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# SANDIA NATIONAL LABORATORIES
# SOLAR THERMOCHEMICAL HYDROGEN PRODUCTION (STCH)

QUARTERLY PROGRESS REPORT FOR JULY 1, 2011–SEPTEMBER 30, 2011

**SUBMITTED BY:** JAY KELLER, (925) 294-3316, JOKELLE@SANDIA.GOV

**RECIPIENT:** SANDIA NATIONAL LABORATORIES

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# SOLAR CAVITY REACTOR SYSTEM EXPERIMENTATION (MATERIALS/OPERATIONS, MODELING AND CONTROL)

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|---|---|
| **COVERING PERIOD:** | JULY 1, 2011–SEPTEMBER 30, 2011 |
| **DATE OF REPORT:** | OCTOBER 28, 2011 |
| **PRINCIPLE INVESTIGATOR:** | ALAN WEIMER, ALAN.WEIMER@COLORADO.EDU |
| **OTHER KEY RESEARCHERS:** | PAUL LICHTY, JANNA MARTINEK, CHRISTOPHER MUHICH, ELIZABETH SAADE |

## BACKGROUND

Previously, a steady state 3D CFD model for the solar receiver was developed and experimentally validated. Both theoretical and experimental results indicated that the current receiver design suffers from low efficiency, large temperature gradients, which could lead to material weakness, and highly non-uniform temperature distributions between tubes, which may prevent useful utilization of the front tubes. A 213-8 fractional factorial design study was set up to identify parameters which significantly impact receiver performance. The base design consisted of a semicircle of tubes near the back cavity wall with nine two-level factors describing receiver geometry and four factors describing operating conditions including gas flow rate, solid flow rate, and solar power input. The geometric factors allowed for variations in cavity height, radius, number of tubes, radius of tubes, and arrangement of tubes. Both staggered and non-staggered arrangements were considered along with factors allowing for offset of tubes toward the window. Each model was solved in two embodiments for an absorbing and a reflective cavity, and all treatment combinations were evaluated on the basis of receiver efficiency.

## STATUS

Results from the 213-8 fractional factorial design with a reflective cavity indicated that cavity radius, solar power input, and the reaction requirements had the largest impact on receiver efficiency. Additional parameters describing receiver geometry were significant through binary interactions, and, as there were no significant interactions between parameters describing receiver geometry and operating conditions, a subset of the geometric parameters were assessed in a second 26-2 fractional factorial design. Results indicated a clear correlation between efficiency and the fraction of the net energy absorbed by the tubes that was used in the reaction.

However, no clear correlation was seen between the efficiency and the fraction of the total solar energy absorbed by the tubes. Rather, the best designs had an intermediate absorption efficiency and allowed a portion of the solar energy to reflect off of the cavity wall, creating a more even distribution of energy around the tube surface. Furthermore, all tubes placed outside of the solar beam did not receive enough energy to carry out the reaction and limited the receiver efficiency. Correspondingly, the best designs had a small number of tubes with intermediate tube radius. Smaller tubes tended to have a better distribution of energy, but this improvement came at the expense of a shorter residence time and an increased energy loss by absorption at the cooled cavity wall surface.

The model was extended to an insulated absorbing cavity by replacing the constant temperature cavity wall boundary condition with a simple one-dimensional conduction model through a layer of insulation. As a whole, absorbing cavity models produced a longer heated tube length due to emission from the cavity wall and, correspondingly, a higher conversion and receiver efficiency. Results for the absorbing cavity again showed a strong impact of cavity radius, solar power input, and solid feed rate, but there was no benefit to allowing energy to reach the cavity wall before being absorbed by the tubes. On the contrary, maximizing the absorption efficiency and residence time was critical to improving the overall receiver efficiency, and the best designs consisted of a small number of tubes with the largest radius possible. Tubes placed slightly outside of the initial solar beam still received enough energy to carry out the reaction. Future work will focus on completing a central composite design containing five factors for both absorbing and reflective cavity configurations in order to quantitatively determine the values of parameters leading to optimal designs.

## H2A ANALYSIS

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|---|---|
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| **OTHER KEY RESEARCHERS:** | MELINDA CHANNEL |

## STATUS

No activity this quarter.

# ALD FERRITE PROCESS STUDIES

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|---|---|
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| **DATE OF REPORT:** | OCTOBER 28, 2011 |
| **PRINCIPLE INVESTIGATOR:** | ALAN WEIMER, ALAN.WEIMER@COLORADO.EDU |
| **OTHER KEY RESEARCHERS:** | DARWIN ARIFIN, PAUL LICHTY, CHRISTOPHER MUHICH, VICTORIA ASTON, XINHUA LIANG, ANTHONY MCDANIEL (SNL) |

## FY 2011 MILESTONES/DELIVERABLES

| Task | Planned | Status |
|---|---|---|
| **Cerium oxide materials for two-step water splitting** | | |
| ***Materials development*** | | |
| Quantify and report the thermochemical performance for two or more reactive materials. We will investigate both thermodynamic and kinetic limits to performance that will allow us to both compare candidate materials and to refine our system-level performance estimates. Both the oxidation and reduction reactions must reach 90% completion in less than two minutes to be considered viable. This supports the evaluation of the technical feasibility of the reactor concept. (SNL) | 9/11 | Complete |

## PROJECT OBJECTIVE

The overall objective of this work is to continue the development of hydrogen-producing thermochemical cycles based on non-volatile metal oxides with the ultimate goal of demonstrating the continuous production of hydrogen in a solar-powered reactor. We have two parallel technical R&D efforts. The first targets the identification and characterization of reactant materials while the second is focused on the development of solar reactor concepts, associated hardware, and system analysis.

## BACKGROUND

Water splitting via two-step, non-volatile metal oxide cycles has been shown to be a potentially efficient pathway to producing hydrogen with solar energy. Past efforts have focused on reactions based on the chemistry of iron oxide using materials broadly characterized as “ferrites.” These materials have been shown to have relatively good thermodynamic performance, but they exhibit insufficient kinetics in cases where high reactive surface area cannot be maintained. In addition, volatility of the active materials at temperatures in excess of 1400 °C is problematic. Cerium oxide has recently been investigated at Sandia National Laboratories as part of an internally funded effort to produce carbon monoxide from carbon dioxide. It is also able to produce hydrogen via a two-step water splitting cycle that is analogous to that used for the ferrite materials. Relative to iron oxide, pure cerium oxide does not perform as well thermodynamically, but the reaction kinetics during water splitting are considerably faster. In addition, volatility is not as great of a concern with cerium oxide-based materials.

