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The CAESAR Project: Experimental and Modeling
Investigations of Methane Reforming in a
CATalytically Enhanced Solar Absorption Receiver
on a Parabolic Dish

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Abstract

A joint U.S./Federal Republic of Germany (FRG) project has successfully tested a unique solar-driven chemical reactor in the CATalytically Enhanced Solar Absorption Receiver (CAESAR) experiment. The CAESAR test was a "proof-of-concept" demonstration of carbon-dioxide reforming of methane in a commercial-scale, solar, volumetric receiver/reactor on a parabolic dish concentrator. The CAESAR design; test facility and instrumentation; thermal and chemical tests; and analysis of test results are presented in detail.

Numerical models for the absorber and the receiver are developed and predicted performance is compared with test data. Post test analyses to assess the structural condition of the absorber and the effectiveness of the rhodium catalyst are presented. Unresolved technical issues are identified and future development efforts are recommended.

MASTER

DO NOT WRITE IN THESE SPACES

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INTRODUCTION

During recent years, the use of solar energy to power high temperature chemical reactions has received increased attention on an international scale [1-7]. Reforming reactions, particularly steam and carbon dioxide reforming of methane, are being investigated at laboratories in Germany (Deutsche Forschungsanstalt für Luft- und Raumfahrt (DLR), Stuttgart), Israel (Weizmann Institute of Science), Spain (Plataforma Solar de Almería), the United States (Sandia National Laboratories (SNL) and the National Renewable Energy Laboratory (NREL)), and the U.S.S.R. (Institute of Catalysis). Potential applications for this technology include thermochemical energy transport and storage, the production of chemical feedstocks and transportation fuels (e.g., methanol), and most recently, the destruction of hazardous chemical waste.

The CAAtalytically Enhanced Solar Absorption Receiver (CAESAR) test was a "proof-of-concept" demonstration of carbon dioxide reforming of methane in a commercial-scale, solar, volumetric receiver/reactor on a parabolic dish concentrator. CAESAR is the largest and first solar direct catalytic absorption receiver (DCAR) reactor [8] to be tested on a dish concentrator.

The CAESAR project was a joint undertaking involving Sandia National Laboratories (SNL), Albuquerque, NM, and DLR-ITT, Stuttgart, Federal Republic of Germany (FRG). It was initiated in 1987, under Task V of the International Energy Agency's Small Solar Power Systems (IEA/SSPS) project, and completed in 1990. Sandia provided the volumetric reactor (a catalyzed porous ceramic absorber) and the gas control, measurement, and analysis equipment. DLR provided the receiver and test facility, including the PAN 17-m parabolic dish concentrator and the gas supply equipment, and was responsible for performing the tests.

Complimenting the tests, simulation models were developed at both laboratories. A one-dimensional, steady-state model of the catalyzed porous volumetric absorber developed at Sandia [9,10] provided guidance in designing the CAESAR absorber. An improved version of this model (described herein), and a coupled one-dimensional, steady-state model of the complete receiver developed at DLR [11,12], were used to aid in interpreting and understanding the test results.

This report describes the design, testing, modeling, and analysis activities that comprised the joint SNL/DLR CAESAR project through the end of fiscal year 1990 (FY90). Both the global performance of CAESAR, and the thermal, chemical, and mechanical performance of the absorber (the catalytic, volumetric reactor), are evaluated and compared with model predictions. Much

of this material is summarized in References [13-15]. Although DLR has continued testing the CAESAR receiver/reactor in FY91 on their own (without SNL participation), the results of these tests are beyond the scope of this report.

CAESAR: CONCEPT AND OBJECTIVES

CAESAR is an integrated solar receiver and chemical reactor that is uniquely suited to the high-temperature/high-flux environments provided by point-focus concentrators. The DCAR is a special type of volumetric receiver/reactor in which absorbed solar radiation is converted from thermal to chemical form, storing solar energy in the chemical bonds of the reaction products rather than as thermal energy in a working fluid [8].

In DCAR reactors, concentrated solar radiation is volumetrically absorbed and chemically converted throughout the catalyst-coated porous absorber matrix. The solar energy is absorbed directly by the catalyst particles, causing the reaction sites to have the highest temperatures. Heterogeneous reactions with reactant gases flowing through the matrix, therefore, are expected to be kinetically limited rather than heat-transfer limited as in conventional tubular reactors. High solar flux capability leads to compact, low-mass receivers with small apertures, reduced heat losses, and fast response. Concurrent, rather than countercurrent, solar radiation and gas flow reduces absorber surface temperatures and reradiation losses. Finally, photolytic enhancement of reaction rates is possible for certain reactions.

