II.C.1 Solar-Thermal Redox-Based Water Splitting Cycles

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Overall Objectives

- Develop efficient robust materials and operation methods for a two-step thermochemical redox cycle that will achieve the DOE cost targets for solar hydrogen
- Develop a scalable solar-thermal reactor design that will achieve the DOE cost targets for solar hydrogen

Fiscal Year (FY) 2014 Objectives

- Synthesize hercynite redox materials that are >80% active by mass
- Characterize "pseudo-isothermal" redox chemistry in a stagnation flow reactor to demonstrate a hydrogen productivity greater than 150 µmole/gram total
- Investigate isothermal and/or "near-isothermal" redox in the High Flux Solar Furnace at the National Renewable Energy Laboratory, demonstrating a hydrogen productivity greater than 150 µmole/gram total on-sun
- Perform robustness testing of "hercynite cycle" redox at ETH Zurich, demonstrating a hydrogen productivity of greater than 150 µmole/g total after 100 cycles.
- Develop an understanding of temperature-swing vs. isothermal redox and the relative efficiency for carrying out each

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(S) High-Temperature Robust Materials

(T) Coupling Concentrated Solar Energy and Thermochemical Cycles

(U) Concentrated Solar Energy Capital Cost

Technical Targets

TABLE 1. Technical Targets for Solar-Driven High-Temperature Thermochemical Hydrogen Production

Characteristics	Units	2020 Target	Ultimate
Plant Gate H_2 Cost	\$/gge H_2	3.70	2.00
Chemical Tower Capital Cost (installed cost)	\$/TPD H_2	2.3 MM	1.1 MM
Annual Reaction Material Cost	\$/yr.-TPD H_2	89,000	11,000
Solar to H_2 Energy Conversion	%	20	26

gge – gasoline gallon equivalent; TPD – tons per day; MM - million

FY 2014 Accomplishments

- Completed computer model for thermodynamic efficiency calculations for isothermal and near-isothermal for cerium oxide
- Demonstrated over 3× H_2 production from "hercynite cycle" materials using near-isothermal Red/Ox cycling (basis of 100 micromole H_2/g in 2013)
- Determined kinetic model and mechanism for CO_2 splitting for "hercynite cycle"
- Performed computational fluid dynamic modeling on SurroundSun™ reactor

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INTRODUCTION

Two-step solar thermochemical processes based on non-volatile metal oxide cycles, as shown in Equations 1 and 2, have the potential to operate at high thermal efficiencies, are chemically simple, and require less land and water to operate than competing biomass, artificial photosynthesis and photovoltaic-driven electrolysis. Traditionally, two types of non-volatile metal oxide redox chemistries are utilized in solar thermochemical H_2O splitting. The first is based on non-stoichiometric oxides of which ceria is a representative example. Such redox materials are thermally reduced without undergoing phase change, as the lattice is able to accommodate the strain induced by oxygen vacancy

formation. These materials are thermally quite stable, although the extent of reduction, and hence cycle capacity, is small compared to other reducible oxides.

$$MO_x \rightarrow MO_{x-\delta} + \delta/2\ O_2 \quad (1)$$

$$MO_{x-\delta} + \delta\ H_2O \rightarrow MO_x + \delta\ H_2 \quad (2)$$

The second prototypical chemistry utilizes materials of the spinel structure that form solid solutions upon reduction. The most common are ferrites where Fe^{3+} in $M_xFe_{3-x}O_4$ is partially reduced to Fe^{2+}; here M can be any number of transition metals that form spinel type oxides with Fe though Co, Zn, and Ni are the most studied. In these redox cycles, the ferrite spinel is heated until it decomposes into a mixture of metal oxide solid solutions that are thermodynamically stable at temperatures above which the spinel decomposes. While these materials theoretically exhibit greater redox potential than non-stoichiometric oxides, in practice deactivation induced by irreversible processes such as sintering or the formation of liquid phases and metal vaporization lead to loss of active oxide.