We are currently developing and characterizing reactive materials based on cerium oxide. There is reason to believe that combining cerium oxide with other materials such as zirconium oxide or ferrites may boost thermodynamic performance. However, this improvement has been shown to come at the expense of kinetic performance. Therefore, we are developing a solar reactor concept that uses a particulate reactive material. We believe that the increase in surface area achieved with a particulate system may offset the reduction in reaction rate that is incurred when cerium oxide is mixed with other compounds. However, significant technical challenges must be addressed with respect to the design and operation of such a reactor. In general, a viable solar thermochemical reactor concept must embody the following characteristics in order to maximize solar conversion efficiency:

- Continuous flow of reactant and production of hydrogen
- Internal recovery of sensible energy between reaction steps (recuperation)
- Direct solar irradiation of the reactant
- Spatial separation of reaction products

In FY11 we are using a new experimental system for evaluating prospective reactive materials under realistic conditions, i.e., thermochemical cycles of duration on the order of seconds to minutes. We will also complete system-level analysis of a particle-based solar thermochemical reactor that will include the identification of major system-level energy losses and the estimation of annual average hydrogen production efficiency. This model is being developed using several tools, including ASPEN.

A relatively small fraction of our efforts are dedicated to performing H2A analyses on cycles developed by the group and to participating in the IEA Task 25 working group.

## PROJECT STATUS

As mentioned above, this task has two main thrusts, materials development and reactor development. Below is a summary of the status of both:

### *Materials Development*

In this quarter, the thermal reduction and oxidation behavior of cobalt ferrite ($Co_{0.9}Fe_{2.1}O_4$) on alumina ($Al_2O_3$) shells was evaluated. When combined in this manner, the redox cycle chemistry is referred to as the “hercynite” cycle.

The material was synthesized by atomic layer deposition (ALD) at the University of Colorado, Boulder. The alumina support is created by performing 50 ALD cycles of $Al_2O_3$ onto a highly porous poly(styrene-divinylbenzene) (PS-DVB) particle template; after the ALD process is completed a thin layer of $Al_2O_3$ covers the PS-DVB. The organic template is burned off leaving a 15 nm thick hollow $Al_2O_3$ shell. A second ALD process is then used to coat the alumina shell with cobalt ferrite spinel. Once completed, this give rise to a 20% mass loading of $Co_{0.9}Fe_{2.1}O_4$ on $Al_2O_3$.

Thermal reduction and oxidation experiments are performed at Sandia National Laboratories, CA. In a typical redox experiment, the material is preheated in a furnace to a desired temperature where oxidation is performed. Thermal reduction is accomplished by rapidly heating the sample with NIR diode laser, at a rate of 17 ºC/sec, to the thermal reduction temperature (typically 1450 ºC). The material is then allowed to cool back to the oxidation temperature and exposed to either $O_2$, $H_2O$, or $CO_2$.

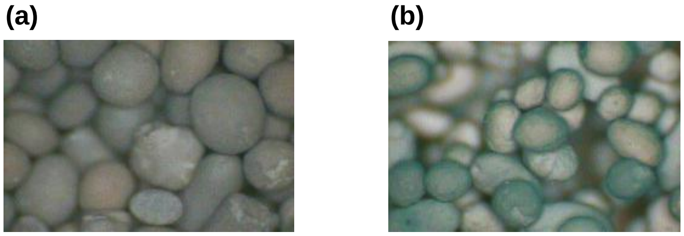

**Figure 1.** (a) $Co_{0.9}Fe_{2.1}O_4$ on $Al_2O_3$ shells before cycling. (b) $Co_{0.9}Fe_{2.1}O_4$ on $Al_2O_3$ shells after thermal reduction. Image is taken with 20X magnification.

Optical microscope images of the sample before and after thermal cycling indicate that the material has high thermal stability. No sintering after exposure to 1450 ºC is observed; the material maintains its semi-spherical shape. Color change of the material is observed. In its oxidized state, the material is brown, in agreement with cobalt ferrite spinel appearance, and in its reduced state, the material is bluish-green, indicative of the formation of cobalt aluminate (Figure 1).

The presence of a cobalt ferrite spinel in the oxidized state, and iron and cobalt aluminates in the reduced state, is confirmed by Raman spectroscopy analysis. The data in Figure 2 reveals that the ALD material, in the oxidized state, has the inverse spinel structure of $CoFe_2O_4$. And in the thermally reduced state, the material has a characteristic phonon mode of cobalt aluminate spinel ($CoAl_2O_4$) and hercynite ($FeAl_2O_4$). Raman spectra of $FeAl_2O_4$ and $CoAl_2O_4$ are provided for comparison. These results confirm the mechanism presented in reactions (1) and (2); that the $CoFe_2O_4$ is thermally reduced to form $CoAl_2O_4$ and $FeAl_2O_4$, thereby releasing $O_2$ and transforming $Fe^{3+}$ to $Fe^{2+}$. Upon re-oxidation by either $CO_2$ or $O_2$, the $CoFe_2O_4$ inverse spinel phase reforms. The Raman data also indicates that $CO_2$ oxidation is incomplete under the conditions of this experiment because the sample exposed to $CO_2$ still exhibits spectral characteristic of $FeAl_2O_4$ and $CoAl_2O_4$.

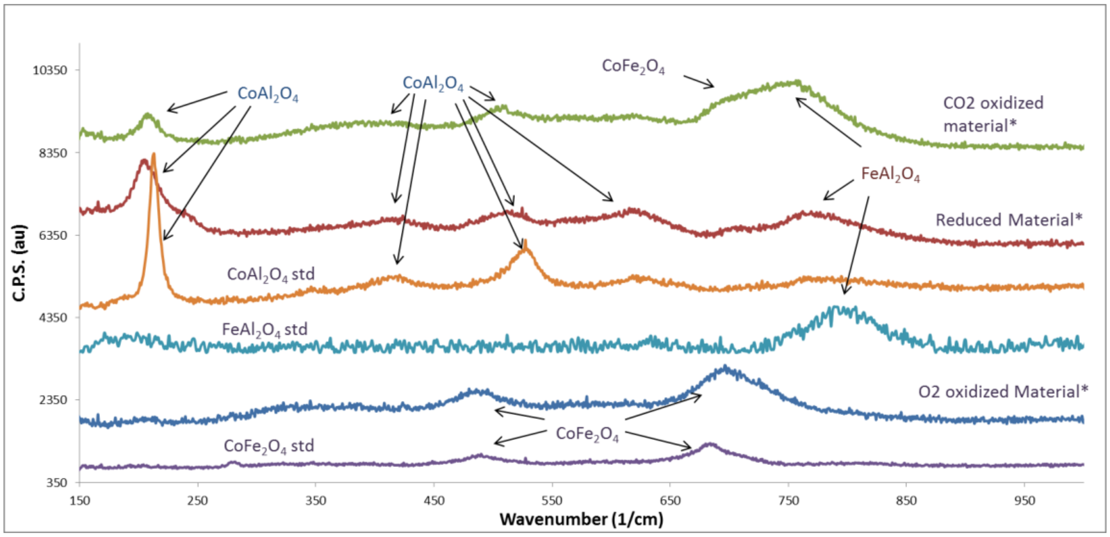

**Figure 2.** Comparison of the $CoFe_2O_4/Al_2O_3$ ALD sample at its oxidized state and reduced state. $CoFe_2O_4$, Cobalt aluminate, and hercynite standard is provided for ease of comparison.