The objective of the CAESAR project was to demonstrate the solar DCAR concept using a commercial-scale receiver/reactor on a parabolic dish. The focus, therefore, was on determining the thermal, chemical, and mechanical performance of the receiver/reactor over a range of steady-state and transient operating conditions (e.g., cloud transients).

It is important to note, however, that the CAESAR "proof-of-concept" test was not designed to provide the basic, comprehensive data required for an in-depth understanding of the processes involved or for validation of simulation models. Such data are better obtained in smaller, less expensive, more controlled experiments in which the boundary conditions and operation can be well controlled, and the important parameters can be independently and systematically varied, to explore the cause and effect relationships that will result in a thorough understanding of the DCAR operation.

TEST AND ANALYSIS

CAESAR DESIGN

The CAESAR test setup included the following major components: dish concentrator, receiver, absorber (reactor), gas supply system (including gas flow control, measurement and sampling), product gas sampling and analysis system, and a flare assembly at the exhaust duct exit. These are shown schematically in Figure 1 (except for the dish) and described in the following sections. Additional components not shown in the figure include the data acquisition and handling equipment and a gas chromatograph for feed and product gas analysis.

Absorber

The heart of the CAESAR reactor is the unique catalyzed volumetric absorber. To provide guidance for the absorber design, model predictions were made for a prototype absorber (20 pores per inch (PPI), 85% porosity) and anticipated operating conditions [10]. The results suggested that:

1. decreasing the optical density (i.e., extinction coefficient) of the porous matrix at the exposed (sunlit) side of the absorber would allow deeper solar penetration and decrease matrix temperatures and temperature gradients at the front of the absorber (reducing thermal stresses and radiation losses) and
2. proportioning of the mass flux through the absorber to the incident solar flux distribution would reduce radial temperature variations within the absorber (preventing unacceptably high local temperatures) and promote more uniform methane conversion.

Two absorbers (reticulated porous ceramic foam disks, 64-cm diameter by 5-cm thick) were designed to incorporate these concepts (shown in Figure 2). They were fabricated of 92% alpha alumina and 8% mullite with a porosity of approximately 85% and were coated with a 6% by weight gamma alumina washcoat to provide several orders-of-magnitude increase in substrate surface area. They were subsequently loaded with rhodium (Rh) catalyst to approximately 0.2% by weight using an incipient wetness technique [16].

The rhodium loading procedure consisted of first immersing the absorber pieces in a rhodium nitrate solution for 30 min. and then firing them in air (~2 hrs. at $>400^{\circ}\text{C}$) to dry the pieces and convert the rhodium nitrate to rhodium oxide (a dark, almost black, deposit). After repeating this cycle three times, the absorber pieces were then fired a final time in hydrogen (2 s. at 1000°C) to reduce the rhodium oxide to rhodium metal.

Figure 1. Schematic of CAESAR Test System

The first absorber was constructed with the same layer configuration throughout (5/10/20 PPI front to back) to provide uniform flow resistance. An exploded assembly of this "radially uniform" absorber is shown in Figure 3 (note that the Rh particles provided a black coating over the white surface of the alumina substrate). Additional photos of the absorber pieces are included in Figures A1 - A4, Appendix A. The second, or "radially nonuniform" absorber used the same central disk but had outer ring pieces of smaller pore sizes (10/30 PPI). This was intended to increase the gas flow through the central disk and reduce the flow through the outer ring, creating a radial mass flux distribution that was more proportional to the expected incident solar flux distribution.

Joints between the absorber pieces were a "V" tongue and groove design for improved structural integrity. Ceramic fiber gaskets, composed primarily of alumina with some silica, were placed in all joints during assembly. A layer of ceramic felt was placed around the periphery of the absorber and the entire assembly was held together by a spring-loaded clamping ring which maintained compression while allowing for thermal expansion and contraction during startup and shutdown.

Receiver

Originally built and tested by DLR-Stuttgart as a volumetric air-heating device, the receiver, as adapted for the CAESAR experiments, is shown schematically in Figure 4. Its principal elements are a 10-mm thick quartz window in a 60-cm diameter aperture, a cylindrical clamshell section of ceramic insulation backed by steel to hold the absorber, and a ceramic backwall that separates and channels the feed and product gas flows.

