmium oxide was observed in the re-solidified cadmium capsule after the experiment. It was determined that the amount of steam available for reaction was not adequate thus little hydrogen was generated. Figure 5.12 shows a plot on the amount of hydrogen produced at various temperatures. There is considerable scattering but it appears that the maximum hydrogen generation rate is obtained at a molten cadmium temperature of around 435°C. The spread in the data is probably due to the low steam fraction in the helium carrier stream, the uncertainty in the degree of vapor saturation and the long residence time. These together contributed to the spread in the data.

Figure 5.11. A flow through system using water vapor saturated carrier gas for molten cadmium hydrolysis.
Figure 5.12. Hydrogen generation rate using a water vapor saturated carrier gas flow through system.

Modifications were made to the system in order to increase the amount of steam in the process stream so a higher rate of reaction could be obtained. First, a syringe pump was added so that the amount of steam that flowed through the system could be accurately controlled. Second, a vaporizer was added to vaporize the water into steam before entering the reactor. The vaporizer was composed of a packed bed of alumina pellets. A schematic of the modified flow through system and a picture of the actual vaporizer and the reactor are shown in Figure 5.13. In addition to the system modifications, the capsule which contained the molten cadmium was also redesigned so that the steam bubbler could rise through the entire molten cadmium column (Figure 5.14). This enables one to change the height of the column and determine the effect of steam-cadmium contact time. 20g of cadmium was used in each experiment and the depth of the nominal molten layer was about 18mm (inner diameter of the tube is 17mm). The molten cadmium temperature was varied to explore its effect and to determine the temperature range at which hydrogen generation was maximum. In addition, the gas flow rate through the system, as controlled by a Mass Flow controller (MFC), was also varied so that the effect of steam and cadmium contact time could be investigated. The nominal carrier gas flow rate was set at between 2-10sccm.
Figure 5.13. A flow through system using steam for molten cadmium hydrolysis.

Figure 5.14. (a) A schematic of the glass capsule for the hydrogen generation reaction using molten cadmium. (b) The actual glass capsule.

Figure 5.15a shows a RGA spectrum from the hydrogen generation experiment with the modified flow through system. As water was injected into the vaporizer by the syringe pump, a hydrogen signal was registered shortly after. This was a result of the steam flowing through the system and reacting with the molten cadmium in the glass capsule. The same hydrogen flow was also measured by the H2 sensor (Figure 5.15b).
Figure 5.15. (a) RGA spectrum showing hydrogen generated from the hydrolysis reaction. The MFC output flow rate is constant at 10sccm. (b) The same output stream as measured by the H2 scan.

Figure 5.16 shows a plot of steam to hydrogen conversion for the steam bubbler experiment at temperatures between 350 and 470°C. In contrast to theoretical prediction based on thermodynamics (Figure 5.10), the conversion increased with reaction temperature. This is because the reaction kinetics, which are proportional to temperature, are dominant over thermodynamics in this reaction. However, the hydrogen to steam ratio measured was significantly less than the 3-5% that was calculated based on an equilibrium reaction. The maximum conversion of 0.6% was obtained at 460°C, which was still below the
predicted equilibrium conversion of 2.8% at this temperature. The lower conversion was probably due to the limited surface contact between molten cadmium and the steam bubble in the present experimental set up. About 20% of the water that flow through the system had been reacted based on the volume collected in the cold trap.

The effect of system gas flow rate is shown in Figure 5.17. At 440°C, the conversion increased from around 0.33% to 0.72% as the flow rate was reduced from 10sccm to 2sccm. The slower flow rate increased the residence time of the steam bubble in molten cadmium thus enhanced the conversion. However, at 490°C, the increase in conversion was only marginal.

![Steam to Hydrogen Conversion](image)

*Figure 5.16. Steam to hydrogen conversion in molten cadmium hydrolysis.*
Figure 5.17. Effect of steam flow rate on the steam to hydrogen conversion ratio for molten cadmium hydrolysis using a bubbler.

Figure 5.18a shows the solidified cadmium that was taken out of the glass capsule. The brownish surface is due to formation of cadmium oxide particles decorating the cadmium metal surface. Figure 5.18b shows an SEM image of the re-solidified cadmium. Small cadmium oxide cubic particles can be seen throughout the surface. Figure 5.19c shows an image of cadmium oxide particles from a two step hydrolysis reaction that was conducted first at 350 and then at 438°C. Results show a grain size distribution between 0.5 to 3 microns and no large scale agglomeration was observed. Hence, this shows that grain size can be controlled via reaction temperature, which can be of significance for decomposer design.

The steam bubbler set up demonstrated that hydrolysis can be carried out using molten cadmium and the optimal reaction temperature for fast hydrogen generation is between 450 – 480°C. Enhancement of steam to hydrogen conversion can be achieved by increasing surface contact between the steam and the cadmium.
5.2.2. Molten cadmium hydrolysis with a rotary kiln.

The results from the steam bubbler experiments demonstrated that the steam to hydrogen conversion depends to a large extent on surface contact between molten cadmium and steam. Based on this concept, it was determined that a rotary kiln would be a logical design to accomplish the hydrogen generation step. New molten cadmium surface is exposed for reaction as the rotational action of the kiln turns the liquid, which should lead to enhanced conversion. Furthermore, this design can be easily scaled up to a larger size for on sun demonstration. A laboratory rotary kiln was designed and constructed to carry out the hydrogen generation experiment. Figures 5.20a and b show a schematic and the actual laboratory rotary kiln furnace system. In this set up, the kiln was single ended with a cavity for reaction, and was fabricated from glass (Figure 5.20c). Hence, all the cadmium materials could be kept inside the cavity for safe handling. Steam was fed directly into the cavity. The experiments were conducted in a
batch mode to probe the effect of various setup and process conditions. In an effort to increase the molten cadmium surface area, inert pellets such as tungsten carbide were added to the cavity of the rotary kiln so that they could disrupt the molten cadmium surface during rotation. Based on the results from the bubbler experiment, the molten cadmium temperature was set at 460°C. The number of WC pellets was varied inside the cavity to gauge its effect. In addition, the water flow rate was varied to determine the effect of residence time.

With the support of this contract, we were able to finish runs using molten zinc as a surrogate to test out the system and a preliminary run with molten cadmium. In the absence of any tungsten carbide pellets, the hydrogen generation rate was very low. Table 5.5 lists a summary of the results using molten cadmium and a RGA spectrum from a molten zinc hydrolysis run is shown in Figure 5.21. The hydrogen generation rate with molten cadmium was very low and the steam to hydrogen conversion ratio is at 0.08% which is significantly lower than the 0.5-0.7% observed in the bubbler system.

Table 5.5 Set up parameters and preliminary molten cadmium hydrolysis results in a rotary kiln (with no WC pellets)

<table>
<thead>
<tr>
<th>Steam (injection rate)</th>
<th>0.011 mole/min (0.66 mole/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium (in rotary kiln cavity)</td>
<td>0.0446 mole (5g)</td>
</tr>
<tr>
<td>Total volume of hydrogen measured</td>
<td>574 cc</td>
</tr>
<tr>
<td>Theoretical $\text{H}_2$ produced with 100% cadmium conversion</td>
<td>999 cc</td>
</tr>
<tr>
<td>$\text{H}_2$ produce rate (at constant output)</td>
<td>0.2 sccm (8.9x10^{-6} mole/min)</td>
</tr>
<tr>
<td>Steam to $\text{H}_2$ conversion</td>
<td>0.08%</td>
</tr>
</tbody>
</table>
Figure 5.20. (a) A schematic and (b) the actual rotary kiln-furnace laboratory set up for cadmium hydrolysis. (c) the single ended glass kiln with a cavity for reaction.
Figure 5.21. RGA spectrum for a molten zinc hydrolysis run with a rotary kiln.

Figure 5.22. RGA spectrum for a molten cadmium hydrolysis run with a rotary kiln.
5.3 High Temperature Cadmium – Oxygen Recombination Experiment

Oxygen and cadmium react with each to form cadmium oxide at temperatures below that of cadmium oxide decomposition. For example, if the temperature of the decomposed gases falls below 1450°C in air, the recombination reaction will take place. The eventual goal is to design a process that can quench the cadmium vapor rapidly to stop this back reaction (Muller 2008, Melchior 2008). The kinetics of the cadmium oxygen reaction is important as it determines the final cadmium yield which in turn affects the thermal efficiency of the cycle. The first step to design the quench process is to study the reaction rate between cadmium and oxygen vapor.

5.3.1 Cadmium – Oxygen Reaction Experimental Set Up

To measure the reaction rate between cad and oxygen, an experimental set up has been designed to adapt a Thermogravimetric Analyzer (TGA) to accomplish this. Figure 5.23a shows a schematic of the set up. A cadmium pellet was melted inside the crucible and vaporized due to the appreciable cadmium vapor pressure at temperatures above 550°C (Figure 5.23a). The crucible sat outside the TGA furnace and was only subjected to radiant heat from the furnace. Its temperature depended on its distance from the furnace which could be raised or lowered by adding and removing spacers. When larger spacers were used, the crucible was further away from the furnace and its temperature became lower for a set furnace temperature. Figure 5.24 shows a plot of the crucible temperature as a function of spacer height for a furnace set point of 1500°C. Hence for this temperature set point, the cadmium in the crucible will be at 750°C for a 10cm spacer and 600°C for an 11cm spacer. The cadmium evaporation rate could thus be roughly adjusted.

The cadmium vapor was carried through the TGA by the flow of an inert carrier gas which was nominally helium. Oxygen gas was introduced at the top of the constant temperature zone of the TGA furnace and was mixed with the cadmium vapor as the gases traveled through the furnace. Reaction between oxygen and cadmium was expected whenever the gas temperature fell below that of decomposition. When this happened, the concentration of oxygen in the gas stream would be reduced accordingly. At the end of the TGA furnace’s constant temperature zone, a sampling tube to collect samples from the flowing gas stream was situated. It was connected to a mass spectroscopy gas analyzer so the oxygen fraction within the gas stream could be determined. In order to halt the cadmium-oxygen reaction, the sampling tube was brazed to a helium cooled bayonet heat exchanger so that the sample gases were quenched at the intake. More importantly, cadmium vapor was condensed, solidified and stopped any reaction with oxygen. Hence, the reaction between cadmium and oxygen should take place only within the heated zone of the furnace in the RGA. The sampling and quench tubing were made
from Hastelloy C276 in order to minimize oxidation at the temperatures they were exposed to. Each set of quench tubes was used for 10 runs to prevent any component failure. A picture of the actual set up is shown in Figure 5.23b. In addition to the test set up, protective equipment had also been added to the TGA test system to ensure safe operation of the cadmium-oxygen reaction experiments. This included an enclosure with a HEPA filter-blower that covered the entire TGA system so that cadmium powder did not escape outside the enclosure (Figure 5.25a). The enclosure was wiped down after each series of experiment. In addition, a quench gas cut off system was also installed (Figure 5.25b). The helium gas that cools the quench tube was set at a pressure of about 500psi. If the bayonet heat exchange cracks due to extensive oxidation, this gas would fill the TGA furnace and push the cadmium vapor out of the furnace into other parts of the TGA. Hence, a system that monitored the TGA furnace pressure was installed so it could cut off the helium flow into the bayonet quench tube instantaneously whenever the pressure exceeded the baseline level. This prevented the TGA from being contaminated in the event of a quench tube failure.

![Figure 5.23a. A schematic of the Cd-O2 recombination experimental set up for use with a TGA.](image-url)
Figure 5.23b. The actual Cd-O$_2$ recombination experimental set up (TC: thermocouple).