$CoFe_2O_4 + 3\ Al_2O_3$ + thermal energy → $CoAl_2O_4 + FeAl_2O_4 + 0.5\ O_2$ Reaction (1)

$CoAl_2O_4 + 2\ FeAl_2O_4 + H_2O$ or $CO_2$ → $CoFe_2O_4 + 3\ Al_2O_3 + H_2$ or CO Reaction (2)

In Figure 3 we show the characteristic behavior of $O_2$ uptake and release. The sample is exposed to a gas atmosphere containing 2000 ppm $O_2$ in helium at a constant temperature of 1000 ºC. Laser pulses lasting 100 seconds heat the sample, thermally reducing it and releasing oxygen as indicated by the train of $O_2$ pulses that are coincident with the leading edge of the temperature square wave. Once the laser is turned off, the material cools off and undergoes oxidation by absorbing the background $O_2$, resulting in a valley in the $O_2$ signal. The re-oxidation is rapid as the valley returns to baseline within 60 seconds. This material exhibits a rapid $O_2$ uptake and release behavior, which is an absolute necessity demonstrating redox activity.

Although the material is capable of fast and complete $O_2$ re-oxidation, $CO_2$ oxidation is much slower. In Figure 4, we show the CO production rate during $CO_2$ oxidation at two different reactor pressures: 75 and 600 torr. Significantly higher CO is produced at the higher pressure. However, at both pressures, $CO_2$ oxidation is slow and incomplete within 7 minutes. This is in agreement with the Raman spectroscopy result mentioned previously. Thus far, it is still unclear why re-oxidation with $O_2$ is significantly faster than with $CO_2$. It is evident that re-oxidation with $CO_2$ is a surface mediated process because of the observed pressure dependence for the CO production rate.