The window is mounted in a water-cooled frame and was initially secured with a high-temperature silicone sealant. The absorber assembly, mounted behind the window, is held firmly in the clamshell casing with the aid of ceramic felt and a ceramic spacer ring. The nine absorber pieces, separated by ceramic fiber gaskets, are visible in the photograph of the assembled receiver presented in Figure 5. Additional photos of the receiver, during assembly and mounted on the dish, are included in Figures A5 - A8, Appendix A.

The feed-gas mixture, CO_2 and CH_4 , enters the annular reservoir at the back of the receiver at ambient temperature and pressure. From there the gases flow forward through an annular gap between the hot absorber framework and the steel clamshell casing, then into the gap between the window and absorber, and finally back through the absorber where they are heated and react (the reforming and water-shift reactions), producing H_2 , CO , and H_2O . The products pass through a stainless steel mixing element, which improves the homogeneity of the flow (composition and temperature) leaving the receiver, and then out through a ceramic-lined exhaust duct where they are

Figure 3. Exploded View of Radially Uniform Absorber

Figure 4. Schematic of CAESAR Receiver/Reactor

Figure 5. Front View of CAESAR Receiver/Reactor

sampled for analysis. Finally, the product gases are burned in the flare before being released to the atmosphere.

TEST APPARATUS

PAN Dish Test Facility

The CAESAR unit was installed in the receiver test bed of the parabolic dish test facility (PAN) at the DLR research center in Lampoldshausen, FRG. A photograph of the facility is presented in Figure 6. The dish, developed by Schlaich & Partner, Engineering Consultant, Stuttgart, FRG, has a diameter of 17 m, a surface area of 216 m², and a focal length of 14 m. It can produce up to 150 kW solar power with flux densities up to 2 MW/m² [17]. Additional photographs of the dish are presented in Figures A8 & A9, Appendix A.

The concentrator consists of a 0.5 mm thick stainless steel membrane, plastically deformed by positive pressure, onto which 0.6 mm thick glass mirror segments (0.4-m²) are bonded. A permanently maintained vacuum (about 25 mbars below ambient) provides mechanical supporting pressure. A grid of cables, forming a 2 m x 2 m mesh, is installed across the dish aperture in front of the mirrors. Pieces of white cotton cloth placed over the 2-m square sections of the grid can be used to cover (shadow) portions of the concentrator thus changing the solar flux distribution incident on the receiver aperture.

To provide flexibility as a test facility, the dish-to-receiver distance can be varied by moving the receiver test bed along the dish axis. Thus, the solar power into the receiver and the flux density and distribution were varied during the tests by translating the receiver along its axis. A second technique for altering the incident flux distribution involved covering some portions of the dish (as described above) thereby reducing the solar flux over selected portions of the aperture. Both of these procedures were used to obtain a more uniform flux distribution across the aperture, and hence more uniform temperatures within the absorber.

An accurate knowledge of the solar input to the receiver, both flux distribution and total power, is essential for proper evaluation of receiver/reactor performance. To characterize the incident solar flux distribution for various combinations of receiver position and concentrator coverings, a series of post-test measurements were made using the DLR HERMES flux-measurement system [17] for conditions similar to tests of interest. The measured solar flux distribution for Test 1L.B34 (tests are listed in Appendix D) is shown in Figure 7.

Figure 6. Parabolic Dish Test Facility (PAN)

Figure 7. Solar Flux Distribution for the Conditions of Test 1L.B34 with the Radially Uniform Absorber

Gas Supply System

Gas storage facilities were installed by DLR at the PAN site to provide the CO_2 and CH_4 feed gases; N_2 for emergency cooling of the receiver/reactor and thermal characterization of the CAESAR system in a nonreacting mode; and CH_4 for the flare pilot light. The N_2 and CO_2 were stored as liquids in large tanks and the N_2 system also contained three evaporator units. The CH_4 feed gas was stored in several gas bottles manifolded together, while a separate bottle was used for the flare pilot light.

From the storage vessels, the three primary gases passed through a gas supply system supplied by Sandia (shown schematically in Figure 1). This unit provided for manual control of each gas flow, measurement and display of the individual flow rates, bottles for collecting samples of the mixed ($\text{CO}_2 + \text{CH}_4$) reactant stream for gas chromatography analysis, and instantaneous switching from methane flow to a much greater flow of nitrogen to cool and purge the complete system in emergency situations (e.g., receiver overtemperature). A detailed description of the gas supply system is given in Appendix B.