APPROACH

Our approach is to develop an efficient cost-effective hydrogen process through (1) an understanding of Red/Ox thermal cycling conditions, (2) the development of improved robust active materials, and (3) a scalable solar thermal reactor system that is optimal for the materials that we develop. First, a thorough understanding of the activity of Red/Ox materials and its impact on type of cycling (isothermal, near-isothermal, and temperature-swing) and reactor efficiency is needed to understand how to produce hydrogen in the most efficient way. This will depend on the specific material being used, as well as different practical and economic constraints on operating conditions. In addition to the reaction cycling conditions, it is important to develop a more detailed understanding of Red/Ox materials mechanisms and, hence, methods to improve materials performance. Different materials and mechanisms (i.e., displacement or oxygen vacancy) can benefit from different operating conditions, and so understanding these fundamental differences is important. Finally, a reactor must be designed which is scalable to large sizes, is comprised of suitable containment materials, and is tunable for specific active materials. This will allow for flexibility in operating the Red/Ox cycle in the most efficient way possible and allow for the hydrogen production process to take advantage of economies of scale.

RESULTS

Determining the most efficient way to operate is an important consideration for solar thermochemical water splitting. Ermanoski et al. and other groups have suggested different ways of finding the overall solar-to-hydrogen efficiency [1], and we have expanded upon the model of Ermanoski et al. in our own analysis. Some of our results are shown in Figure 1, and indicate that isothermal cycling is theoretically the most efficient way to operate ceria Red/Ox, assuming perfect gas-gas heat recuperation. This gas-gas heat recuperation efficiency is an important factor in the overall solar-to-hydrogen efficiency, and in determining the best possible combination of operational parameters. This heat recuperation deals with the water entering the system into the oxidation reactor, some of which reacts to form hydrogen and then exits the oxidation reactor along with any excess steam and is cooled to ambient temperatures. The

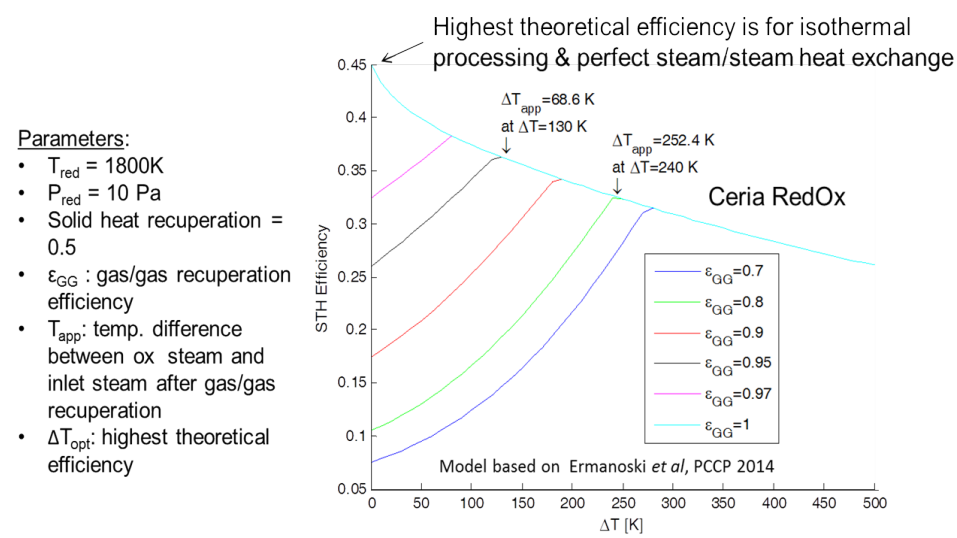

FIGURE 1. Solar-to-hydrogen efficiency calculations for cerium oxide based on thermodynamic compositions for a single reduction temperature and pressure with different oxidation temperatures and gas-gas heat recuperation efficiencies.

gas-gas heat recuperation efficiency is a lumped parameter of how much heat form the cooling of the steam/H_2 mixture can be used to pre-heat the water. Here we show that for ceria, as the heat recuperation approach temperature between the steam to be fed to the oxidizer and the exiting steam/H_2 mixture is minimized and approaches zero (meaning the gas-gas heat recuperation efficiency approaches 100%), the overall efficiency of the process is improved and more isothermal-like operating temperatures are suggested.