Figure 5.24. The effect of spacer height on the TGA crucible temperature.

\[ y = -174.9x + 2517. \]
5.3.2 Cadmium – Oxygen Reaction Experiment Results

In the absence of the quench tube, the temperature of the TGA furnace heat zone was constant throughout the furnace and the length of this heat zone was measured to be about 7cm long from the top of the furnace (Figure 5.26a). The thermocouple which monitored the temperature of the furnace was situated at 2cm from the top of the furnace and was used as the furnace temperature set point. However, once the quench tube was introduced; the temperature profile was no longer constant through the heated zone. It began to drop after about 3cm from the top of the furnace. The range of the decrease was relatively constant at between 180-195°C for furnace temperature set points between 600-1500°C. (Figure 5.26b). Hence, this temperature variation must be taken into account when determining the effect of temperature on the cadmium oxygen reaction rate.
Molten zinc was used as a surrogate to test out the experiment. To investigate the kinetics of the reaction, the oxygen concentration in the flow gas, the reaction zone temperature and the residence time were varied. For the molten cadmium runs, the temperature of molten cadmium was also varied so that the evaporation rate changed accordingly. Figures 5.27a and b show a typical TGA output from a cadmium-oxygen reaction experiment. In Figure 5.27a, the red line is the set temperature of the furnace and blue line is the weight of the TGA balance. As the furnace ramped up in temperature, the crucible temperature...
increased correspondingly. When the crucible temperature reaches 321°C, the cadmium began to melt and evaporation commenced. This continued as the furnace temperature ramped up and the crucible temperature increased. The evaporation resulted in a decrease of the crucible weight as measured by the TGA balance (blue line). Figure 5.27b shows the oxygen level (green line) in the gas stream as measured by mass spectroscopy. The oxygen gas was introduced in the TGA chamber to mix with the carrier gas at either just before or at the onset of significant evaporation. The timing of this was essential as premature introduction of oxygen would cause an oxide crust to form, due to gas diffusion, on the surface of the molten cadmium before it assumed a certain degree of volatility. If the crust had complete coverage and was thick enough, it could stop cadmium evaporation even at high crucible temperatures. As the gas stream flowed through the furnace heat zone, the oxygen and cadmium began to react, thus resulting in a reduction in the oxygen level as illustrated in Figure 5.27b. Once all the cadmium was evaporated, the balance weight ceased to decrease. As there was no more cadmium to react with the oxygen, the oxygen signal returns to the baseline level. The oxygen gas was then turned off so that the background level could also be determined.
The evaporation rate of cadmium (or zinc) was calculated from the weight change of the TGA balance with respect to time. Since the oxygen flow rate had been preset, the reaction rate between the cadmium and oxygen at the furnace set temperature could thus be calculated based on the cadmium evaporation rate, reduction in the oxygen level and the oxygen flow rate. Table 5.6 shows the results from the zinc oxygen reaction at three different furnace set temperatures and oxygen concentrations. The measured reaction rate was between 0.65 – 1.3%/s. The total reaction time was between 1.24 – 1.54s. The reaction rate increased with the concentration of oxygen concentration but no recognizable trend could be derived from that of the furnace temperature (Figure 5.28). The measured rate was similar to those obtained by other researchers in the solar furnace quenching experiments (Muller 2008). These results showed that the zinc vapor would need to be quenched from the decomposition temperature down to low temperature in the span of a few second in order to minimize recombination and obtain an adequate yield of zinc for hydrogen generation. Table 5.7 shows the preliminary measurement results for the cadmium-oxygen vapor reaction experiments. A plot of the cadmium reaction rate at 1035°C for different oxygen flow rates is shown in Figure 5.29. The cadmium reaction rate decreases with increasing oxygen flow rate which is in contrast to the conventional trend. Hence, there could be other subtle factors...
that determine the reaction rate. Additional experiments at other reaction temperatures are on going and the order of reaction will be determined using the entire data set.

Figure 5.28. Zinc-oxygen vapor reaction rate as a function of oxygen flow rate and TGA furnace set temperature.
Figure 5.29. Cadmium-oxygen vapor recombination reaction rate for various oxygen flow rate at 1035°C.
Table 5.6. Measurement results from zinc-oxygen reaction at various TGA furnace set temperatures and oxygen concentrations.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1020</th>
<th>1210</th>
<th>1340</th>
</tr>
</thead>
<tbody>
<tr>
<td>evap. Rate (mg/min)</td>
<td>12.8</td>
<td>11.2</td>
<td>8.5</td>
</tr>
<tr>
<td>evap. Rate (mole/min)</td>
<td>2.0E-04</td>
<td>1.7E-04</td>
<td>1.3E-04</td>
</tr>
<tr>
<td>oxygen flow rate (ml/min)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>oxygen flow rate (mole/min)</td>
<td>2.2E-04</td>
<td>1.3E-04</td>
<td>2.2E-04</td>
</tr>
<tr>
<td>amount of oxygen reacted %</td>
<td>26%</td>
<td>30%</td>
<td>22%</td>
</tr>
<tr>
<td>amount of oxygen reacted (mole/min)</td>
<td>5.9E-05</td>
<td>6.8E-05</td>
<td>4.9E-05</td>
</tr>
<tr>
<td>amount of zinc reacted (mole/min)</td>
<td>1.2E-04</td>
<td>1.4E-04</td>
<td>9.7E-05</td>
</tr>
<tr>
<td>Zn reaction rate (%)</td>
<td>60%</td>
<td>79%</td>
<td>74%</td>
</tr>
<tr>
<td>Zn reaction rate (%)</td>
<td>1.00%</td>
<td>1.32%</td>
<td>1.24%</td>
</tr>
<tr>
<td>Zinc/oxygen ratio</td>
<td>87%</td>
<td>76%</td>
<td>58%</td>
</tr>
<tr>
<td>amount of zinc reacted (mole)</td>
<td>3.0E-06</td>
<td>3.0E-06</td>
<td>2.0E-06</td>
</tr>
<tr>
<td>% of Zn reacted</td>
<td>1.55%</td>
<td>1.78%</td>
<td>1.53%</td>
</tr>
<tr>
<td>total gas flow (ml/min)</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Total reaction time (s)</td>
<td>1.54</td>
<td>1.35</td>
<td>1.24</td>
</tr>
</tbody>
</table>
Table 5.7. Measurement results from cadmium-oxygen reaction at various TGA furnace set temperatures and oxygen concentrations.

<table>
<thead>
<tr>
<th>Run</th>
<th>38</th>
<th>39</th>
<th>40</th>
<th>41</th>
<th>42</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>1474</td>
<td>1032</td>
<td>1032</td>
<td>1030</td>
<td>1035</td>
</tr>
<tr>
<td>Cd evap. Rate (mg/min)</td>
<td>9.4</td>
<td>12.8</td>
<td>14.2</td>
<td>16.5</td>
<td>14.1</td>
</tr>
<tr>
<td>Cd evap. Rate (mole/min)</td>
<td>8.4E-05</td>
<td>1.1E-04</td>
<td>1.3E-04</td>
<td>1.5E-04</td>
<td>1.3E-04</td>
</tr>
<tr>
<td>oxygen flow rate (ml/min)</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>oxygen flow rate (mole/min)</td>
<td>8.9E-05</td>
<td>8.9E-05</td>
<td>4.5E-05</td>
<td>2.2E-04</td>
<td>4.5E-04</td>
</tr>
<tr>
<td>amount of oxygen reacted (%/min)</td>
<td>22%</td>
<td>45%</td>
<td>102%</td>
<td>19%</td>
<td>3%</td>
</tr>
<tr>
<td>amount of oxygen reacted (mole/min)</td>
<td>2.0E-05</td>
<td>4.0E-05</td>
<td>4.5E-05</td>
<td>4.2E-05</td>
<td>1.4E-05</td>
</tr>
<tr>
<td>amount of Cd reacted (mole/min)</td>
<td>3.9.E-05</td>
<td>8.0.E-05</td>
<td>9.1.E-05</td>
<td>8.4.E-05</td>
<td>2.7.E-05</td>
</tr>
<tr>
<td>Cd reaction rate (%/min)</td>
<td>47%</td>
<td>70%</td>
<td>72%</td>
<td>57%</td>
<td>22%</td>
</tr>
<tr>
<td>Cd reaction rate (%/s)</td>
<td>0.78%</td>
<td>1.16%</td>
<td>1.20%</td>
<td>0.96%</td>
<td>0.36%</td>
</tr>
<tr>
<td>cadmium/oxygen ratio</td>
<td>0.94</td>
<td>1.28</td>
<td>2.83</td>
<td>0.66</td>
<td>0.28</td>
</tr>
<tr>
<td>cadmium reacted mole (through hot zone)</td>
<td>7.5.E-07</td>
<td>2.0.E-06</td>
<td>2.3.E-06</td>
<td>2.2.E-06</td>
<td>7.0.E-07</td>
</tr>
<tr>
<td>% of Cd reacted</td>
<td>0.90%</td>
<td>1.78%</td>
<td>1.85%</td>
<td>1.48%</td>
<td>0.56%</td>
</tr>
<tr>
<td>total gas flow (ml/min)</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>time travel through reaction zone at temperature (s-6cm length)</td>
<td>1.14</td>
<td>1.53</td>
<td>1.55</td>
<td>1.55</td>
<td>1.55</td>
</tr>
</tbody>
</table>
5.4 Cadmium Oxide (CdO) and Cadmium Carbonate (CdCO₃) Decomposition

The decomposition of cadmium oxide is a key step in the cadmium oxide cycle (Reich 1989, Behrens 1981). Conditions which allow full decomposition with minimal process temperature and back reaction will not only help to enhance the overall thermal efficiency but also reduce the cost of the hydrogen due to decreased associated solar field cost. Previous works have demonstrated the decomposition process using both a simulated solar source and a Knudsen cell (Sibieude 1982, Ambriz 1982, Miller 1975). To better understand the details of the decomposition process, non-isothermal decomposition experiments were carried out at UNLV utilizing the TGA (Thermogravimetric Analysis) similar to what had been carried out on the Zn/ZnO system (Weidenkaff 2000, Perkins 2007). There were three goals of the experiments:

- Decomposition mechanism determination i.e. whether the decomposed oxygen species is atomic or molecular:
  \[
  \begin{align*}
  & \text{CdO(s)} \rightarrow \text{Cd(g)} + \frac{1}{2}\text{O}_2(\text{g}) \quad \text{Ea: 241 kJ/mole} \quad \text{——— 5.8} \\
  & \text{CdO(s)} \rightarrow \text{Cd(g)} + \text{O(g)} \quad \text{Ea: 305 kJ/mole} \quad \text{——— 5.9}
  \end{align*}
  \]

- Determine the minimum cadmium decomposition temperature.

- Examine the effects of process environments and sample configuration on CdO decomposition.

These tests will provide data on both the decomposition temperatures and rates in various environments. Such data will be used to define the design concepts for a preliminary decomposer design.