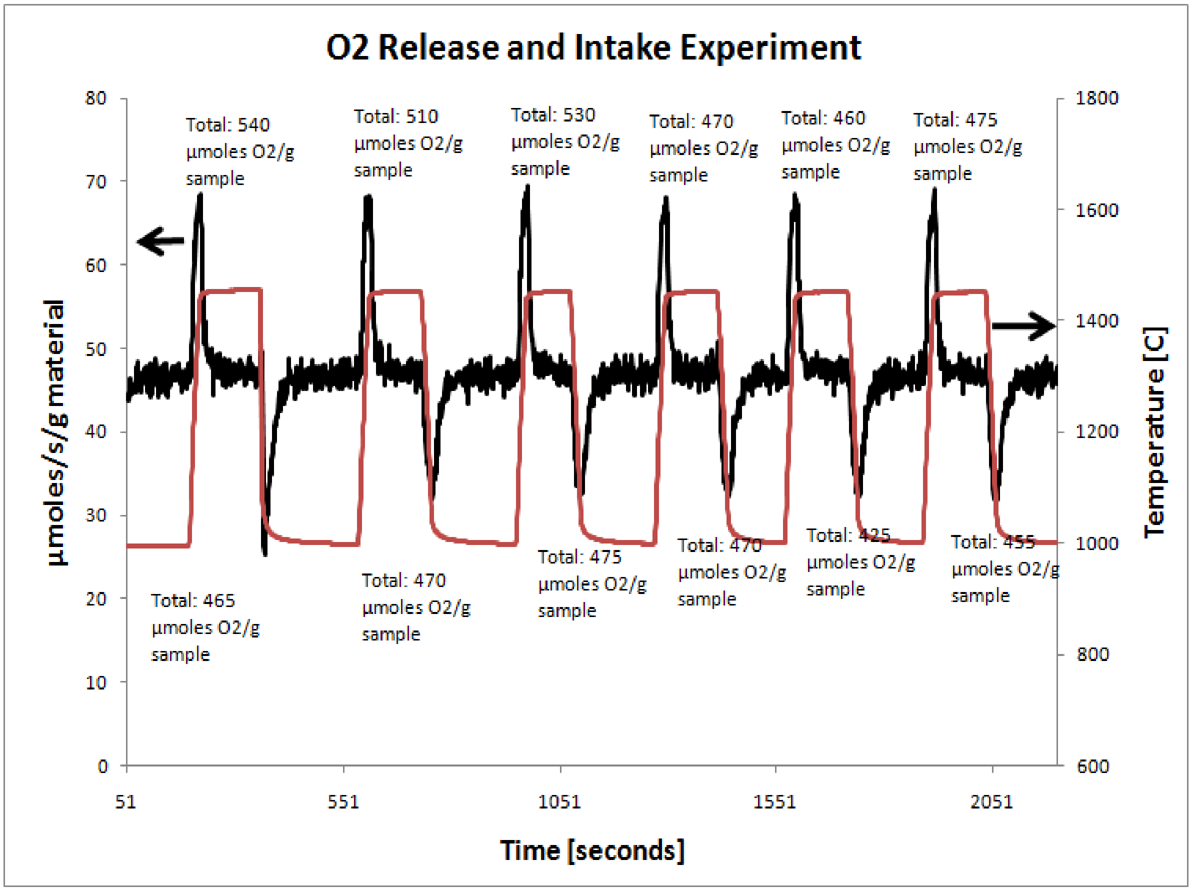

**Figure 3.** $O_2$ intake and uptake experiment at 1000 ºC–1500 ºC.

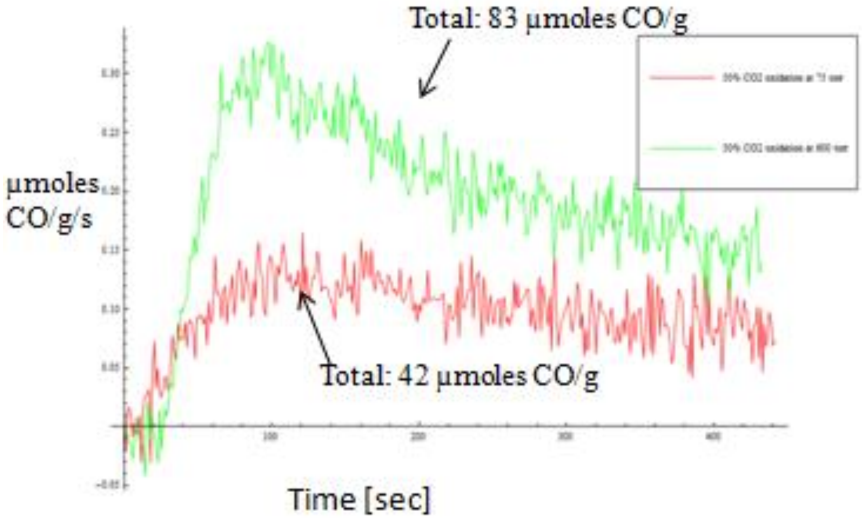

**Figure 4.** CO production with: thermal reduction at 1460 ºC and $CO_2$ oxidation at 1000 ºC at two different pressures: 75 and 600 torr.

The main benefit of a “hercynite” cycle is its ability to be thermally reduced at lower temperature than ceria or iron/YSZ. Approximately 80% of the $O_2$ oxygen capacity in the material is expelled at temperatures below 1300 ºC. This in turn enables the design of a thermochemical cycle that operates at or below 1300 ºC, potentially operating the oxidation chemistry between 1000 ºC and 1200 ºC. Figure 5 shows CO production at two different oxidation temperatures: 1200 ºC and 1000 ºC, both after thermal reductions at 1310 ºC. The 1200 °C oxidation temperature affords significantly higher CO production due to a catalytic effect: the concurrent production of CO and $O_2$. Since the material is already rejecting oxygen at 1200 ºC, it is not surprising that under this particular experimental condition CO and $O_2$ co-evolve and will continue to do so once the stoichiometric part of the reaction has completed. It is unclear whether this would be a desired outcome for a large-scale industrial process.

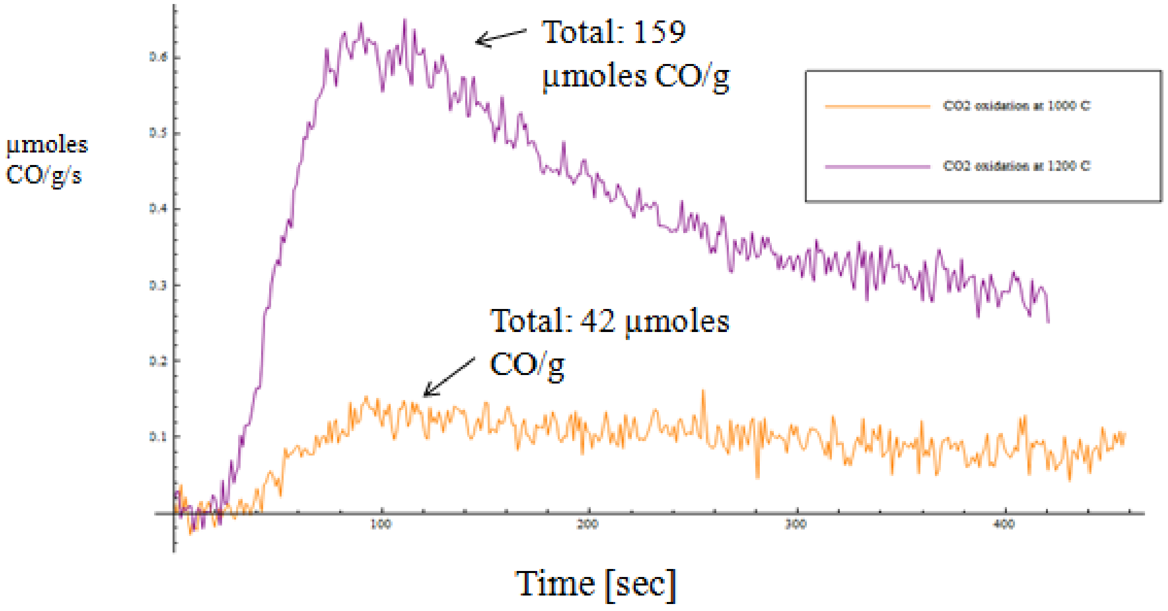

**Figure 5.** CO production with: thermal reductions at 1310 ºC and $CO_2$ oxidation at 1000 ºC and 1200 ºC.

Our experiments suggest that the $CO_2$ oxidation step is limited by the dissociation of $CO_2$ on the surface, and, thus, partial pressure of the oxidant and oxidation temperature have a large effect on the oxidation rate. The kinetics of this chemical reaction are complex as they involve the transport and reaction of $Co^{2+}$, $Al^{2+}$, and $Fe^{3+}/Fe^{2+}$ in a continuous manner. Further work will be performed to better understand the oxidation kinetics with $H_2O$ as opposed to $CO_2$.

### *Reactor Development*

In the 4th quarter, through a contract with Jenike and Johanson, we experimentally evaluated a key component of the particle reactor: the particle conveyor/heat exchanger. We produced three conveyor screws with varying height/depth aspect ratios, in order to evaluate the ability of these unusually dimensioned conveyors to efficiently move the particles from the fuel production chamber to the thermal reduction chamber. We also evaluated gravity-flow of $CeO_2$ powder through a finned tube.

We have established an upper limit of the screw aspect ratio of approximately 1:3, beyond which material is no longer conveyed. Even at this aspect ratio, conveying is inefficient, and higher aspect ratios will have to be considered for a working reactor. Powder particle size does not seem to have an important effect on the upward material conveyance.

Experiments with the return powder flow through a finned tube showed a critical dependence on particle size. Flow was evaluated with powders with average particle sizes of 5μm and 70μm. While powder flow was essentially unimpeded for the larger particles, it was completely absent with the smaller particles, except under severe mechanical agitation. These results are very encouraging from the heat exchange viewpoint, which should be relatively easy to accomplish provided powder of a desired particle size can be used.

We also further investigated the compatibility of ceria with prospective reactor materials—specifically, alumina and alumina-coated silicon carbide. Alumina was found not to react with ceria up to 1550 ºC in stagnant air. Alumina-coated silicon carbide was tested up to 1450 ºC and also found to be unreactive. These experiments also showed that a minimal thickness of alumina coating is needed before the surface can be passivated. When coating thickness is insufficient, ceria reacts vigorously with the underlying $SiC/SiO_2$. Thick coatings, however, were found to be increasingly unstable. The optimal coating thickness and deposition method will need to be established if SiC is to be used as a reactor material.