Achieving very high gas-gas heat recuperation efficiencies is a considerable challenge. Metal alloy heat exchangers are able to heat the steam from ambient to 1,000°C using high-temperature Ni alloys, such as Inconel. These would be followed by ceramic heat exchangers that are being developed by a number of companies to take the steam to even higher temperatures in order to minimize the approach temperature, or the difference in temperature between the hot steam and hydrogen entering the heat exchanger and the fresh water leaving the heat exchanger. We've contacted some of these companies and have been told that heating gases to 1,200°C is almost guaranteed, 1,300°C should work, 1,500°C should be possible and even hotter may be possible. This would then become an economic argument (as with everything else in the system), and the cost/benefit tradeoffs will need to be considered.

As discussed in the previous section, it may be desirable to operate in a near-isothermal mode, where the temperature difference between the oxidation and reduction steps is relatively small (<150°C). This will minimize simultaneous Red/Ox formation of O_2 and H_2 while increasing theoretical efficiency if the perfect gas/gas heat exchange is not achieved. Therefore, we experimentally investigated the hydrogen production capacity under near isothermal conditions where the reduction step is carried out at 1,350, 1,400, 1,450, and 1,500°C while oxidation occurred at 1,350°C. This was done using 85% active hercynite skeletal material. As expected, we were able to achieve ~100 µmol H_2/total gram of material for 1,350°C isothermal water splitting, and as we increased the reduction temperature we were able to increase the H_2 produced, achieving over 350 µmole H_2/total gram of material under 1,500°C reduction, as seen in Figure 2. The increased reduction temperature increases the extent of hercynite material reduction, thereby increasing the hydrogen production capacity, while the high 1,350°C oxidation temperature reduces the deleterious kinetic effects of lower oxidation temperatures, leading to the high quantity of hydrogen generated.

In the past fiscal year, we studied isothermal carbon dioxide splitting using the laser assisted stagnation flow reactor at the Livermore branch of Sandia National Laboratories. We collected data using "hercynite cycle" material for isothermal operation with temperatures of 1,280-1,420°C and partial pressures of CO_2 in the range of 316-576 Torr. During experimental runs catalytic CO_2

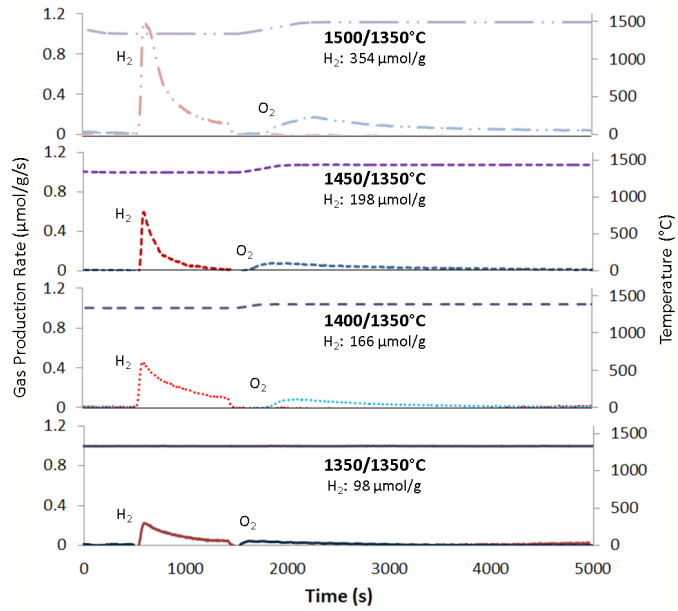

FIGURE 2. Near isothermal water splitting gas production. The H_2 and O_2 generation rates under isothermal or near isothermal water splitting conditions for reduction temperatures of 1,350-1,500°C and an oxidation temperature of 1,350°C.

splitting occurred along the inside of the reactor walls at the high operating temperatures. In order to correct for this material-independent splitting, blanks were run at each of the experimental conditions. The CO curves generated with the blanks were subtracted from the overall signal in order to determine corrected CO generation data. The corrected curves were then used to model the CO_2 splitting behavior of the "hercynite cycle" material and the dispersion of CO as the gas moves through the analytics section as outlined by Scheffe et al. [2]. However, because of the catalytic CO_2 splitting and O_2 uptake by the hercynite materials from O_2 resulting from CO_2 splitting on the walls of the reactor, we were unable to fit the CO_2 production curves using only one of the traditional solid state reaction models (F1, F2, D1, D2, etc.) shown in Equation 3, where α is the extent of reaction (in this case the extent of re-oxidation), t is time, k_0 is kinetic rate coefficient, Y is the CO_2 concentration, γ is the reaction order with respect to the CO_2 concentration, and f(α) is the reaction model.