5.4.1 Experimental Set Up for CdO and CdCO₃ Decomposition Experiments

In experimental set up, 200 mesh cadmium oxide powder was pressed into a 5mm diameter platinum crucible. It was found that alumina crucibles react with cadmium oxide at around the decomposition temperature. The furnace temperature was increased at different heating rates up to 1550°C. The nominal CdO decomposition temperature in air based on HSC chemistry is 1450°C at atmospheric pressure. The effects of various carrier gases, flow rates and furnace heating rates on the decomposition of cadmium oxide were investigated. Table 5.8 shows a summary of the conditions used in the decomposition experiments:
Table 5.8 Experimental set up conditions for all the cadmium oxide decomposition experiment.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier Gas</td>
<td>He, Ar, Air, CO₂ and O₂</td>
</tr>
<tr>
<td>Heating Rate</td>
<td>1 – 20 °C/min</td>
</tr>
<tr>
<td>Gas Flow Rate</td>
<td>20-150 ml/min</td>
</tr>
<tr>
<td>CdO Sample Weight</td>
<td>10-70 mg</td>
</tr>
</tbody>
</table>

5.4.2 CdO and CdCO₃ Decomposition Experimental Results

Figure 5.30 shows a typical TGA decomposition plot. The furnace temperature was ramped up at a constant rate and when it reached around 850°C, cadmium oxide began to decompose into cadmium and oxygen vapors. This was reflected by the reduction in crucible weight. As the temperature increased, the kinetics of decomposition process also accelerated resulting in further reduction in the crucible weight. When all the cadmium oxide inside the crucible had decomposed, the crucible weight stopped decreasing. It should be noted that the furnace was still ramping up after decomposition had been completed. Figure 5.31 shows the decomposition curves of cadmium carbonate (CdCO₃) under different gas environments. Completion of decomposition from cadmium carbonate into cadmium oxide and carbon dioxide ranges between 688 and 713 ºK (415 and 440ºC). Thus, thus the gas environment did not have a significant effect on the decomposition temperature. However, the carbon dioxide that was generated from the decomposition reaction would need to be captured for the cadmium carbonate cycle to be closed.
The key step in the cadmium based cycles is the decomposition of cadmium oxide at high temperature. Using the raw data obtained from the experiment, we were able to determine the effect of
carrier gas on the start and completion temperature ranges for the non-isothermal decomposition process (Figure 5.32). The use of helium had been found to decrease the decomposition temperature range. This is because under an inert gas environment, the oxygen partial pressure will be minimized as the only source of oxygen comes from the decomposition. As a result, the back/recombination reaction rate will also be at its lowest allowing the decomposition reaction to be completed much sooner. However, it is not entirely clear why argon gas did not have a similar impact as helium, as the decomposition temperature range in argon was higher. This could be due to the fact the diffusivity of oxygen in the helium is higher than that in argon (Landolt-Börnstein 2007). At room temperature, the diffusion coefficient variance is more than 3 fold. Table 5.9 shows the diffusion coefficient of helium in various gases (the volume fraction of He is 20%).

The decomposition rate (normalized by the initial cadmium weight) in pure helium, air and oxygen are plotted in Figures 5.33-35 respectively. The rate was highest in helium, followed by air and oxygen respectively at each temperature. This measured decomposition rate was useful for the design of the decomposer. It was also observed that the decomposition completion temperature in the TGA can be further reduced by using a slower furnace ramp up temperature and this effect is shown in Figure 5.36. With a slow heating rate of 1°C/min, the decomposition temperature in helium decreased to below 1150°C. Using a low heating rate is similar to a longer residence time. This reaction temperature suggests the possibility that the decomposition reaction could be conducted using heat from heated particles instead of high temperature concentrated solar power.

![Effect of Gas Environment on CdO Decomposition Completion Temperature](image)

Figure 5.32. Effect of carrier gas on the start and end decomposition temperature for cadmium oxide.
Table 5.9. Diffusivity of oxygen in various gases at ambient conditions.

<table>
<thead>
<tr>
<th>Gas*</th>
<th>D (x 10^4 m^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.753</td>
</tr>
<tr>
<td>Ar</td>
<td>0.220</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.214</td>
</tr>
<tr>
<td>Air</td>
<td>0.153</td>
</tr>
</tbody>
</table>

*volume fraction of helium is at 20%

Figure 5.33. CdO decomposition rate in helium a function of temperature.
Figure 5.34. CdO decomposition rate in air a function of temperature.

Figure 5.35. CdO decomposition rate in pure oxygen a function of temperature.
In order to determine the effect of process conditions on the activation energy and the kinetics of the decomposition process, the approach outlined by Perkins et al. (Perkins 2007) was used. The solid to gas decomposition rate has previously been defined by Galway and Brown (Galway and Brown 1999):

\[
\frac{d\alpha}{dt} = k_o \times \exp\left(\frac{E_a}{RT}\right) \times (1 - \alpha)^n
\]

--- 5.10

in which
\(\alpha\) is the degree of decomposition
\(k_o\) is the pre-exponential related to the kinetics
\(E_a\) is the activation
\(R\) is the gas constant
\(n\) is defined by the decomposition mechanism

The equation can be transformed into an Arrhenius equation by adding a constant \(T_0\) and the resulting equation becomes:
In which $\frac{d\alpha}{dT}$ is the degree of decomposition with respect to temperature change

$\beta$ is the temperature ramp rate

$k^* = k_0 \cdot \exp \left( \frac{E_a}{RT_0} \right)$

For the analysis of the cadmium oxide decomposition experimental results, $T_0$ was set at the temperature for which $\alpha = 0.5$. Hence, the decomposition curve in Figure 5.30 was then re-plotted based on eq. 5.9 and the slope of the linear portion equals $E_a/R$ and the intercept at the x-axis is $\ln k^*$. A typical plot is shown in Figure 5.37 in which the y axis is in units of K which is defined as

$$K = \frac{\left( \frac{d\alpha}{dT} \beta \right)}{\left( 1 - \alpha \right)^b}$$

Figure 5.37. Arrhenius plot and data fitting for CdO non-isothermal decomposition.

Thus, the effect of the various processing factors on the activation energy and the kinetics related pre-exponential term in eq. 5.11 can be determined. Table 5.10 and Figure 5.38 show the effect of carrier gases on $E_a$ and $k^*$. The calculated activation energy varies significantly depending on the carrier gas.
For both helium and argon, the activation energy was close to the theoretical value of 241kJ/mole which was similar to that observed by L'vov (L'vov 2001, 2004). However, the presence of oxygen in the other environments promoted the back reaction and resulted in higher apparent calculated activation energy. The effect of heating rate on $E_a$ and $k^*$ are shown in Figure 5.39. The activation energy is insensitive to the heating rate whereas $k^*$ is proportional to it. This is because more energy (per unit time) was pumped into the system resulting in faster kinetics. Table 5.11 shows the effect of sample configuration on $E_a$ and $k^*$. This experiment was based on those of L'vov and Perkins, in which the sample volume was double so the configuration dependence could be quantitatively determined. Results showed that $E_a$ is basically insensitive to the geometric set up but $k^*$ is extremely sensitive. The doubling of volume lead to two orders of magnitude decrease in $k^*$ compared to an expected drop of 50%. This shows that gas diffusion plays an extremely important role in the cadmium oxide decomposition process.

In conclusion, the decomposition of cadmium oxide is effected to a large extend by two factors, diffusion of oxygen away from the CdO/vapor interface and the partial pressure of oxygen in the carrier gas. The former can be enhanced by using as a carrier gas, such as helium, in which oxygen has high diffusivity and also through optimal reactor design. The oxygen partial pressure can be reduced via an inert carrier gas or with a reduced atmosphere.
Table 5.10 Calculated apparent activation energy for CdO decomposition in various gas environments

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>$E_a$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>248 ± 6</td>
</tr>
<tr>
<td>He</td>
<td>241 ± 10</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>268 ± 8</td>
</tr>
<tr>
<td>Air</td>
<td>363 ± 10</td>
</tr>
<tr>
<td>O$_2$</td>
<td>384 ± 4</td>
</tr>
</tbody>
</table>

Table 5.11. Effect of loading geometry on cadmium oxide decomposition kinetics

<table>
<thead>
<tr>
<th>Sample weight (mg) *</th>
<th>$E_a$</th>
<th>$k^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.6</td>
<td>250.5</td>
<td>7.48E-01</td>
</tr>
<tr>
<td>65.7</td>
<td>237.3</td>
<td>9.13E-03</td>
</tr>
</tbody>
</table>

*carrier gas is helium

Figure 5.38. Effect of carrier gas environment on $E_a$ and $k^*$ for CdO decomposition.
Figure 5.39. Effect of heating rate on $k^*$ and $E_a$.

Effect of heating rate on $k^*$ and $E_a$ (100% He)
6. Process Flowsheet Design and CdO Decomposer Design Concept

6.1 Solar Cadmium Hydrogen Process Flowsheet

In order to determine the thermal efficiency of the solar cadmium oxide cycle, process flowsheets for the cycle have been designed using AspenPlus software. The program takes into account the heat duty requirements for the various process steps and carries out a heat and mass balance for the entire cycle by iterations, finally reaching an equilibrium solution. The thermal efficiency can be maximized by the resourceful utilization of solar heat input but due to equipment associated with this method, the cost of hydrogen may not be lowest when one achieves the highest efficiency. Highest efficiency and lowest hydrogen cost may not go hand in hand. When merged with the appropriate solar field design, the final cost of hydrogen can thus be calculated.

For the present studies, the flowsheet was based on a production rate of a solar plant that produces 100,000 kg of hydrogen per day. The process was put together using the Aspen Plus software. The studies used a solar cadmium oxide decomposer and the hydrolysis step was carried out with molten cadmium. By completing a process flowsheet, a more accurate thermal efficiency of the overall process could thus be obtained. Furthermore, the flowsheets enabled us to determine the size of process equipment for a 100,000 kg of hydrogen per day plant. At the onset on the project, a baseline flowsheet was established. This flowsheet assumed a constant heat source and did not take into account the diurnal nature of the solar heat source. The process was set up so that the entire cycle, including the decomposition portion, ran 24 hours a day. A schematic block diagram of this flowsheet is shown in Figure 6.1 with the detailed Aspen Plus output shown in Figure 6.2. For 100,000 kg H₂/day, the required thermal input is 702 MW and the daily turnover of cadmium was estimated to be 5.6 million kg. Using this flowsheet, the thermal efficiency of the cadmium cycle was calculated to be 70% HHV (59% LHV). The required electricity required to operate various equipment within the plant was taken from the grid. Since the heat within the process streams can be used to power internal power generation circuits, a more advanced flowsheet was developed in which all the heat flow streams within the process were integrated. It incorporated the power generation circuit as part of the cycle and the electricity requirement was thus supplied internally. Excess electricity would be put back into the grid. This reduces the electricity dependence on the grid. A detailed flowsheet is shown in Figure 6.3.

However, since the solar heat is only available during daylight hours, the flowsheet had to take into account a diurnal cycle. A more advanced, second generation flowsheet was thus established and a block diagram of it is shown in Figure 6.4. In addition to integrating the various heat streams, it incorporated thermal heat storage using three different media: cadmium at 325°C, cadmium oxide at 325°C or cadmium at 700°C so that the process efficiency can be maximized. In the flowsheet, cadmium decomposition is carried out only during the day and the decomposed cadmium vapor is quenched into liquid cadmium at 700°C. The heat from this molten cadmium was used to generate electricity 24 hours a
day which consequently dropped the molten cadmium to between 350-450°C. This cadmium was then used to drive the hydrolysis step around the clock. The hydrogen plant components have been sized and costed for a 100,000 kg/day. In order to complete the flowsheet design, the solar field design will need to be completed. Work is under way with the Weizmann Institute to establish the solar field for a beam down tower design. The decomposer design will be incorporated into the flowsheet to complete the process design for an on sun demonstration of the cadmium cycle. In addition, the completion of the solar field design will enable us to arrive at a more rigorous cost estimate of hydrogen using H2A.

Figure 6.1. A simplified block diagram of the cadmium cycle flow sheet.
Figure 6.2. The detail flowsheet for a cadmium hydrogen cycle created with Aspen Plus.
Figure 6.3. The detail flowsheet for a cadmium hydrogen cycle with integrated heat flow and power generation circuit.
Figure 6.4. A block diagram of a 24 cadmium hydrogen flowsheet that takes into account the diurnal nature of the solar heat source.
Figure 6.5. The detailed flowsheet for a cadmium hydrogen cycle that takes into account the diurnal nature of the solar heat source.
6.2 Solar Reactor Design

There are various options to designing a cadmium oxide decomposer. One alternative is to employ a flow through reactor utilizing indirect solar radiation with nano zinc oxide particles (Perkins 2008). Reactor tubes are heated by concentrated solar radiation. Zinc oxide nano-particles flow through these reactor tubes and are decomposed as they are subjected to the irradiative heat from the tube wall. This design relies on the fast decomposition kinetics of very small nano zinc oxide particles. The drawback to this approach is the requirement to make nano zinc oxide particles during the hydrolysis process. Another decomposer design using a rotating cavity has been constructed (Muller 2006). In this design, solar radiation is concentrated and channeled into a rotating cavity that is lined with zinc oxide bricks. Zinc oxide powder is continuously fed into the cavity and as the cavity rotates, the powder is thrown around and eventually decomposed under high heat. This design is relatively sophisticated and faces scale up issue.