Instrumentation/Measurements

Measurements made during the tests, and the instruments used, were selected to provide data that would insure safe operation of the CAESAR system and yield information on the global performance (methane conversion and efficiencies) of the receiver/reactor and on the thermal and chemical performance of the absorber. Brief descriptions of the principal measurements and instruments are given below. Additional details of the instruments and the measurement uncertainties are presented in Appendix C.

Knowledge of temperatures within the absorbers is essential for both a thorough evaluation of absorber performance and detailed comparisons with the simulation models. To this end, holes for thermocouples were drilled in the back of both absorbers at numerous radial-azimuthal ($r-\theta$) locations and at six axial (z) locations ($z = 0.0$ at front surface of absorber). Fifteen 1/16" diameter, stainless steel sheath, type K thermocouples were installed at the locations shown in Figure 8 (nominal axial locations in the different absorber layers are illustrated in Figure 9).

Temperatures of the product gases leaving the absorber were measured with a cross-array of 21 thermocouples located immediately downstream of the absorber. Temperatures of the mixed product gases leaving the receiver were measured with a cross-array of 5 shielded thermocouples mounted behind the mixing element.

As mentioned above, flow rates of the CO_2 and CH_4 feed gases (as well as the N_2 gas) were measured in the gas supply module and presented on panel-

TC NO.	R(CM)	θ (DEG)	Z (CM)	
			1st ABS.	2nd ABS.
1	0	-	3.7	3.9
2	2.5	0	4.0	4.0
3	2.5	60	2.8	2.7
4	2.5	120	0.7	2.4
5	2.5	180	4.3	4.4
6	2.5	240	3.3	1.4
7	2.5	300	2.3	0.6
8	10.0	0	4.1	3.5
9	10.0	90	4.0	3.9
10	10.0	180	4.4	4.0
11	10.0	270	4.1	3.5
12	17.5	0	4.2	3.7
20	27.5	0	4.1	4.1
23	17.5	180	4.1	4.2
24	27.5	180	4.0	4.3

Figure 8. Thermocouple Locations in First (Uniform) and Second (Nonuniform) Absorbers

Figure 9. Nominal Axial Locations of Absorber Thermocouples

mounted digital display units. In addition, samples of the mixed reactant stream were collected in bottles for gas chromatography (GC) analysis.

The product gas stream was sampled continuously through a water-cooled probe mounted in the exhaust duct on the duct axis downstream of the receiver exit (see Figure 1). The sample stream passed through a gas analysis system (shown schematically in Figure 1) mounted in a metal box behind the receiver (in approximately the center of the photo in Figure 10). This unit cooled the gas, removed water, collected samples in remotely operated sample bottles (not shown in Figure 10), and provided on-line measurement of the CH_4 , CO_2 , and CO concentrations using an infrared (IR) gas analyzer. Samples collected in the bottles were subsequently analyzed by gas chromatography.

Additional details of the gas supply and analysis systems, including diagrams, instrumentation, and operating and calibration procedures, are presented in Appendix B.

Data Acquisition and Handling System

All transducers were connected to a data scanner (OPTILOG unit) mounted on the back of the receiver test bed - the box in the lower right hand corner of

Figure 10. Gas Analysis and Data Acquisition Systems Mounted behind the Receiver

Figure 10. The OPTILOG was equipped for 50 thermocouple channels and another 20 voltage channels. All active channels were scanned every five seconds. Each channel was programmed individually to transform the measured electric signal into the desired units. The transformed data were then stored on an output file. The data files were subsequently converted to ASCII format and transferred to the host computer at DLR in Stuttgart for evaluation and analysis. From the DLR host, these data files were also sent via electronic mail to the host at SNL for analysis by Sandia participants.

The OPTILOG unit was connected via an RS-232 interface to an IBM PC XT-286 in the PAN dish control room for processing of the data and control of the measurement process. A safe operation range was specified for those channels carrying data critical to the safe operation of the CAESAR system. When a signal exceeded the limits of this range, a warning message was displayed on the PC screen. This was done for the following critical measurements:

- absorber temperatures too high (to prevent substrate and/or catalyst destruction)
- cooling water temperature too high (reduction or loss of water flow)
- receiver pressure drop too high (possible coking of the absorber)
- temperature at flare exit too low (no combustion of product gases)

TESTS OF THE CAESAR SYSTEM

Emergency Operating Procedure

Since the tests involved highly concentrated solar radiation and combustible gases, certain safety procedures were designed into the system that would be implemented in the event of an emergency. The most dangerous modes of failure were determined to be: cracking of the window and leaking of combustible gases. In either occurrence, the following emergency procedures were to be implemented immediately to minimize damage to, or destruction of, the receiver:

1. The flow of methane into the system would be stopped.
2. The system would be purged with a high flow rate of nitrogen (along with the CO₂ already flowing).