$$\frac{d\alpha}{dt} = \kappa_0 Y_{CO_2}^{\gamma} f(\alpha) \tag{3}$$

The models had to be expanded to include the reaction of O_2 produced on the walls, along with that produced by the "hercynite cycle" active materials and catalytic CO_2 splitting. The overall rate expression for material re-oxidation is shown in Equation 4, where the first and second terms are the CO_2 and O_2 oxidation contributions, respectively.

$$\frac{d\alpha_o}{dt} = \kappa_1 Y_{CO_2}^{\gamma}(1-\alpha_0)^{n_1} + \kappa_3{}^1 Y_{CO_2}^{\gamma_3}(1-\alpha_0)^{n_3} \tag{4}$$

We have complete modeling of isothermal CO_2 splitting based on surface limited models (Equation 2) and system dispersion as can be seen in Figures 3 a-d. The surface limited models give reasonably good fits to the experimental data. Additionally, Figures 3f-g shows the reaction progression without dispersion effects. Overall, we found that the CO_2 reaction is roughly third and second order with respect to the CO_2 pressure, and material respectively, and the O_2 reaction is roughly first and second order with respect to the O_2 pressure, and material respectively.

Over the past several years, we have developed the SurroundSun™ reactor design which is simple to operate and maintain. In this design, the active material is fixed within heated reaction tubes which are themselves housed in an insulating cavity. Concentrated sunlight enters through a window and directly irradiates the tubes containing