Based on the results from the cadmium oxide decomposition kinetics studies, a design concept for a decomposer has been established. A schematic of the decomposer is shown in Figure 6.6. This proposed design is based on a fluidized bed. The reactor cavity will be heated directly by concentrated solar radiation. Windows will be used in the cavity with a protective gas sweep over the inside of the windows to prevent metal vapor condensing on them. The use of a similar reactor has been demonstrated for other high temperature thermochemical hydrogen systems (Kodama 2008). The application of windows can prevent cadmium based material from escaping into the environment and allows for the use of carrier gases other than air. The skin of the reactor will be constructed from carbon steel and the inside wall will be lined with high temperature bricks. Cadmium oxide particles will be fed into the decomposer cavity and are then fluidized by a carrier gas, which can be either air or an inert like helium. Experiments have shown that the cadmium oxide particles formed by molten cadmium hydrolysis ranged between 1 to 10 \( \mu \)m in size, a size range that can be readily fluidized. The fluidized particles are subjected to the high temperature inside the cavity and decomposed accordingly. The advantages of this design are as follows:

- Fluidization allows for fast gas diffusion and heat transfer, which have been shown to be important to cadmium oxide decomposition
- The window design enables operation with either an inert carrier gas or sub-atmospheric pressure conditions, both of which can reduce the temperature required for decomposition
- Fluidized bed can be scaled easily to match the size of the solar tower
- The present design is based on a beam down solar tower design but can also be adapted to a tower top reactor.
Using this design, cadmium vapor quenching is incorporated into the decomposer design. The concept is to evacuate the decomposed cadmium and oxygen vapors from the chamber and quench them with a low temperature fluid. As a result, cadmium will be cooled into molten form and the recombination will then be reduced. The baseline concept is to use molten cadmium for quenching but other fluids such as air and helium are also being considered.

Work is ongoing to size and adapt the decomposer design concept to the solar field design. A cost estimate utilizing H2A will be conducted once these design parameters have been defined.
Figure 6.6. A multi-concentrator cadmium decomposer design which incorporates molten cadmium quenching.
7. SUMMARY

A literature survey was carried out and had identified more than 360 published thermochemical hydrogen production cycles. The list was narrowed down to the 12 most promising cycles based on the process thermal efficiencies, economic considerations and other operational criteria. The 12 cycle can be divided into 5 different categories: sulfuric acid cycles (e.g. sulfur iodine), metal sulfate cycles (e.g. manganese sulfate), volatile metal oxide cycles (e.g. cadmium oxide), non-volatile oxide metal oxide cycles (e.g. iron oxide) and low temperature cycles (e.g. hybrid copper). Experimental studies were carried out in order to reduce the number of selected cycle from twelve down to a manageable two to three cycles for on sun demonstrations.

GA along with UNLV performed laboratory experiments on the sulfate and cadmium based cycles to determine their feasibility. It was concluded from hydrolysis experiment results that sulfate based TCs were not viable candidates because the low temperature hydrogen generation step did not proceed as proposed. This was due to the existence of other, more thermodynamically favorable side reactions.

The feasibility studies for the cadmium oxide cycle were divided into three areas: i) cadmium oxide decomposition, ii) cadmium-oxygen vapor reaction and iii) cadmium hydrolysis. It was found that the cadmium oxide decomposition kinetics were very sensitive to the diffusion of oxygen gas away from the solid-gas interface. The diffusivity could be enhanced by either the use of an inert carrier gas or by highlighting geometric factors that could increase gas diffusivity. It was shown that decomposition could be completes at temperatures as low as 1150°C. A design concept utilizing a fluidized bed decomposer inside the solar cavity has been developed based on the findings. The motion of the particles in a circulating fluid provides enhanced mass and heat transfer which will help to maximize the decomposition rate.

The reaction rates between cadmium and oxygen vapors were measured at elevated temperatures. Preliminary measured reaction rates showed that 2% of the cadmium vapor has reacted per second. Further measurements are required in order to determine the effect of temperature, flow rate and oxygen concentrations. This, along with future quench modeling results, will provide inputs to design a quench process.

Experimental results have shown that carbon dioxide and shear deformation were essential to achieve a high hydrogen generation rate using solid cadmium. The carbon dioxide turned the impervious cadmium hydroxide surface layer into granular cadmium carbonate. This, along with mechanical deformation, made available fresh cadmium surfaces for reaction. Laboratory studies have also successfully demonstrated the use of molten cadmium to carry out the hydrogen generation reaction. The optimal temperature for fast hydrogen generation was determined to be between 460 – 480°C and
hydrogen production could be boosted further by increasing the surface contact between cadmium and steam. A rotary kiln loaded with inert pellets was used to demonstrate this. Based on the results obtained, a conceptual design for a high pressure rotary kiln that can be scaled up to carry out the hydrolysis step was made.

The flowsheet for the solar cadmium cycle has also been modified and improved based on the design concepts for the various process steps. First, the heat flow within the cycle was integrated so that a power generation circuit could be added. Next, thermal storage using molten cadmium was incorporated to run this circuit. The most up to date flowsheet separated the cycle into daytime processes (cadmium oxide and post decomposition vapor quenching) and 24 hour operations (molten cadmium hydrolysis and electricity generation). Overall thermal efficiency of this flowsheet was calculated to be at 58% (LHV).
8. ACCOMPLISHMENTS

- A database which contains all published thermochemical cycles for hydrogen production has been established.

- An evaluation into the applicability of more than 360 thermochemical cycles for solar based hydrogen production had been carried out. A set of criteria which took into account the economics, solar characteristics, scientific understanding and the environmental impact of the TCs were established. The list was narrowed down to the 50 most promising cycles and detailed flowsheet studies to determine their thermal efficiencies were carried out. A final set of 12 TCs with high thermal efficiency and the best chance to succeed were selected for laboratory studies.

- Feasibility studies on sulfate based hydrogen cycles have been completed. Experimental studies on sulfate based thermochemical cycles showed that they were not viable candidates. This was because the hydrogen generation step did not proceed as expected due other thermodynamically more favorable, non hydrogen generating reactions.

- Feasibility studies on cadmium based cycles have been carried out. Pathways for hydrogen generation using both solid and molten cadmium have been established based on laboratory studies.

- The role of carbon dioxide in the solid cadmium hydrolysis process was identified for the first time. The mechanism through which the protective cadmium hydroxide surface layer was broken up was demonstrated via experimental studies.

- It was shown that the combination of mechanical deformation and carbonate formation can greatly enhance the oxidation rate of solid cadmium in water.

- It was demonstrated that molten cadmium can be used to generate hydrogen via reaction with steam and surface contact between them played an important role. A concept to use a rotary kiln to accomplish this has been developed and other means to enhance the reaction rate have also been identified. Furthermore, a design concept for a large scale production unit was also proposed.

- A novel concept to measure the reaction rate of metal vapor with oxygen have been developed and demonstrated using a TGA. The reaction rates between zinc-oxygen and cadmium-oxygen gases at various temperatures and oxygen concentrations have been measured. This forms the baseline of the quench modeling studies going forward.
The cadmium oxide decomposition kinetics in various gaseous environments have been measured. The importance of kinetics and the back reaction in the decomposition process was demonstrated. Pathways to lower the decomposition temperature to below 1150°C have been found.

A process flowsheet for a 24 hour solar cadmium cycle has been established. Based on this layout, cadmium decomposition and cadmium vapor quenching takes place during daylight hours; the hydrolysis step and electricity generation run around the clock. The thermal efficiency of this process was calculated to be 58% (LHV).

A cadmium decomposer design concept, based on a fluidized bed, have been developed. The decomposer includes windows to prevent cadmium release and it also incorporates the idea of quenching decomposer vapors using molten cadmium.
9. ISSUES AND RECOMMENDATION

Most of the key process steps in the cadmium oxide cycle have been demonstrated but some issues remain. In addition, some of the design concepts will require demonstration to prove out their viability. The list of issues and corresponding recommendations for the next phase of the project are as follows:

- The main outstanding question in the cadmium cycle is whether quenching of cadmium vapor can be carried out at a sufficient rate using practical means. The reaction rate measurements should be completed. Furthermore, modeling studies should be carried out to understand the quenching process via the use of different quench fluids such as molten cadmium, air etc. The results will feed into the design of the quench process and enable one to determine whether it can be accomplished in a practical manner.

- The decomposition experiments to date were all based on a non-isothermal set up. To improve the design and define the operating conditions of the decomposer, isothermal measurements should also be made to further explore the decomposition process under varying conditions.

- A prototype decomposer based on the design concept should be constructed to verify its effectiveness in improving the decomposition process. Fluidization processes are often complicated to design and predict, thus the only means of obtaining valuable data is through testing of a laboratory scale prototype. A simulated solar source can be used for the application.

- It is beneficial to conduct the molten cadmium hydrolysis process under pressure so one can employ a hydrogen separation membrane to extract the hydrogen from the flowing stream without the need to condense the steam. Verification of the molten cadmium hydrolysis at elevated pressures is needed.

- Experimental results have shown that the use of an inert carrier gas, especially helium, can enhance the decomposition kinetics and lower the decomposition temperature. The use of an inert gas requires a gas separation step to be carried out in order to recover the inert gas for reuse. A flowsheet study will need to be carried out to determine whether such an added step is economically viable.

- New hydrogen generation cycles are being proposed in the literature based on new research. The project should retain resources so it has the ability to evaluate these new cycles and add them to the database.
10. PUBLICATIONS AND PRESENTATIONS

Publications

Barry W. McQuillan, Gottfried E. Besenbruch, Lloyd C. Brown, Roger A. Rennels, Bunsen Y. Wong;
“Metal Sulfate Water-Splitting Thermochemical Hydrogen Production Cycles”, Proceedings of the 16th

Bunsen Wong, Lloyd C. Brown, Gottfried E Besenbruch, Yitung Chen, Richard Diver, B. Earl, Sean H. T.
Hsieh, K. Kwan, Barry W. McQuillan, C. Perkins, P. Phol, Roger Rennels, N. Siegel, Alan Weimer;
International Symposium on Concentrated Solar Power and Chemical Energy Technology (SolarPACES),
Seville, Spain, June 20-23, 2006

Presentations

Lloyd Brown; “Solar Production of Hydrogen Using a Cadmium Based Thermochemical Cycle”, American
Institute of Chemical Engineers Spring Meeting, Orlando, FL, April 23-27, 2006

Lloyd C. Brown; “Metal Sulfate Water-Splitting Thermochemical Hydrogen Production Cycles”, 16th World

Lloyd C. Brown; “SHGR Cycle Evaluation Process”, International Program for the Hydrogen Economy

Lloyd C. Brown; “Solar Production of Hydrogen Using a Cadmium Based Thermochemical Cycle”,
International Program for the Hydrogen Economy (IPHE) Solar Hydrogen Working Group, Seville, Spain,

Bunsen Wong “Evaluation of Water-Splitting Cycles Applicable to Solar Thermal Systems”, 13th
International Symposium on Concentrated Solar Power and Chemical Energy Technology (SolarPACES),
Seville, Spain, June 20-23, 2006,
11. REFERENCES

Stéphane Abanades, Patrice Charvin, Gilles Flamant, Pierre Neveu
“Screening of water-splitting thermochemical cycles potentially attractive for hydrogen production by concentrated solar energy”
*Energy, Volume 31, Issue 14, November 2006, Pages 2805-2822*

J.J. Ambriz, M. Ducarroir, F. Sibieude
“Preparation of cadmium by thermal dissociation of cadmium oxide using solar energy”

B.J. Asirvatham and Z.A. Munir
“The decomposition of cadmium carbonate in air and in vacuum”

Robert G Behrens, Caroline F.V Mason
“A mass spectrometric investigation of the vaporization thermodynamics and vapor composition of cadmium oxide”

A. Berman, M. Epstein
“The kinetics of hydrogen production in the oxidation of liquid zinc with water vapor”

M. W. Breiter
“Effect of scraping on the anodic oxidation of cadmium in alkaline solutions”
*Electrochimica Acta, Volume 12, Issue 6, June 1967, Pages 679-686*