The results of these experiments were used to further refine the reactor performance characteristics on the prototype scale. A system-level model for a dish-based fuel production system extensible to 100,000 kg $H_2$ per day has been completed. The model for the tower-based version is still under development.

## PLANS FOR NEXT QUARTER AND KEY ISSUES

### *Materials Development*

In Q1FY12 we will continue to evaluate the performance space, with respect to temperature and pressure, of doped cerium oxide powder reactants as well as various versions of hercynite material provided by CU. The goal is to identify a rigorous metric upon which to evaluate all materials and reactive structures so that a meaningful comparison can be made between different chemistries and structures. This rubric can then be used to evaluate the efficacy of a proposed non-volatile metal oxide system within the context of proposed reactor designs for concentrated solar power (CSP) hydrogen production.

### *Reactor Development*

None.

# CERIUM OXIDE MATERIALS FOR TWO-STEP WATER SPLITTING

**COVERING PERIOD:** JULY 1, 2011–SEPTEMBER 30, 2011

**DATE OF REPORT:** OCTOBER 28, 2011

**PRINCIPLE INVESTIGATOR:** NATHAN SIEGEL (505) 284-2033, NPSIEGE@SANDIA.GOV)

**TEAM MEMBERS:** TONY MCDANIEL (SNL/CA), IVAN ERMANOSKI (SNL/NM), VICTORIA ASTON (CU), DARWIN ARIFIN (CU), GREG KOLB (SNL/NM) XINHUA LIANG (CU), ALAN WEIMER (CU)

## FY 2011 MILESTONES/DELIVERABLES

| Task | Planned | Status |
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| **Cerium oxide materials for two-step water splitting** | | |
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## BACKGROUND

Water splitting via two-step, non-volatile metal oxide cycles has been shown to be a potentially efficient pathway to producing hydrogen with solar energy. Past efforts have focused on reactions based on the chemistry of iron oxide using materials broadly characterized as “ferrites.” These materials have been shown to have relatively good thermodynamic performance, but they exhibit insufficient kinetics in cases where high reactive surface area cannot be maintained. In addition, volatility of the active materials at temperatures in excess of 1400 °C is problematic.

Cerium oxide has recently been investigated at Sandia National Laboratories as part of an internally funded effort to produce carbon monoxide from carbon dioxide. It is also able to produce hydrogen via a two-step water splitting cycle that is analogous to that used for the ferrite materials. Relative to iron oxide, pure cerium oxide does not perform as well thermodynamically, but the reaction kinetics during water splitting are considerably faster. In addition, volatility is not as great of a concern with cerium oxide-based materials.

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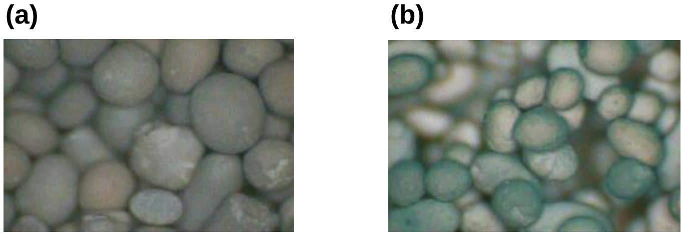

**Figure 6.** (a) $Co_{0.9}Fe_{2.1}O_4$ on $Al_2O_3$ shells before cycling. (b) $Co_{0.9}Fe_{2.1}O_4$ on $Al_2O_3$ shells after thermal reduction. Image is taken with 20X magnification.

Optical microscope images of the sample before and after thermal cycling indicate that the material has high thermal stability. No sintering after exposure to 1450 ºC is observed; the material maintains its semi-spherical shape. Color change of the material is observed. In its oxidized state, the material is brown, in agreement with cobalt ferrite spinel appearance, and in its reduced state, the material is bluish-green, indicative of the formation of cobalt aluminate (Figure 6).

The presence of a cobalt ferrite spinel in the oxidized state, and iron and cobalt aluminates in the reduced state, is confirmed by Raman spectroscopy analysis. The data in Figure 7 reveals that the ALD material, in the oxidized state, has the inverse spinel structure of $CoFe_2O_4$. And in the thermally reduced state, the material has a characteristic phonon mode of cobalt aluminate spinel ($CoAl_2O_4$) and hercynite ($FeAl_2O_4$). Raman spectra of $FeAl_2O_4$ and $CoAl_2O_4$ are provided for comparison. These results confirm the mechanism presented in reactions (1) and (2); that the $CoFe_2O_4$ is thermally reduced to form $CoAl_2O_4$ and $FeAl_2O_4$, thereby releasing $O_2$ and transforming $Fe^{3+}$ to $Fe^{2+}$. Upon re-oxidation by either $CO_2$ or $O_2$, the $CoFe_2O_4$ inverse spinel phase reforms. The Raman data also indicates that $CO_2$ oxidation is incomplete under the conditions of this experiment because the sample exposed to $CO_2$ still exhibits spectral characteristic of $FeAl_2O_4$ and $CoAl_2O_4$.

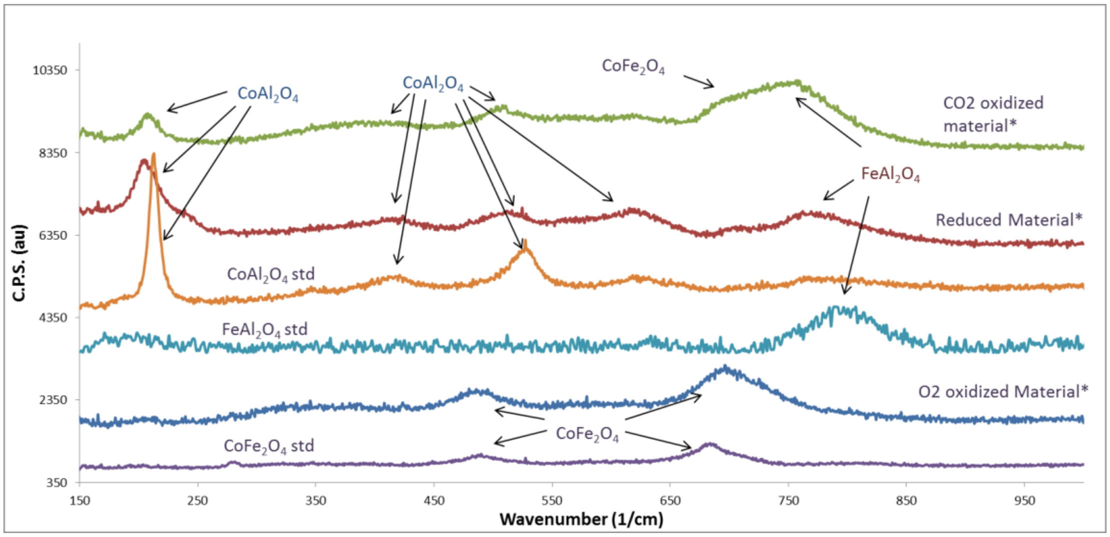

**Figure 7.** Comparison of the $CoFe_2O_4/Al_2O_3$ ALD sample at its oxidized state and reduced state. $CoFe_2O_4$, Cobalt aluminate, and hercynite standard is provided for ease of comparison.