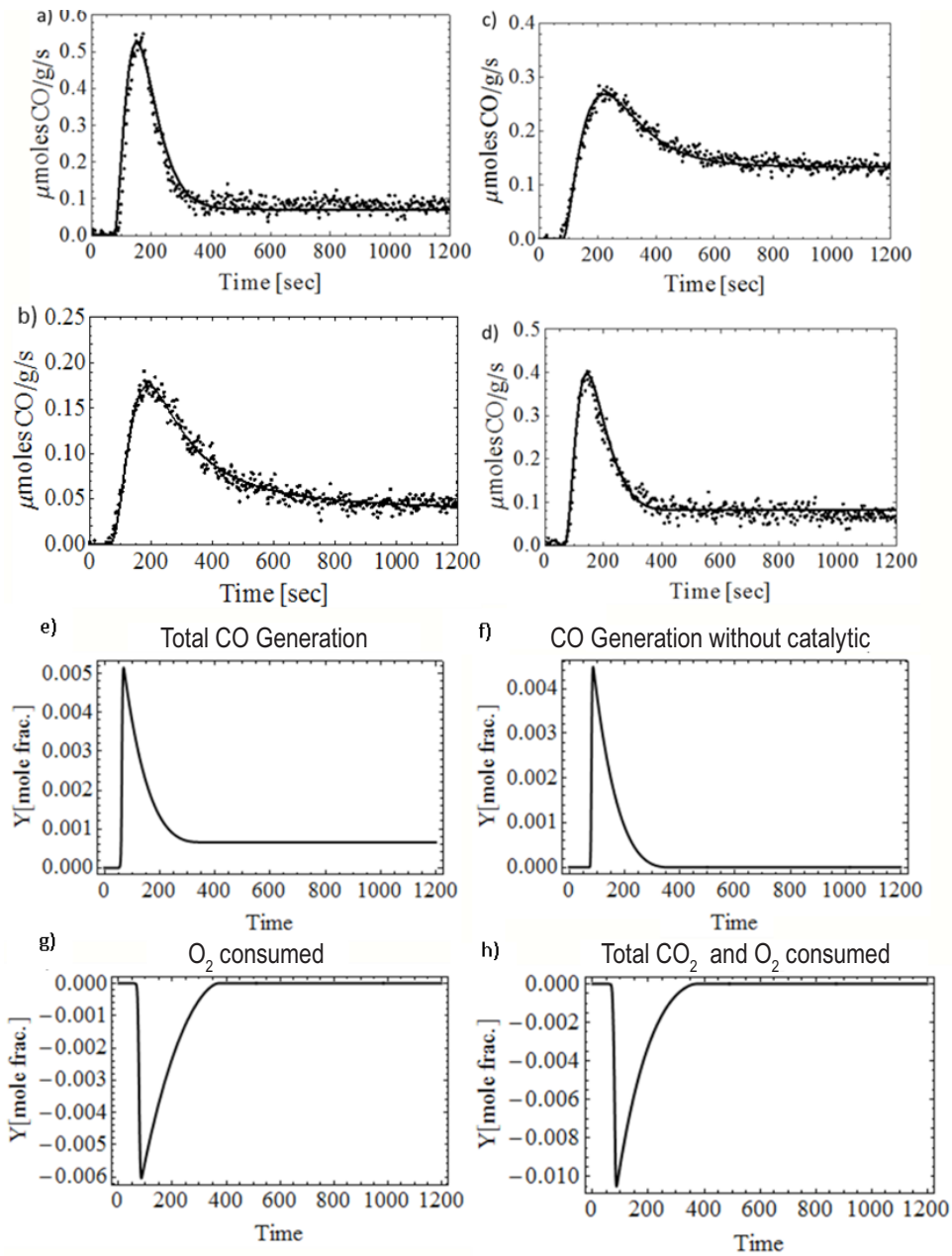

FIGURE 3. Result of kinetic molding analysis for isothermal CO_2 splitting using hercynite materials. CO_2 production curves as experimentally observed (dots) and modeled (straight lines) for a) 1,420°C and b) 1,280°C at 450 Torr CO_2, and at 1,350°C under c) 576 and d) 310 Torr. Modeled CO_2 production curves as modeled using Equation 2 for isothermal splitting at 1,350°C under 310 Torr. e) total CO generated, f) CO generated without including the catalytic activity, g) O_2 oxidation and h) total O_2 and CO_2 oxidation. These curves are un-corrected for dispersion.

the active materials, as shown in Figure 4. One great benefit to this design is that there are no moving parts. For temperature-swing operation, the concentrated sunlight is moved from one half of the reaction tubes to the other with reduction occurring in the irradiated tubes while steam is fed to the other, oxidizing tubes producing H_2. For isothermal operation, concentrated sunlight is directed such that all reaction tubes are heated uniformly and the steam is fed into the desired tubes to drive oxidation.
This past year we carried out detailed computational fluid dynamics modeling of the operation of this reactor design under isothermal and temperature swing conditions, which indicate major challenges in the operation of this reactor design. For temperature swing operation, it is impossible to achieve substantial differences in temperature between the reduction and oxidation reaction tubes, while for isothermal operation there is a substantial temperature variation with the tubes, thus preventing all of the active material to hold at a constant temperature. This indicates two major drawbacks of the SurroundSun™ design: 1) limited control over the operating temperature within the reactor, as indicated by the small temperature change achieved during temperature swing operations modeling; and 2) inefficient use of the material because it is not efficiently heated all the way through to the center of the reducing tubes, as illustrated by the large temperature gradients across individual reaction tubes undergoing reduction under both temperature swing and isothermal water splitting operation. Based on these results, we have concluded that a new reactor design should be considered based on the following principles: 1) flowing particles to enable even material heating, 2) separate reduction/oxidation reaction containment and 3) decoupled reduction/oxidation times.