Brown LC, Besenbruch GE, Lentsch RD, Schultz KR, Funk JF and Pickard PS

S. Ciampi, V. di Castro, G. Polzonetti
“XPS study of cadmium oxidation in air,”

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

R. Gauer and U. Gut
“Thermodynamische und morphologische aspek der corrosion in trinkwasseraehnlchen losungen – II. Cadmium in hydrogencarbonatloesungen bie temperature von 25 bis 80°C”
*Corrosion Science, 1970. Vol. 10, pp. 503 to 511*

N. Gokon, S. Takahashi, H. Yamamoto, T. Kodama
“Thermochemical two-step water-splitting reactor with internally circulating fluidized bed for thermal reduction of ferrite particles”
J. Henning, H. D. Lutz
“Order-disorder phase transitions in β-MnSO₃·3H₂O-type hydrates: isotopic effects-vibrational, x-ray, thermoanalytical and permittivity measurement”
_Thermochimica Acta, Volume 150, Issue 1, 15 September 1989, Pages 141-152_

K.E. Heusler
“Growth and dissolution of passivating films”
_Corrosion Science, Volume 31, 1990, Pages 597-606_

E. Juzeliunas and M. Samuliavicien,
“Investigation of cadmium oxygen corrosion in acid sulphate solutions,”

Landolt-Börnstein
**Group IV/15A: Diffusion of Gases in Gases, Liquids and their Mixtures**
_Springer Berlin Heidelberg 2007_

Boris V. L’vov
“A physical approach to the interpretation of the mechanisms and kinetics of analyte release in electrothermal atomic absorption spectrometry”

Boris V. L’vov, Valery L. Ugolkov, Fedor F. Grekov
“Kinetics and mechanism of free-surface vaporization of zinc, cadmium and mercury oxides analyzed by the third-law method”

C. F. V. Mason, J. D. Farr and M. G. Bowman
“The cadmium-cadmium carbonate cycle for the thermochemical production of hydrogen”

C.F.V. Mason and M.G. Bowman
“The cadmium-cadmium carbonate cycle for the thermochemical production of hydrogen”
_Proc. 3rd World Hydrogen Conf, Japan 1980 pg. 537-549_

“High Efficiency Generation of Hydrogen Fuels Using Solar Thermo-chemical Spliting of Water”
_GA Report GA-A24972, May 2005_

T. Melchior, N. Piatkowski, and A. Steinfeld
“H₂ production by steam-quenching of Zn vapor in a hot-wall aerosol flow reactor”
_Chemical Engineering Science, Volume 64, Issue 5, March 2009, Pages 1095-1101_

A.R. Miller
“Vaporization of cadmium oxide by Knudsen effusion”
_High Temp. Sci., v. 7, no. 2, pp. 126-130_
R. Müller and A. Steinfeld
“H₂O-splitting thermochemical cycle based on ZnO/Zn-redox: Quenching the effluents from the ZnO dissociation”
Chemical Engineering Science, Volume 63, Issue 1, January 2008, Pages 217-227

Reto Müller, Peter Haeberling, Robert D. Palumbo
“Further advances toward the development of a direct heating solar thermal chemical reactor for the thermal dissociation of ZnO(s)”

J. Pangborn and J. Sharer
“Thermo-electrochemical process for producing hydrogen and oxygen from water”
United States Patent 3907980

Christopher Perkins, Paul Lichty, Alan W. Weimer
“Determination of aerosol kinetics of thermal ZnO dissociation by thermogravimetry”
Chemical Engineering Science, Volume 62, Issue 21, November 2007, Pages 5952-5962

Christopher Perkins, Paul R. Lichty, Alan W. Weimer
“Thermal ZnO dissociation in a rapid aerosol reactor as part of a solar hydrogen production cycle”

Leo Reich, S. H. Patel, S. S. Stivala
“Factors affecting the thermal decomposition of cadmium carbonate by TG”
Thermochimica Acta, Volume 138, Issue 1, 8 February 1989, Pages 147-160

M. Ristić, S. Popović, S. Musić
Formation and properties of Cd(OH)₂ and CdO particles
Materials Letters, Volume 58, Issue 20, August 2004, Pages 2494-2499

F. Sibieude, M. Ducarroir, A. Tofighi, J. Ambriz
High temperature experiments with a solar furnace: The decomposition of Fe₃O₄, Mn₃O₄, CdO

W.J. Tomlinson, N. Wardle
“Electrochemical equilibria of cadmium and water and the dissolution of cadmium as a function of pH”
Corrosion Science, Volume 15, Issues 6-12, 1975, Pages 663-665

A. Weidenkaff, A. W. Reller, A. Wokaun, A. Steinfeld
“Thermogravimetric analysis of the ZnO/Zn water splitting cycle”
Thermochimica Acta, Volume 359, Issue 1, 21 August 2000, Pages 69-75

T. Whaley, B. Yudow, R. Remick, J. Pangborn, A. Sammells
“Status of the cadmium thermoelectrochemical hydrogen cycle”

Irina Vishnevetsky, Michael Epstein
“Production of hydrogen from solar zinc in steam atmosphere”
J. O. Zerbino, S. B. Saidman, J. R. Vilche, A. J. Arvia

“Ellipsometric changes produced by oxidation—reduction potential cycles applied to cadmium in sodium hydroxide solutions”


**Project Title:** Solar Thermo-Chem for H$_2$ (STCH)

**Date of Report:** April 6, 2008

**Recipient:** Sandia National Laboratories

**Award Number:** DE-AC04-94AL85000

**Working Partners:** Sandia National Laboratories

**Cost-Sharing Partners:** None

**Contact:** Nathan Siegel, 505-284-2033, npsiege@sandia.gov

**DOE Managers:** Rick Farmer

**Patents/IP:** No patents were issued as part of this work.

**EXECUTIVE SUMMARY**

The solid particle receiver (SPR) is a direct absorption central receiver that can provide a solar interface with thermal storage for thermochemical hydrogen production processes requiring heat input at temperatures up to 1000 °C, which is beyond the capability of traditional heat transfer fluids. In operation, a curtain consisting of ceramic particles ranging in size from 100 µm-1,000 µm is dropped within the receiver cavity and directly illuminated by concentrated solar energy. The heated particles exit the receiver and may either be stored in silos or sent through a heat exchanger to provide process heat input (Figure 1). Because the energy is directly absorbed on the particles the receiver is capable of operating at high flux levels relative to other receiver concepts where the heat transfer media is confined to tubes. The performance of the SPR is dependent on several factors including the characteristics of the particle flow velocity (residence time) and opacity (optical density), the geometry of the receiver, and the operating temperature. In addition, because this type of receiver has an open aperture it is possible that convective losses to the environment can be significant.
Producing hydrogen using a thermochemical (TC) process typically requires a heat input in excess of 1000 °C. This heat can be supplied by using either solar or nuclear energy. There has been significant work done to identify viable water splitting processes [1-2]. Historically, processes receiving the most attention were those having a maximum temperature of around 900 °C that could be linked with a nuclear energy input. The Sulfur-Iodine and Hybrid Sulfur processes (Figure 2), developed by General Atomics and Westinghouse, respectively, are two examples [3-4]. Processes requiring still higher temperatures are achievable only with a solar energy input. The Zinc-Oxide [5] and Ferrite [6] processes require heat input at a temperature of 2000 °C and 1600 °C, respectively, and may be considered “solar-only”.

**Figure 1.** a) The solid particle receiver and b) one possible system configuration. Note that HX is a particle to process heat exchanger.

**Figure 2.** The process diagrams for the Sulfur Iodine (SI) and Hybrid Sulfur (HyS) cycles. The maximum temperature of heat addition is 950°C, consistent with the operating temperature of an SPR.
Integrating a TC process with a solar energy input requires a suitable solar interface. The prevailing wisdom with regard to the design of TC hydrogen production facilities is that bigger is better due to the economies of scale and operational considerations. Because of this, TC processes suitable for a central receiver platform tend to have more favorable economics [7]. In addition, a central receiver facility has the potential to offer thermal storage and “round-the-clock” operation. The principal challenges involved with the central receiver solar interface for TC processes are 1) identifying a suitable heat transfer and storage media and 2) designing a receiver that is efficient at the required temperatures (keeping in mind that adding secondary concentrators will boost efficiency and system cost). The solid particle receiver addresses both of these challenges.

The Solid Particle Receiver (SPR) was initially developed in the early 1980’s in an effort to create a direct absorption central receiver capable of efficiently achieving temperatures greater than those possible with molten nitrate salt receivers [8]. Early work on the SPR was done primarily by Sandia National Labs (SNL) and focused on identifying an appropriate particle material with respect to optical properties and structural stability [9], evaluating the heat absorption characteristics of particle flows using a radiant heat source [10], and creating computational models to simulate receiver operation and aid in design efforts [11-12]. This initial work at SNL was concluded in 1986 with the recommendation to proceed to on-sun testing on a central receiver platform. More recent SPR work included testing and optical characterization of a 30cm wide curtain heated using a solar furnace [13].

Over the last several years, as part of the Solar Thermochemical Hydrogen (STCH) project, we have continued the development of the SPR culminating in a series of tests conducted on-sun in 2007-2008. The purpose of these tests was to generate a dataset that could be used to validate existing and planned computational models. In this report we discuss:

- Initial off sun testing and evaluation of the optical properties of the solid particle curtain.
- The design and on-sun testing of the solid particle receiver prototype.
- The development and validation of computational models of the receiver.
- Plans for continued development leading up to a demonstration that will determine the ultimate feasibility of the technology for either Thermochemical or high temperature power generation processes.

If the solid particle receiver is ultimately proven to be a successful technology it would provide a critical component in a low-cost solar hydrogen fuel production facility.

PROJECT PLAN, GOALS, AND ACCOMPLISHMENTS

This project began in 2004 when the solid particle receiver was identified as a possible solar interface for the SI and HyS cycles. From there the project proceeded in the following stages:

- Initial modeling using previously developed codes. These include PSI-Cell, which was used in the 1980s by Sandia to do performance modeling of the SPR. We also began collaborating with the National Energy Technology Lab (NETL) to use their multi-phase code MFIX to perform some comparative analysis. The purpose of this work was to estimate the level of performance that might be expected of a prototype device tested at Sandia’s Central Receiver Test Facility (CRTF).
- Receiver design: The design process for the prototype was initiated in 2005 and concluded in June of 2006.
- Off-sun studies: a small off-sun test fixture was build to investigate the optical properties of the falling particle curtain and provide some additional data for the modeling efforts. This work was begun in 2005 and included collaborators from UNLV working onsite at Sandia. The work concluded in early 2007.
Prototype construction: The construction of the on-sun test prototype began in 2005 and was completed in December of 2007.

On-sun testing: Testing at Sandia’s CRTF was conducted from December 2007 through February 2008.

Computational modeling: These efforts have been ongoing and have included collaboration from researchers at UNLV and DLR (Germany). We began validating models developed at Sandia and DLR in early 2008 using experimental data from the on-sun testing.

The initial project plan was significantly different from the end result. Most notably, on-sun testing was originally planned for late 2005 (as opposed to late 2007, when it actually took place). Additionally, there were some changes made to the prototype test platform that restricted the maximum achievable temperature. However, the initial project goals, listed below, were all achieved:

1. Gain a firm understanding of the factors affecting particle flow dynamics and develop methods to control particle flow and maintain stability.
2. Demonstrate that the solid particle receiver can efficiently collect high temperature heat and provide thermal storage.
3. Provide empirical data necessary for the accurate formulation of advanced computational models. Modeling efforts to be undertaken at UNLV and SNL will focus on simulating particle dynamics within the receiver and also on the design of large-scale solid particle receivers for thermochemical cycles. These models must be developed alongside experimental work to assure accuracy.
4. Provide hands-on experience with the handling of solid particle materials in the context of solar thermal applications. The test platform will allow researchers to gain much needed information about solid particle behavior and handling that will be valuable to the balance of plant design of solid particle receiver.