To facilitate these emergency procedures, the gas supply system was designed to provide two operating modes: normal operation and emergency operation. In normal operation, the CO₂ and CH₄ feed gas flow rates were controlled manually using valves mounted on the gas supply console. In emergency operation, methane flow was automatically cut-off, CO₂ flow remained unchanged, and nitrogen flow was set to approximately 400 scfm (the

maximum for which the gas supply system was designed). This combined CO₂ and N₂ emergency flow rate ranged from approximately 6 to 34 times the total feed gas flow rate over the range of conditions tested.

Emergency operation was initiated either automatically (by signals from various sensors to detect such things as electric power failure, window overtemperature, absorber overtemperature, loss of feed gas flow, etc.) or manually (in response to warning messages displayed on the PC screen (see above) or the occurrence of critical, unforeseen operating conditions) from various locations around the test facility. The emergency signal simultaneously opens a bypass valve in the N₂ line and closes a cut-off valve in the CH₄ line.

System Check-Out Tests

Once assembly and instrumentation of the system were completed, the individual components, as well as the overall system, were checked for proper operation and safety. These tests included: leakage test of the gas supply system; instrument performance and calibration; proper operation of the data acquisition and handling system; feed gas control (flow rate response to changes in the manual valve settings); stable operation of the flare; tests of the various automatic and manual emergency shut-down procedures and proper functioning of the emergency operation mode; and agreement among the feed gas flowmeter readings, IR analyzer measurements of the product gases, and GC measurements of gas samples collected from both the feed and product gas streams.

Thermal Tests

The first on-sun tests were performed to evaluate the behavior of the system, especially during start-up and shut-down (going on- and off-sun), determine system control strategies, and characterize the thermal performance of the CAESAR absorber. These non-chemical tests, conducted with only nitrogen flowing through the system, were performed over a range of gas flow rates and insolation conditions. A total of 13 cold and on-sun tests were conducted accumulating over 2 1/2 hours of operation.

Chemical Tests

Reforming tests with the radially uniform absorber began in mid June 1989 and continued for three months. During this time, forty-two tests were conducted accumulating almost 12 hours of on-sun operation. The insolation during these tests ranged from approximately 500 to 850 W/m². The start-up procedure during these tests was to put the receiver on-sun and bring it up to operating temperature with only nitrogen flowing through the system. At this point, the carbon dioxide and methane flows were started and increased to their desired values while the nitrogen flow was decreased to zero. A photograph of CAESAR during one of the chemical tests is presented in Figure 11. The flame produced by the burning product gases leaving the exhaust duct

Figure 11. On-Sun Operation of CAESAR during a Chemical Test

is visible just to the right of the receiver unit. Additional photos of CAESAR during testing are presented in Figures A9 & A10, Appendix A.

The silicone window sealant decomposed after approximately 9.4 hours of testing and was replaced with a ceramic rope gasket. At this time, visual inspection of the absorber revealed considerable discoloration of the front surface (portions of the black absorber surface exhibited shades from white to gray) and cracks of random lengths and directions in all pieces of the absorber. After three more tests (2+ hours), fracturing of the absorber precluded further testing with the radially uniform absorber. Consequently, this absorber was removed and the second (radially nonuniform) absorber was installed in the receiver.

Chemical tests with the second absorber, sixteen in all, were conducted from mid October to mid November 1989. These tests were generally of longer duration and also resulted in almost 12 hours of on-sun operation. The insolation for these tests varied from about 600 to 820 W/m². After some experimentation, a revised start-up procedure was adopted for these tests: the carbon dioxide and methane flows were set to values appropriate for the insolation available, with zero nitrogen flow, before the receiver was placed on-sun. Once the feed gas flows were established, the receiver was put on-sun - a process that took about 5 seconds.

A list of all of the system check-out, thermal, and chemical tests, giving the test number, date, start time, insolation, and pertinent system parameters, is presented in Table D-I (Appendix D).