CONCLUSIONS AND FUTURE DIRECTIONS

- Determined that isothermal Red/Ox is possible, enabling large design space for optimization
- Determined that optimal change in temperature (ΔT) is dependent on active materials, gas/gas heat transfer efficiency and temperature of H_2/H_2O separation
- Developed oxidation kinetics for high temperature CO_2 splitting

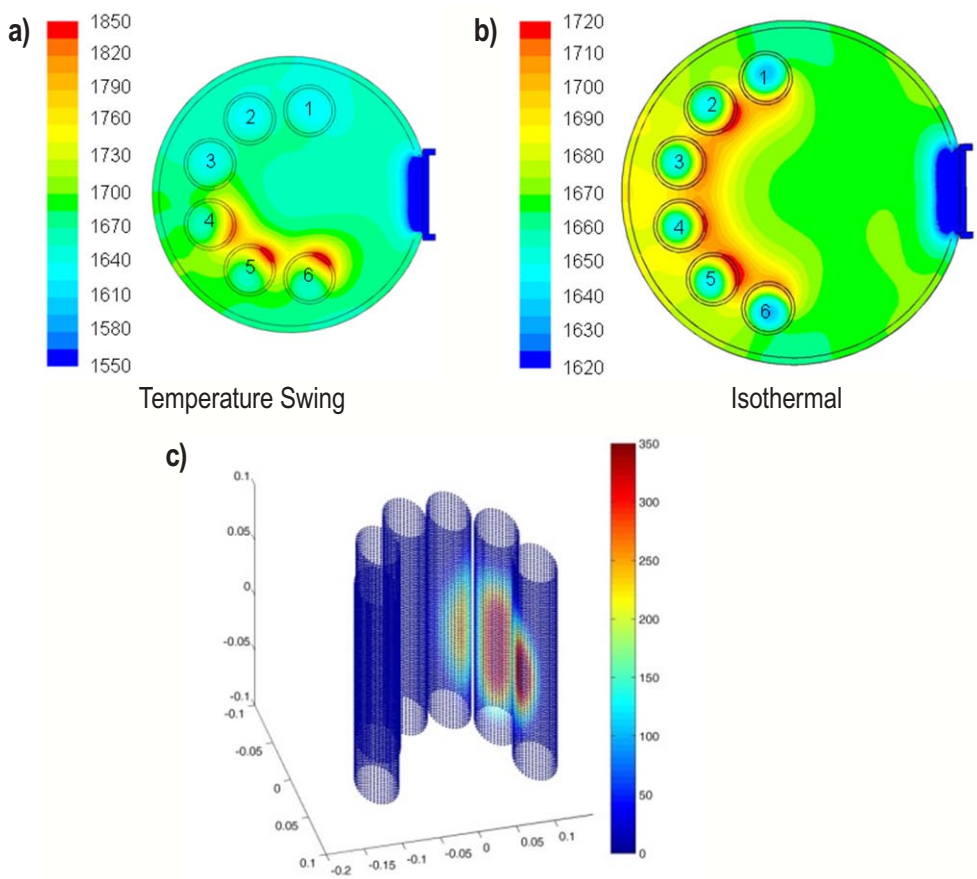

FIGURE 4. Computational fluid dynamics modeling results of SurroundSun™ reactor. a) and b) show the temperature profile with in the reactor under temperature swing and isothermal conditions. c) shows the directional focus of the concentrated sunlight during temperature swing operations.

- Determined that "near-isothermal" processing enables high reduction extent and rapid oxidation kinetics without simultaneous reduction/oxidation occurring
- Determined that a packed bed, stationary tube, SurroundSun™ reactor does not enable considerable ΔT, and materials heating is uneven across the reactant tubes
- Will incorporate Red/Ox extents from "hercynite cycle" and new materials into model to determine "optimal" ΔT
- Will develop improved "hercynite cycle" and perovskite materials using high through-put screening methods and investigate extent of reduction for various P_{O2} and P_{H2O}

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Martinek, J., R. Viger, and A.W. Weimer, "Transient Simulation of a Tubular Packed Bed Solar Receiver for Hydrogen Generation via Metal Oxide Thermochemical Cycles," Solar Energy, 105, 613-631 (2014).

2. Saade, E., D.E. Clough, and A.W. Weimer, "Use of Image-Based Direct Normal Irradiance Forecasts in the Model Predictive Control of a Solar-Thermal Reactor," Journal of Solar Energy Engineering – Transactions of the ASME, 136 (1), Article 010905 (February, 2014).

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2. J.R. Scheffe, *et al.*, "Kinetics and mechanism of solar-thermochemical H2 production by oxidation of a cobalt ferrite-zirconia composite," *Energy & Environmental Science*, **6**, pp. 963-973, 2013.

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