The most notable accomplishment of this project was the first ever on-sun demonstration of a solid particle central receiver. In addition, the experimental dataset gathered during the on-sun test program has provided valuable information needed for further development of the technology.

PUBLICATIONS

The following papers were directly related to the work outlined in this document:


¹ This paper received “Best Paper” honors at the ASME Energy Sustainability conference.
COLLABORATIONS

We have developed a working collaboration with DLR in Germany through this project. Researchers from DLR have developed receiver models and participated in the on-sun test stage of this project. Their interest in the technology is motivated primarily by the desire to develop a high temperature receiver interface to support advanced, higher temperature power cycles such as the Brayton cycle.

SECTION 1: INITIAL TESTING AND DEVELOPMENT

Prior to completing the design of the prototype receiver we performed some initial testing off sun the purpose of which was to more fully characterize the falling particle curtain. This involved the measurement of certain flow parameters of an unheated solid particle curtain over a drop height of approximately three meters. The particles used in this work are commercially available sintered bauxite “proppants” from CarboCeramics [14]. The relevant material properties of the proppants are given in Table 1. The test platform (schematic shown in Figure 3) consists of 1) an upper discharge hopper with a machined slot to control flow rate, 2) a 3 m high three sided cavity through which the particles fall, and 3) a collection hopper at the base. Tests were run in 45-68 kg batches over a mass flow rate range of 1.2 kg/s-m to 22.3 kg/s-m. The width of the curtain at the discharge point is 30 cm. Preliminary testing confirmed that the mass flow rate out of the discharge hopper was independent of the bed height within the hopper (no hydrostatic affect on discharge rate). We had previously constructed a larger scale discharge hopper with a 1m slot width and a capacity of 1800 kg The discharge characteristics of the smaller 30 cm wide curtain were found to be an accurate representation of discharge from the larger hopper.

Table 1. Material Properties for CarboHSP®[14]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material composition</td>
<td>Aluminosilicate with ~7% Fe₂O₃</td>
</tr>
<tr>
<td>Median particle diameter</td>
<td>697 µm</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3.56</td>
</tr>
<tr>
<td>Bulk density</td>
<td>2.0 g/cc</td>
</tr>
<tr>
<td>Roundness</td>
<td>0.9</td>
</tr>
<tr>
<td>Sphericity</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Figure 3. Schematic of the off-sun drop test platform.
Experimental Methods

Velocity and Curtain Thickness

Measurement of particle velocity along the drop height was accomplished using the Phantom v5.1 high speed digital camera from Vision Research Inc [15]. The camera was mounted on a tripod that was positioned either in front of or to the side of the falling particle curtain. We used an AF Nikkor lens for all imaging. For images taken from the front of the curtain, a diffuse reflector was used to backlight the particles. In order to achieve an appropriate depth of field, the focal length of the camera was adjusted between 200-300 mm with the f/stop at f/8 and the position from the subject at 2.45 m. Images were taken at 1000 frames per second (1024x1024 resolution) with a digital exposure time of 100 µs. For images on the side of the curtain, the camera was first aligned with the curtain and positioned approximately 2.5 m from its center. The focal length and f/stop of the lens were 70 mm and f/8, respectively, and the image rate and exposure times were unchanged from the front imaging.

Analysis of the images for velocity measurement was done using the Particle Image Velocimetry (PIV) method and the software PIV Sleuth [16]. The thickness of the particle curtain was measured simply by counting the number of pixels across the dense portion of the curtain\(^2\) and then converting with the appropriate length scale. The measurement of curtain thickness becomes more difficult as the curtain becomes more diffuse and/or turbulent at either low mass flow or for drop distances greater than 2 m.

Solids Fraction

Solids fraction was measured using an impedance technique typically used in fluidized bed applications [17]; in this method, represented as a circuit schematic in Figure 4, the particles flow between the power and sensing electrodes and act as the dielectric in a capacitor. As the solids fraction changes so does the dielectric permittivity, which results in a change in the capacitance and output voltage of the circuit. The output voltage can be related to the solids fraction. This method relies on accurate measurement of curtain thickness, which as mentioned previously can be difficult. In addition, the measured curtain thickness using optical techniques may not be the same as the effective thickness seen by the electrodes.

---

\(^2\) The curtain cross-section typically has a dense core region containing the bulk of the particles bounded by a diffuse region with far fewer particles. The curtain thickness is assumed to be that of the core.
**Curtain Opacity**

Backlit images taken from the front of the curtain during velocity measurement tests were used to measure curtain opacity, which is defined as the ratio of frontal area covered by particles to the total frontal area of the curtain. A previous study has shown that light scattering by particles of the size used in this testing is negligible [9].

**Results and Discussion**

**Mass Flow Rate**

The flow rate of particles out of the discharge hopper was controlled using a 3.2 mm thick metal plate with a machined rectangular slot. The mass flow rate of the particles as a function of the slot width is shown in Figure 5.

![Figure 5. Particle discharge mass flow rate.](image)

Initial computational models of the 1MW, on-sun receiver currently in development have shown that the optimal mass flow rate, defined as that which achieves the highest efficiency at the desired particle exit temperature, is in the range of 2-5 kg/s-m.

**Particle Velocity**

Measured velocity data are particularly important to model validation because they offer a point of comparison for the relatively complicated two-phase momentum equations. In addition, the velocity of the particles, along with the drop height, fixes the residence time within the receiver and is directly related to the amount of heat that can be absorbed by the particles. The curtain density just downstream of the discharge slot is high enough to make the curtain opaque, thus preventing velocity measurements from being taken using backlit images from the front of the curtain. In these cases, images taken with a side view were used instead. Subsequent analysis showed that velocity measured from images taken from the front and side is nearly identical for the conditions tested. Figure 6 shows the velocity distribution for five particle mass flow rates.
The initial velocity at the discharge point is 0.4 m/s and is the same for all flow rates. The particles appear to be nearing a terminal velocity after a drop of only three meters. The particle velocity, which reflects a balance between the gravitational force and particle-air drag forces, increases with flow rate due to air entrainment by the particle curtain, which lowers the relative velocity difference between the particles and the air thereby reducing drag forces [18].

**Curtain Thickness and Solids Fraction**

As mentioned previously, the evaluation of the solids fraction using the impedance method requires the measurement of the curtain thickness. Figure 7 shows the data for curtain thickness as a function of drop distance and flow rate.

In all cases the curtain continues to spread as the particles fall. However, initial behavior near the discharge point does have a dependence on flow rate. Three images were taken within 25cm of the discharge to closely examine the flow during initial acceleration. The curtain thickness initially decreases at the two highest flow rates. The opposite is true for the lower flow
rates. Figure 8 shows a side by side comparison of the flow at 22.3 kg/s-m (B) and 1.23 kg/s-m (A) for the first 25 cm of drop.

**Figure 8.** Variation in curtain thickness near the discharge point for the lowest (A) and highest (B) mass flow rates tested.

The flow behavior seen in Figure 8 is similar to what one would expect for liquid flow through a sharp edged orifice plate and highlights the affect of the discharge geometry on the character of the curtain. In addition, the data presented in Figure 7 indicate that this effect is propagated downstream given that the widest curtain at 3m downstream corresponds to the 1.23kg/s-m flow whereas the narrowest corresponds to 22.3 kg/s-m.

Combining the measured values for the curtain thickness with the data for dielectric permittivity allows for the calculation of solids fraction, which is shown in Figure 9 for three mass flow rates.

**Figure 9.** Solids fraction variation along drop.
The solids fraction ranges from a maximum of ~2.5% at a position 30 cm downstream of the discharge point to a minimum of less than 1% near the terminal velocity. In general, particle-gas flows having a solids fraction in this range may be considered to be dilute; meaning that momentum exchange between particles is negligible compared to the momentum exchange between the particles and the gas through which they are falling [19]. This is an important result because it helps to identify the appropriate physical models to be used in the computational analysis of the receiver.

Curtain Opacity

An efficient solid particle receiver is one having a fairly opaque curtain where most of the incoming solar energy is absorbed by the particles. Any energy not absorbed by the particles will be incident on the back wall where it is either reflected, eventually exiting the aperture, or absorbed by the back wall and potentially damaging the receiver. In general, a minimum curtain opacity is needed to protect the back wall. This is especially true for large central receiver where peak flux values can reach 200 W/cm² and considering that passive insulation materials have a flux limit of around 100 W/cm². In this situation, and assuming that the particles are very close to the back wall of the receiver, a minimum opacity of 0.5 would be needed to maintain an acceptable flux level on the back wall. In practice, an opacity value greater than the minimum is desired for increased efficiency; how much greater depends largely on the optical design of the receiver cavity. Figure 10 shows the measured curtain opacity variation for several mass flow rates as well as some of the images taken along the drop length.

Figure 10. a) The variation in opacity along the drop height b) backlit images taken at the positions noted for a flow rate of 4.5 kg/s-m and c) backlit images taken at the positions noted for a flow rate of 1.2 kg/s-m.

The trend shown in Figure 10 is similar to that shown in Figure 9. This is because, for a non-scattering particle flow, the opacity of the curtain scales with the product of the solids fraction and the curtain thickness as per a modified version of Bouguer’s law, given as Equation 1. The results in Figure 10 also show that both the relative change in opacity between discharge and exit and the average value of opacity increase with mass flow rate. In addition, the opacity approaches a constant value as the particle flow nears the terminal velocity. The fact that the opacity does not appear to continue to decrease indefinitely is fortunate because,
outside of increasing the flow rate, there is not yet any other practical means of maintaining a relatively opaque curtain over an extended drop distance.

\[ \text{Opacity} = 1 - \frac{I}{I_0} = 1 - e^{-\frac{3f_w}{2d}} \]  

(1)

**Off-sun testing conclusions**

An experimental characterization of a falling particle curtain was performed to support ongoing solid particle receiver design and analysis efforts. These tests were performed using a small scale receiver model with a drop distance of 3 m. The principle conclusions can be summarized as follows:

1) The falling particle flow accelerates from 0.4m/s to between 6-7 m/s, approaching the terminal velocity, within the first 3 m for the range of mass flow rates tested.
2) The particle flow exiting the discharge slot shifts from diverging to converging as the mass flow rate is increased (coinciding with an increase in the discharge slot width)
3) The solids fraction for all mass flow rates over the entire drop length was less than 3%, indicating that the flow is dilute and than interparticle momentum exchange is negligible.
4) The opacity of the particle curtain increases with mass flow rate and approaches a constant value near the terminal velocity.

The data collected in this work will help us to improve and validate existing computational models as well as to provide design input for the planned 1 MWt on-sun test program. We plan to continue to refine our experimental methods with an increasing emphasis on developing techniques suitable for use during on-sun testing.

**Nomenclature**

\( I \)  Attenuated intensity, W/m\(^2\)
\( I_0 \)  Initial intensity, W/m\(^2\)
\( f \)  Solids fraction
\( w \)  Curtain thickness, cm
\( d \)  Particle diameter, cm

**SECTION 2: THE DESIGN AND ON-SUN TESTING OF A SOLID PARTICLE RECEIVER PROTOTYPE**

*Receiver design and construction*

The prototype SPR was designed to be tested on top of Sandia’s 61 m tall central receiver located at the National Solar Thermal Test Facility (NSTTF) in Albuquerque, NM. The heliostat field at the NSTTF can provide an estimated 5 MWt from 212 heliostats each with an area of 37 m\(^2\). The optics of the field are such that ~75% of the concentrated flux can be intercepted by an aperture measuring 1.5 m in diameter. The receiver cavity itself measures 6.3 m in height by 1.85 m in width and 1.5 m in depth. Figure 11 shows front, side, and top views as well as the position of the particle curtain within the cavity and the illuminated length determined by the angles of the reflected sunlight from the front and back row heliostats.
The interior and front surface of the cavity bordering the aperture is covered with a 5 cm thick layer of Duraboard HD from Unifrax [20]. This material is a rigid alumina-silica insulation that can tolerate up to 1000 kW/m$^2$ once the organic binders have been baked out. It is a relatively low cost option for rigid insulation compared with high-alumina products.