$CoFe_2O_4 + 3\ Al_2O_3 +$ thermal energy $\rightarrow CoAl_2O_4 + FeAl_2O_4 + 0.5\ O_2$ Reaction (1)

$CoAl_2O_4 + 2\ FeAl_2O_4 + H_2O$ or $CO_2 \rightarrow CoFe_2O_4 + 3\ Al_2O_3 + H_2$ or CO Reaction (2)

In Figure 8 we show the characteristic behavior of $O_2$ uptake and release. The sample is exposed to a gas atmosphere containing 2000 ppm $O_2$ in helium at a constant temperature of 1000 ºC. Laser pulses lasting 100 seconds heat the sample, thermally reducing it and releasing oxygen as indicated by the train of $O_2$ pulses that are coincident with the leading edge of the temperature square wave. Once the laser is turned off, the material cools off and undergoes oxidation by absorbing the background $O_2$, resulting in a valley in the $O_2$ signal. The re-oxidation is rapid as the valley returns to baseline within 60 seconds. This material exhibits a rapid $O_2$ uptake and release behavior, which is an absolute necessity demonstrating redox activity.

Although the material is capable of fast and complete $O_2$ re-oxidation, $CO_2$ oxidation is much slower. In Figure 9, we show the CO production rate during $CO_2$ oxidation at two different reactor pressures: 75 and 600 torr. Significantly higher CO is produced at the higher pressure. However, at both pressures, $CO_2$ oxidation is slow and incomplete within 7 minutes. This is in agreement with the Raman spectroscopy result mentioned previously. Thus far, it is still unclear why re-oxidation with $O_2$ is significantly faster than with $CO_2$. It is evident that re-oxidation with $CO_2$ is a surface mediated process because of the observed pressure dependence for the CO production rate.

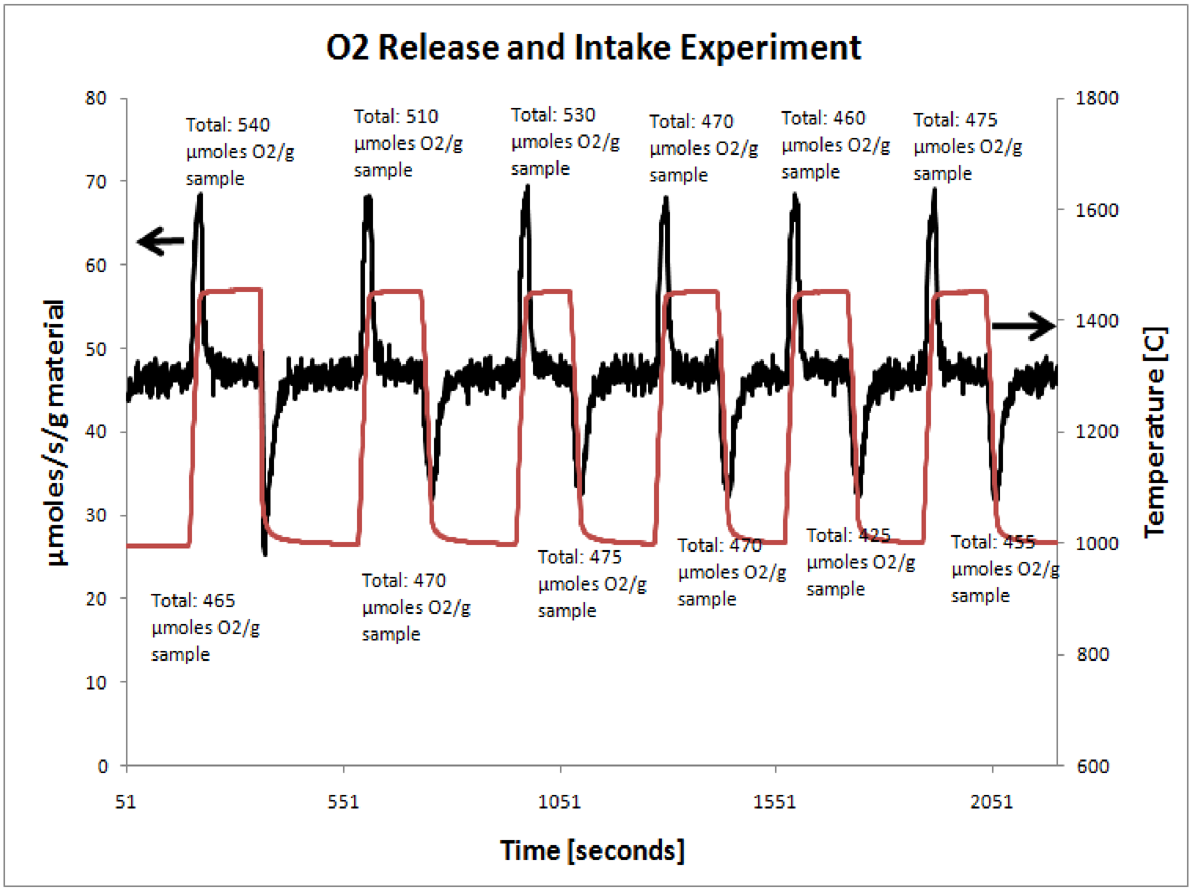

**Figure 8.** $O_2$ intake and uptake experiment at 1000 ºC–1500 ºC.

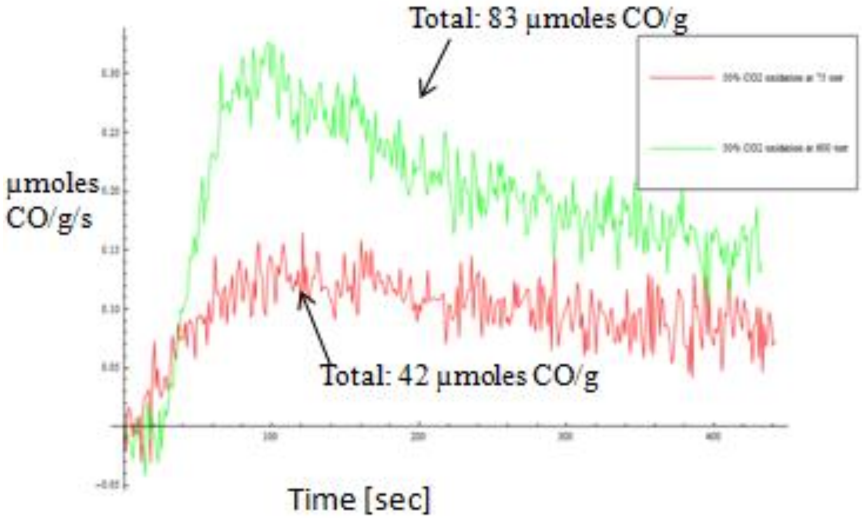

**Figure 9.** CO production with: thermal reduction at 1460 ºC and $CO_2$ oxidation at 1000 ºC at two different pressures: 75 and 600 torr.