The SPR currently operates in batch mode with a total particle inventory of roughly 1800 kg. The particles are commercially available from CarboCeramics and marketed as CARBO HSP 20/40. The cost in 2007 was less than $0.5/lb. A listing of the properties of the particles is given in Table 2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material composition</td>
<td>Aluminosilicate with $\sim$7% Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Median particle diameter</td>
<td>697 $\mu$m</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3.56</td>
</tr>
<tr>
<td>Bulk density</td>
<td>2.0 g/cc</td>
</tr>
<tr>
<td>Roundness</td>
<td>0.9</td>
</tr>
<tr>
<td>Sphericity</td>
<td>0.9</td>
</tr>
<tr>
<td>Mean specific heat (0-300 °C)</td>
<td>760 J/kg-K</td>
</tr>
<tr>
<td>Estimated solar absorptivity</td>
<td>0.85</td>
</tr>
<tr>
<td>Estimated thermal conductivity</td>
<td>2.0 W/m-K</td>
</tr>
</tbody>
</table>

Depending on the flow rate, tests can run from roughly three minutes to just over seven minutes. The decision to run in batch mode was made primarily due to the thermal limits of the
bucket elevator used to move the particles from the bottom of the receiver to the top. In this case, moving particles at a temperature greater than 170 °C would damage the elevator. In operation, particles are first loaded into the discharge hopper above the receiver cavity via the bucket elevator. A sliding gate at the bottom of this hopper allows particles to drop through a machined slot that controls the flow rate over the 1 m wide curtain. Previous studies have shown that a machined slot offers repeatable control over mass flow rate and that the rate does not change as the level of particles in the hopper drops during discharge [22]. The particles fall through the open cavity where they are heated and finally collected in an internally insulated lower hopper. A sliding gate on the lower hopper allows the particle flow to be metered into a fluidized cooler that lowers their temperature to within the limits of the bucket elevator. The major system components are shown in Figure 12.

![Figure 12. The SPR system layout](image)

Data Acquisition

The receiver cavity was instrumented with Type K thermocouples (TCs) at several positions along the back and side walls. These TCs were installed just below the outer surface of the rigid insulation to avoid exposure to direct flux. Additional TCs were installed 15 cm above the insulation to measure the air temperature near the walls. These TCs were only placed in areas within the cavity that did not see direct flux. Finally, the particle temperature at the discharge slot as well as at five vertical positions within the bottom hopper was also measured. A high speed camera (Phantom v7.1 @ 500 frames/second) was used to acquire on-sun images of the particles as they fell past the aperture. The particle image velocimetry (PIV) method was then used to calculate a velocity distribution from the set of images. Previous cold-flow testing had shown that after falling 3 m the particles are near their terminal velocity. We expect that the same is true of on-sun testing, although the terminal velocity might be slightly higher due to the reduced density of heated air.
Table 3. SPR test conditions

<table>
<thead>
<tr>
<th>Date</th>
<th>DNI, W/m²</th>
<th>Flow rate, kg/s-m</th>
<th>Input power, MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-8-08</td>
<td>1050</td>
<td>8.72</td>
<td>1.90</td>
</tr>
<tr>
<td>2-8-08</td>
<td>1070</td>
<td>8.72</td>
<td>2.28</td>
</tr>
<tr>
<td>2-11-08</td>
<td>1002</td>
<td>5.32</td>
<td>1.52</td>
</tr>
<tr>
<td>2-11-08</td>
<td>1038</td>
<td>5.32</td>
<td>2.28</td>
</tr>
<tr>
<td>2-11-08</td>
<td>1040</td>
<td>3.84</td>
<td>2.28</td>
</tr>
<tr>
<td>2-13-08</td>
<td>1050</td>
<td>3.84</td>
<td>1.52</td>
</tr>
<tr>
<td>2-18-08</td>
<td>1000</td>
<td>8.72</td>
<td>2.56</td>
</tr>
<tr>
<td>2-22-08</td>
<td>962</td>
<td>5.32</td>
<td>2.56</td>
</tr>
<tr>
<td>2-28-08</td>
<td>953</td>
<td>3.84</td>
<td>2.56</td>
</tr>
</tbody>
</table>

Experimental results and discussion

Testing was conducted in January and February of 2008. In Albuquerque, during this time of year, the levels of direct normal insolation (DNI) are typically above 1040 W/m² sometimes reaching 1080 W/m². All tests were done with a single aimpoint in the center of the aperture. The heliostats used for testing were concentrated in the center of the field to maximize intercept. The maximum number of heliostats used in a test was set at 140, roughly 65% of the field. Analysis indicated that above this level the spillage on the back wall would exceed 1000 W/m² and result in damage to the cavity insulation. The test plan called for running three particle flow rates at three flux levels and is summarized in Table 3.

The amount of power entering the aperture is estimated using the code DELSOL [21]. Parameters within the code have been adjusted, based on experimental data, so that the output is an accurate prediction of the performance of the field at the NSTTF. The temperature increase ($\Delta T$) of the particles during on-sun testing ranged from 100 °C to nearly 250 °C for a single pass through the cavity. These data are summarized in Figure 13.
In general, for a given amount of power the temperature change of the particles increases as the flow rate is reduced. This is primarily a result of decreased particle shading i.e. a lower density curtain allows each particle to receive more direct flux. The increased temperature rise comes at the expense of absorption efficiency since at low flow rates a larger relative fraction of the incident energy strikes the back wall as opposed to the particles, violating a cardinal rule of receiver design which is to “put the flux on the absorber”. Data for peak back wall temperature are shown in Figure 14. An image of SPR aperture during on-sun testing is shown in Figure 15 and illustrates the difference in curtain transparency at the three flow rates.

Figure 13. Single pass temperature rise of the particles.

Figure 14. The temperature distribution along the back wall of the receiver cavit
Excessive heating of the back wall can be problematic with respect to the cavity insulation. The Duraboard HD used during these tests is tolerant to flux up to 1000 kW/m². We observed the formation of substantial cracks through the insulation board in the vicinity of the region of peak temperature shown in Fig. 14. Although it is unlikely that flux on the back wall ever exceeded 1000 kW/m², it is possible that cycling of the back wall temperature combined with water deposited in the cavity during storms caused the degradation. Research on more durable cavity insulation materials is merited since, in a commercial device, the frequent replacement of the insulation within the cavity is likely to be an unacceptable O&M cost.

![Figure 15. The particle curtain as it passes through the cavity. Wind is disturbing the flow in the left corner of the 3.84 kg/s-m case.](image)

One concern prior to testing on-sun was the potential impact on curtain stability of buoyancy driven flow within the cavity. Although the particles are dense and acquire a relatively large amount of momentum as they fall there is a chance that air currents could be set up within the cavity that would disturb the uniformity of the particle curtain. We did not observe this during testing even though the air within the cavity achieved temperatures in excess of 800°C, through contact with the hot cavity walls.

A related concern is the impact of ambient wind on the particle flow within the open cavity receiver. In commercial scale systems, the receiver cavity might be located 250 m or more above the ground and exposed to almost constant winds. We measured wind speed at the aperture prior to most tests. The maximum measured wind speed was in excess of 13 m/s, with most tests conducted when winds exceeded 5 m/s. In most cases the wind came either directly out of the north or the south and had little effect on the curtain regardless of speed. Winds that were not directly normal to the aperture did produce some instability in the curtain. This observation is consistent with some of the qualitative predictions of our computational models and is evidence enough that we should analyze this affect further and develop mitigation strategies.

**Conclusions of the initial on-sun testing**

The on-sun test program concluded in March of 2008 provided a foundational data set for the validation of existing and future computational models. The demonstration of a single
pass temperature increase in excess of 200 C at practical particle mass flow rates is an encouraging result, as is the relative stability of the curtain when exposed to wind and buoyant flows. We are, however, reluctant to say that the overall feasibility of the concept has sufficiently demonstrated by these tests. That can only be accomplished using a redesigned and optimized receiver system.

SECTION 3: THE DEVELOPMENT AND VALIDATION OF COMPUTATIONAL MODELS OF THE SPR

Computational Approach

A computational fluid dynamics model was developed using FLUENT [24] to simulate the coupled processes of gas flow, particle flow, solar irradiation, and heat transfer within the solid particle receiver. Figure 16 shows the model of the solid particle receiver that was used in FLUENT. Sensitivity studies of flow within the cavity were performed using different numbers of hexahedral elements (up to ~1 million), and it was found that a mesh resolution with 169,200 cells was sufficient to yield grid independence.

Gas Flow Model

As the particles fall through the receiver, air is entrained into the particle flow. Cool air from outside the receiver cavity is pulled into the receiver and circulated within the hot cavity. FLUENT solves the governing partial differential equations for gas-phase conservation of mass, momentum, and energy.

![Figure 16. Drawing of the model used in FLUENT.](image)

Turbulent flow (and closure for the turbulent viscosity term) was modeled using the k-\( \varepsilon \) realizable turbulence model (using default values) with the standard wall function, which provides a commonly used approximation for the near-wall velocity for turbulent flows. The term "realizable" refers to the fact that the model satisfies mathematical constraints on the Reynolds stresses (must remain positive) by making a previously defined constant in the definition of the turbulent viscosity a function of the mean flow and turbulence quantities. Neither the standard k-\( \varepsilon \) model nor the RNG k-\( \varepsilon \) model is realizable and can violate the positive value of the
Reynolds stress terms. The realizable k-ε model has been validated for a wide range of flows including jets, mixing layers, channel and boundary layer flows, and separated flows. The realizable k-ε model is likely to provide superior performance flow flows involving rotation, boundary layers with strong adverse pressure gradients, separation, and recirculation. Surfaces representing the front aperture and bottom outlet of the receiver were specified as fixed pressure boundaries where air could enter and exit (see Figure 16).

Particle Flow Model

The motion of the particles falling through the receiver is governed in FLUENT by a time-integrated force balance on each particle that relates particle acceleration, drag, and gravity in a Lagrangian reference frame. The formulation assumes that the interaction between particles is negligible, which is valid for particle volume fractions less than approximately 10%. Previous tests of falling particles have shown that the particle volume fraction (volume of particles divided by total volume occupied by particles and air) is less than several percent [22]. However, the particles do interact with the continuous gas phase and entrain air as they fall through the receiver. Two-way turbulence coupling was activated in FLUENT.

The particles were released from 300 points defined by the narrow slot at the top of the receiver (see Figure 16). The inlet temperature of the particles was prescribed based on measured discharge temperatures. The mass flow rate of the particles was also prescribed (Table 3), and this value was used in FLUENT to determine the rate of particle release (particles/second) based on the mass of each particle and the number of release points. Sensitivity studies showed that the number and location of release points defined along the slot did not significantly impact the results as long as the number of release points was greater than 100. A surface representing the bottom opening of the cavity, as well as the aperture in the front of the receiver, were defined as outlets where particles could escape (see Figure 16). All other wall surfaces were defined as reflecting surfaces for the solid particles.

Convection and radiative heat transfer (discrete ordinates radiation) were also included in the discrete-phase particle model. The particles were assumed to be spherical, and the particle radiation scattering factor in FLUENT was assumed to be 0.3. The particles absorb irradiation, reducing the amount of solar flux that reaches the walls of the receiver. The mass flow rate of the particles, which impacts the particle concentration, also impacts the amount of irradiation received by the particles and cavity walls.

Solar Irradiation and Heat Transfer Models

A discrete-ordinates radiation model in FLUENT was used to simulate the solar irradiation onto the falling particles from the heliostat field. The discrete-ordinates radiation model solves the radiative transfer equation over a domain of discrete solid angles. The model does not perform ray tracing; instead, the radiative transfer equation is transformed into as many transport equations as there are solid angles. It calculates the radiation intensity as a result of absorption, scattering, and emission within the fluid, along with reflection and emission from surfaces. The solution method is the same as that used for the momentum and energy equations.