The main benefit of a “hercynite” cycle is its ability to be thermally reduced at lower temperature than ceria or iron/YSZ. Approximately 80% of the $O_2$ oxygen capacity in the material is expelled at temperatures below 1300 ºC. This in turn enables the design of a thermochemical cycle that operates at or below 1300 ºC, potentially operating the oxidation chemistry between 1000 ºC and 1200 ºC. Figure 10 shows CO production at two different oxidation temperatures: 1200 ºC and 1000ºC, both after thermal reductions at 1310 ºC. The 1200 ºC oxidation temperature affords significantly higher CO production due to a catalytic effect: the concurrent production of CO and $O_2$. Since the material is already rejecting oxygen at 1200 ºC, it is not surprising that under this particular experimental condition CO and $O_2$ co-evolve and will continue to do so once the stoichiometric part of the reaction has completed. It is unclear whether this would be a desired outcome for a large scale industrial process.

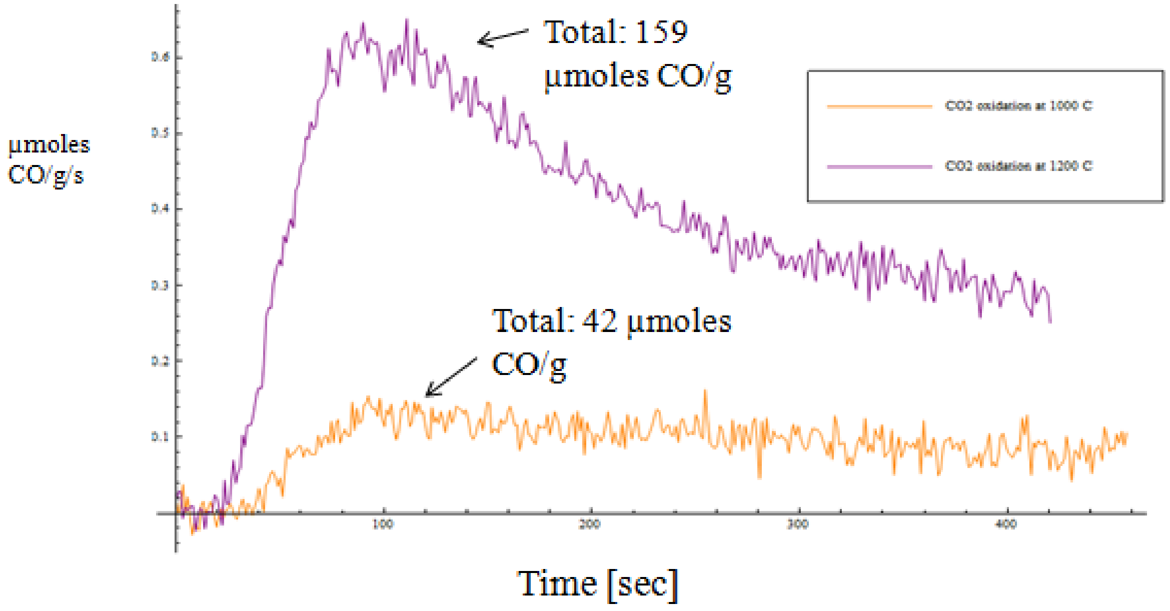

**Figure 10.** CO production with: thermal reductions at 1310 ºC and $CO_2$ oxidation at 1000 ºC and 1200ºC.

Our experiments suggest that the $CO_2$ oxidation step is limited by the dissociation of $CO_2$ on the surface, and, thus, partial pressure of the oxidant and oxidation temperature have a large effect on the oxidation rate. The kinetics of this chemical reaction are complex as they involve the transport and reaction of $Co^{2+}$, $Al^{2+}$, and $Fe^{3+}/Fe^{2+}$ in a continuous manner. Further work will be performed to better understand the oxidation kinetics with $H_2O$ as opposed to $CO_2$.

### *Reactor Development*

In the 4th quarter, through a contract with Jenike and Johanson, we experimentally evaluated a key component of the particle reactor: the particle conveyor/heat exchanger. We produced three conveyor screws with varying height/depth aspect ratios, in order to evaluate the ability of these unusually dimensioned conveyors to efficiently move the particles from the fuel production chamber to the thermal reduction chamber. We also evaluated gravity-flow of $CeO_2$ powder through a finned tube.

We have established an upper limit of the screw aspect ratio of approximately 1:3, beyond which material is no longer conveyed. Even at this aspect ratio, conveying is not efficient, and higher aspect ratios will have to be considered for a working reactor. Powder particle size does not seem to have an important effect on the upward material conveyance.

Experiments with the return powder flow through a finned tube showed a critical dependence on particle size. Flow was evaluated with powders with average particle sizes of 5μm and 70μm. While powder flow was essentially unimpeded for the larger particles, it was completely absent with the smaller particles, except under severe mechanical agitation. These results are very encouraging from the heat exchange viewpoint, which should be relatively easy to accomplish provided powder of a desired particle size can be used.

We also further investigated the compatibility of ceria with prospective reactor materials—specifically, alumina and alumina-coated silicon carbide. Alumina was found not to react with ceria up to 1550 ºC in stagnant air. Alumina-coated silicon carbide was tested up to 1450 ºC and also found to be unreactive. These experiments also showed that a minimal thickness of alumina coating is needed before the surface can be passivated. When coating thickness is insufficient, ceria reacts vigorously with the underlying $SiC/SiO_2$. Thick coatings, however, were found to be increasingly unstable. The optimal coating thickness and deposition method will need to be established if SiC is to be used as a reactor material.

The results of these experiments were used to further refine the reactor performance characteristics on the prototype scale. A system-level model for a dish-based fuel production system extensible to 100,000 kg $H_2$ per day has been completed. The model for the tower-based version is still under development.