This approach is an improvement over previous modeling of a solid particle receiver by Chen et al. [25]. In that study, a solar ray-tracing algorithm in FLUENT was used to predict the solar illumination energy on the walls. In Chen et al., heating of the falling particles was simulated by reradiation from the walls to the particles, but direct irradiation from the heliostat beams was not modeled since the solar ray-tracing solar-load model does not interact directly.
with the discrete-phase particles. In contrast, the use of the discrete-ordinates radiation model to apply the solar load on the model domain allows for direct irradiation of the particles.

In the current study, a small “solar patch” was applied in the middle of the aperture to simulate the concentrated solar irradiation entering the receiver via the discrete-ordinates radiation model. The beam width, direction, and diffuse fraction of the irradiation received through the solar patch were used as calibration parameters. The diffuse fraction (between 0 and 1) dictates how much radiation from the solar patch is emitted specularly (along the beam direction) or diffusely (in all directions from the surface). The magnitude of the solar irradiation [W/m²] applied to the solar patch was calculated using the estimated input power [MW] for each test from [23] and the size of the solar patch (0.1 m² – 1 m²). The entire solar irradiation was applied to a single wavelength band (0 – 4.5 microns) in a two-band model in FLUENT. The second wavelength band (4.5 – 100 microns) was used to account for the higher thermal emission at higher wavelengths from the cavity walls.

Heat conduction was also simulated within the walls of the cavity, and convective heat loss to the ambient was simulated assuming a heat transfer coefficient of 5 W/m²-K and a free-stream temperature of 300 K on the outside of the walls.

The temperature of the aperture boundary surface was set equal to the measured ambient temperature during each test. This temperature was used as a blackbody boundary temperature (with an emissivity of one) to calculate reradiation from the internal walls of the cavity to the aperture (and bottom outlet). Sensitivity studies were performed and showed that the use of a variable ambient temperature (relative to a fixed ambient temperature of 300 K) did not significantly change the results.

Solution Procedure

For each of the nine on-sun tests listed in Table 3, the FLUENT model was simulated until a converged solution was achieved for the continuity, velocity, energy, turbulence, and discrete-ordinates intensity residuals. The discrete-phase particle sources (momentum and heat sinks/sources generated by the particles and applied to the continuous phase equations) were updated every flow iteration, and one continuous phase iteration was applied per discrete-phase iteration. Ten flow iterations were run per radiation iteration. In some runs, the solar irradiation was omitted so that unheated particle velocities and concentrations could be compared to experimental measurements of the same quantities [22].

For the on-sun test comparisons, the particle and wall temperatures were used as metrics to calibrate the parameters that governed the shape (but not magnitude) of the solar irradiation entering through the solar patch. The irradiation beam width, beam direction, and diffuse fraction were varied until the comparisons between the predicted and measured particle and wall temperatures were qualitatively optimized. The following solar irradiation and discrete-ordinates radiation parameters yielded the best matches to the data:

- **Beam Width**: theta (vertical) x phi (horizontal) = 30 x 150 degrees
- **Beam Direction**: (0, 0.5, -0.866) or 30 degrees from horizontal
- **Diffuse Fraction**: 0.15
- **Angular Discretization of Solid Angles**: theta x phi divisions = 7 x 7, theta x phi pixels = 3 x 3

The calibrated values for the simulated beam shape and direction were within the range of the actual beam shape entering the receiver as dictated by the number and location of heliostats used in each test. The angular discretization of the solid angles was refined sufficiently to yield smooth temperature and incident radiation distributions.
Results and Discussion

Simulated results were compared to measured particle velocities, volume fractions, wall temperatures, and particle temperatures recorded during a series of unheated tests [22] and on-sun tests [23].

Particle Velocity and Concentration

Simulations of unheated particle velocity and concentration (volume of particles divided by total volume occupied by particles and air) were compared to measured values from previous tests. Figure 17 shows a plot of the simulated and measured particle velocities as a function of particle distance from the release point. Simulation results for two different mesh resolutions are shown, and both yield very similar results to the measured velocities (average relative error ~6%). The particle velocity increases rapidly after being released (reaching 4 m/s within 1 m of the release point), and continues to increase more slowly thereafter.

Figure 17. Simulated vs. measured particle velocities for unheated test.

Figure 18 shows a plot of the simulated and measured particle volume fraction at different locations beneath the release point. As the particles fall downward, they disperse and decrease in concentration. The maximum volume fraction is less than 3% near the top, and decreases to less than 0.5% within 3 m from the release point. The average relative error between the simulated and measured particle volume fractions was ~8%.
Figure 18. Simulated vs. measured particle volume fraction for unheated test.

On-Sun Test Comparisons

Figure 19 shows representative images from the simulations of the nine on-sun tests listed in. The left image shows the simulated incident radiation on the walls of the receiver. No “spillage” occurs on the front walls of the receiver because the source of the irradiation is the small patch in the center of the aperture. However, because the beam shape emanating from the patch was defined by vertical and horizontal angles of 30 and 150 degrees, respectively, with a diffuse fraction of 0.15, the solar flux is spread laterally and vertically on the walls. In addition, the direction of the beam is aligned 30 degrees above horizontal, so the beam enters the cavity in an upward direction. The simulated beam shape and direction is approximately the same as the actual concentrated flux entering the receiver based on the location of the heliostats used in the tests.

Figure 19. Simulated wall incident radiation (left), particle tracks colored by temperature (middle), and gas flow colored by velocity (right).
The middle image in Figure 19 shows simulated particle tracks (colored by temperature) of particle streams released along the discharge slot. As the particles pass near the aperture, they are irradiated by the concentrated solar flux and increase in temperature.

The right image in Figure 19 shows simulated contours of gas-phase velocity within the receiver. The falling particles entrain airflow downward (up to ~5 m/s). Air enters the receiver through the cavity and is pushed primarily downward with the particles, although some air entering the top of the aperture flows upward along the front wall before recirculating back down with the particle flow. Behind the particle curtain, hot air rises upward along the back wall and recirculates back down with the falling particles.

Figure 20 shows a plot of the simulated and measured vertical temperature distributions along the center of the back wall of the receiver for the test conducted on 2/22/08, which is representative of the wall temperature distribution for each test. The wall temperature increases from the bottom of the receiver to a point approximately 2.3 m above the bottom. This is the point where the maximum solar flux was incident on the back wall. The location of the maximum temperature was used to calibrate the solar beam direction used in the simulations. Above this location, the temperature decreases with increasing height. Near the top of the cavity, the wall temperature begins to increase again slightly, probably due to lower convective heat transfer to the adjacent air flow, which has a lower buoyant upward velocity near the top of the receiver where the vertical wall meets the top wall.

The data in Figure 20 show that the measured wall temperatures were still increasing during the duration of the test. Nevertheless, the trend in the transient temperature distribution is similar to the simulated steady-state wall temperature distribution.

The data in Figure 20 show that the measured wall temperatures were still increasing during the duration of the test. Nevertheless, the trend in the transient temperature distribution is similar to the simulated steady-state wall temperature distribution.

Figure 20. Simulated and measured vertical temperature distributions along the center of the back wall of the receiver for the test conducted on 2/22/08 (5.32 kg/s-m, 2.56 MW).

Figure 21 shows the simulated and measured increase in particle temperatures for all nine on-sun tests. The particle-temperature increase ranged from ~100 K – 250 K. As discussed in Siegel and Kolb [23], factors impacting the observed increase in particle temperatures included the input power and particle mass flow rate. Higher particle temperatures were observed during tests with higher input power and lower mass flow rates. It was postulated that at lower particle mass flow rates, less shading occurred with a lower concentration of particles, and the particles received more direct solar irradiation.
The measured increase in particle temperature is within the range of simulated values for eight out of the nine tests. The simulated particle-temperature increase follows the observed trends as a function of input power and particle mass flow rate. For a given mass flow rate, the simulated particle-temperature increase was positively correlated with simulated input power (for example, compare the results for the two runs at 8.72 kg/s-m on 2/8/08). For a given input power, the simulated particle-temperature increase was negatively correlated with the particle mass flow rate (for example, compare the results of the runs at 2.56 MW on 2/18/08, 2/22/08, and 2/28/08).

Figure 21. Simulated vs. measured increase in particle temperatures for nine on-sun tests.

Figure 22 shows the simulated and measured solid-particle-receiver efficiency for each test, where the efficiency is defined as follows:

$$
\eta = \frac{Q_{\text{particles}}}{Q_{\text{in}}} = \frac{1}{N} \sum_{i} m_i c_p \left( T_{i,f} - T_{i,o} \right)
$$

where $m_i$ is the mass flow rate of particle stream, $i$, $c_p$ is the particle specific heat, $T_{i,f}$ and $T_{i,o}$ are the final and initial particle temperatures, $Q_{\text{particles}}$ is the power absorbed by the particles, and $Q_{\text{in}}$ is the total power entering the receiver (Table 3). The mass flow rate of each particle stream, $i$, is defined as the prescribed total mass flow rate (Table 3) divided by the number of particle streams tracked in the simulation (300).

As discussed in Siegel and Kolb [23], the efficiency improves with increasing particle mass flow rate at higher rates of input power (> 1.75 MW, Fig. 4) due to the increased opacity of the particle curtain and its ability to intercept a greater fraction of the incident solar energy. However, at lower input power, the efficiency decreases with increasing particle mass flow rate due to the increased particle shading and reduced particle-temperature increase. The interactions between these parameters and additional factors warrants a thorough parametric evaluation, which is currently underway.
**Conclusions**

A computational model of particle flow through a solid particle receiver has been developed. As the particles fall through the receiver cavity, they are irradiated by concentrated solar energy entering the receiver through an aperture. Solar irradiation, reradiation and emission from the cavity walls, convection, wall conduction, and two-phase particle/air flow are simulated in the model. Simulated results are compared to measured temperatures of the particles and walls during nine on-sun tests. Results are also compared to particle velocities and concentrations measured during unheated tests with good matches to the data. Results show that the model accurately predicts the salient distributions and trends in particle temperatures and efficiencies as a function of input power and particle mass flow rate.

**SECTION 4: FUTURE WORK: DEMONSTRATING TECHNICAL FEASIBILITY**

In order to demonstrate the ultimate feasibility of the SPR either for thermochemical fuel or electric power production, the following milestones must be achieved.

1. The demonstration of a particle exit temperature in excess of 900 °C. This is the minimum temperature required to produce hydrogen with sulfuric-acid-cracking cycles. To achieve 900 °C we must optimize the optical design of the receiver. For example, in the current test the average flux on the particle curtain was 400 suns. Our performance models indicate that an 800 sun average will be required to achieve 900 °C given an inlet temperature of 600 °C. Achieving 900 °C may also require recirculation to increase residence time for a receiver of the size that we’re likely to test. In larger systems having a greater drop distance it may not be necessary.
2. The demonstration of receiver efficiency in excess of 70% (heat absorbed/power into aperture)
3. The development of a rigorous multi-phase analysis of the impact of ambient wind on curtain stability in an open cavity and the demonstration of strategies to mitigate this issue.
4. The demonstration of the physical stability of the particles i.e. that particle attrition due to self abrasion is within acceptable limits for economical plant operation.

Achieving these milestones will require a mix of computational and experimental efforts. We currently plan to use our validated computational models to design an optimized cavity receiver based on our current test platform (5 MW$_n$, central receiver). This receiver design will incorporate a high temperature bucket lift and enable hot particle recirculation. Assuming that the four milestones can be achieved, the next step is to proceed with scale-up and balance of plant design with an eye towards the eventual demonstration of an integrated solar hydrogen system, likely based on the hybrid sulfur (HyS) cycle. We believe that much of the technology needed for a demonstration already exists. Some components, such as the receiver, electrolyzer, and the particle-to-process heat exchanger still require R&D investment, but much of the system design and construction can be handled through known technical solutions.

REFERENCES


20. Unifrax Duraboard HD specs retrieved from [www.unifrax.com](http://www.unifrax.com)

21. DELSOL


**ACKNOWLEDGEMENTS**

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.