## PLANS FOR NEXT QUARTER AND KEY ISSUES

### *Materials Development*

In Q1FY12 we will continue to evaluate the performance space, with respect to temperature and pressure, of doped cerium oxide powder reactants as well as various versions of hercynite material provided by CU. The goal is to identify a rigorous metric upon which to evaluate all materials and reactive structures so that a meaningful comparison can be made between different chemistries and structures. This rubric can then be used to evaluate the efficacy of a proposed non-volatile metal oxide system within the context of proposed reactor designs for concentrated solar power (CSP) hydrogen production.

### *Reactor Development*

None.

# IEA TASK 25: HIGH TEMPERATURE HYDROGEN PRODUCTION PROCESSES

| | |
|---|---|
| **COVERING PERIOD:** | JULY 1, 2011–SEPTEMBER 30, 2011 |
| **DATE OF REPORT:** | OCTOBER 28, 2011 |
| **PRINCIPLE INVESTIGATOR:** | GREG KOLB, (505) 844-1887, GJKOLB@SANDIA.GOV |
| **INDUSTRIAL PARTNERS:** | DOE STCH PROJECT CONSORTIUM AND IEA MEMBER COUNTRIES AND THEIR INDUSTRIAL PARTNERS |
| **DOE MANAGERS:** | SARA DILLICH, HYDROGEN PRODUCTION & DELIVERY TEAM LEAD |

## PROJECT OBJECTIVE

The objective of this Task 25 expert group working within the IEA/HIA (International Energy Agency/Hydrogen Implementing Agreement) is to enhance and create synergy between the different international research institutes and potential industrials involved in hydrogen production using high-temperature processes (HTPs, >500 °C). This project also provides the opportunity to gather the nuclear and solar community in a common task.

## BACKGROUND

The Task 25 work program is divided into 4 subtasks:

(A) Technical review of the different HTPs,
(B) Comparative analysis of the HTPs,
(C) Definition of a HTP project to be deployed within the next 10 years to demonstrate industrial feasibility and to validate techno-economic evaluations,
(D) Development of communication tools. The task is led by the French atomic energy commission (CEA).

## STATUS

The seventh and final official meeting of the group occurred on September 26th, 2011, in Almeria, Spain. The meeting gathered 11 participants from eight countries. The attendees and contact information are given at the end of this report. The meeting time was selected to occur directly after the SolarPACES 2011 conference nearby in Granada, Spain.

The primary focus of the meeting was to discuss the preparation of the final Task 25 report. The report will be submitted to the IEA ExCo by CEA before the end of the calendar year. The results of each of the four project subtasks will be summarized in the final report. In addition, separate sections will be provided by each member country on their current national R&D plan related to hydrogen-production, as well as recent results using high-temperature approaches.

The USA hydrogen-generation plan to the year 2020 was recently updated on the DOE website (9/11) and G. Kolb made the group aware of it. In addition, he informed the group that since we last met one year ago, an error in the Aspen analysis for the CuCl-hybrid cycle was found that resulted in a significant drop in the efficiency of the cycle. The current efficiency estimate for CuCl is now similar to low-temperature alkaline electrolysis (AE), making it much less interesting from an R&D point of view.

The group believes that AE powered by nuclear reactors will produce the lowest-cost $CO_2$-free hydrogen in the near term. However, with a cost of ~3 Euro/kg, this is still not competitive with the $CO_2$-generating methane-reforming method at 1.6 Euro/kg. The group believes that high-temperature electrolysis (HTE) will be the first high-temperature $CO_2$-free process that will be implemented. France predicts an eventual cost of 3.6 Euro/kg. The next step for France is to demonstrate a 100 kWe stack, but a precise schedule for the demonstration was not presented.

The most exciting R&D news was presented by Sune Ebbesen from RISO national lab in Denmark. He reported that Denmark has solved the cell stack degradation issue within their HTE; their new cells have been operating at 800 °C and currents of 0.75 amp/cm$^2$ for many thousands of hours with no degradation. (This was not the case during our first meeting four years ago, in which he reported ~4% degradation at lower current levels after a few thousand hours.) Removing impurities from the gases and improved thermal management of the stack were the keys to success. RISO is working with the company Haldor Topsof to build a demonstration HTE plant by 2013.

The IEA group published a multi-criteria evaluation of 13 hydrogen generation processes of interest to STCH and other international organizations. The results also favor HTE, as documented in a report prepared by CEA [1] and in a recently published journal article [2]. Based on the promising news from RISO and on our multi-criteria work, G. Kolb suggested to the group that a good demonstration project would be to interface a HTE with a solar dish. As described within a Task D subtask document developed earlier [3], that combination is expected to achieve ~25% solar-to-hydrogen annual efficiency (vs. ~14% for solar interfaced with a low-temperature AE.) Ferrite and cerium cycles currently under investigation in the USA and Germany also have the potential to achieve solar-to-hydrogen efficiencies greater than 20% but early reactors are demonstrating efficiencies of only a few percent "heat-to-hydrogen" and are many years behind the progress demonstrated with HTE.

This was the final meeting of the group. There are no current plans to develop a follow-on task.

| Country | Name | Surname | email |
|---|---|---|---|
| Australia | HINKLEY | Jim | Jim.Hinkley@csiro.au |
| Finland | LOKKILUOTO | Anu | anu.lokkiluoto@aalto.fi |
| France | LE NAOUR | François | francois.le-naour@cea.fr |
| France | MANSILLA | Christine | christine.mansilla@cea.fr |
| Germany | SATTLER | Christian | Christian.Sattler@dlr.de |
| Italy | GIACONIA | Alberto | alberto.giaconia@enea.it |
| Italy | LIBERATORE | Raffaele | raffaele.liberatore@enea.it |
| Switzerland | VOGT | Ulrich | Ulrich.Vogt@empa.ch |
| Switzerland | MEIER | Anton | Anton.Meier@psi.ch |
| US | KOLB | Gregory | gjkolb@sandia.gov |
| Denmark | EBBESEN | Sune | sueb@risoe.dtu.dk |

## PUBLICATIONS

1. Galzim, O. and C Mansilla, et. al., “A multicriteria methodology for assessing high temperature hydrogen production processes,” *International Journal Multicriteria Decision Making*, Vol. 1 No. 2, 2011.

2. “A multicriteria methodology for assessing high temperature hydrogen production processes – first results,” *CEA Report RT/10-009*, August 25, 2010.

3. “Screening Analysis of Solar Thermochemical Hydrogen Concepts,” IEA/HIA Task 25: High Temperature Hydrogen Production Process, draft prepared by Sandia National Laboratories, November 2008. The final version will be included within final Task 25 report to be delivered to the IEA ExCo.