The combination of shorter days and inclement weather, with the approach of winter, brought these tests to a close. The second absorber was still intact at this point (catastrophic fracturing had not occurred) and the receiver was still functional.

Problems Encountered

As with most experiments, a variety of unanticipated problems arose during the tests. Two which have already been identified were:

1. Decomposition of the high-temperature silicone window sealant after approximately 9.4 hours of testing with the radially uniform absorber, which is believed to have caused discoloration of the front surface of the absorber.
2. Fracturing of the uniform absorber, and the resulting separation of the front layer, allowed a piece of the central disk front layer to fall toward the window forcing termination of these tests after more than 11 1/2 hours of testing.

Additional problems encountered included:

1. Failure of the CH_4 flowmeter early in the tests required repair and recalibration of the instrument.
2. Water accumulation in the tubing of the gas analysis system caused erratic readings of the IR gas analyzer. Two sources of water were identified: a leak in one of the dryer units and condensation downstream of the compressor. Replacing the defective dryer, modifying the piping network, and installing an additional valve upstream of the compressor eliminated this water problem.
3. Time variations in the feed gas flow rates were observed. Two possible causes were identified:
 - a. excessive variations in the pressures upstream of the gas regulators during a test, which would produce changes in the downstream pressures, and hence in the flow rates, and
 - b. ice formation and buildup on the outside of pipes and valves in the gas supply lines leaving the storage vessels (upstream of the gas supply module).Frequent adjustment of the manual control valves was required to alleviate these problems and maintain stable flows.
4. The number of gas bottles used for methane storage proved to be inadequate. This resulted in excessive CH_4 pressure drop during a test, which contributed to the gas flow stability problem described above, and also limited test time to between one and two hours depending on the operating conditions.

TEST RESULTS

The test data were examined to determine which tests were suitable for in-depth analysis. Two criteria were used in making these selections: the test must have good data for at least several minutes of steady-state operation, and solar flux data must be available from HERMES measurements for operating conditions similar to those of the test. A total of 7 tests satisfied these criteria and were selected for analysis: four of the uniform absorber tests, during the period from 7 to 10.7 hours of testing, and three of the nonuniform absorber tests, from 4.7 to 11.8 hours of testing. These tests are indicated in Table D-I, Appendix D.

As an essential aid to interpreting and understanding the data, a set of data plots was prepared for each of the selected tests. Each set includes the following variations with time:

- insolation,
- feed gas flow rates (CH_4 , CO_2 , and N_2),
- product gas composition (CO , CH_4 , and CO_2),

- product gas temperatures along the horizontal diameter ($\theta = 0^\circ - 180^\circ$) 0.5 cm downstream of the absorber exit,
- axial temperatures near the center of the absorber ($r = 0$ and 2.5 cm), and
- radial temperatures along the horizontal diameter near the back of the absorber;

and the following plots at each of several selected times:

- center-of-absorber temperatures ($r = 0$ and 2.5 cm) versus axial distance (z) and
- azimuthal temperatures near the back of the absorber ($z \approx 4.0$ cm) at $r = 10$ cm,
- azimuthal product gas temperatures 0.5 cm downstream of the absorber exit at $r = 5$ and 10 cm,
- radial temperatures along the horizontal diameter near the back of the absorber ($z \approx 4.0$ cm), and
- product gas temperatures along the horizontal diameter 0.5 cm downstream of the absorber exit.

Receiver performance data were analyzed at nine specific times during these tests (near the end of periods of steady-state operation). The pertinent measured data and calculated performance parameters for each of these times are included in Table D-II, Appendix D. Receiver performance results are discussed and summarized below.

Absorber Performance

Detailed performance aspects of the absorber (i.e., its thermal response and substrate and catalyst behavior) were investigated only for the radially uniform absorber. Overall performance of the CAESAR receiver/reactor, with both uniform and nonuniform absorbers, is presented in the Receiver Performance section.

Thermal Performance. As mentioned previously, considerable discoloration of the front surface of this absorber, which undoubtedly altered its optical properties, was observed following decomposition of the silicone window sealant after approximately 9.4 hour of testing. Furthermore, post-test analyses of the absorber, described below, revealed extensive physical cracking and substantial reductions in catalyst activity as a result of the tests. For these reasons, absorber thermal performance was analyzed at steady state conditions during one of the earlier tests (Test 1L.B34) of the uniform absorber in the hope that pretest estimates of absorber properties would be applicable. Insolation was essentially constant for more than 40 min. (see Figure 12); good steady-state data were obtained (feed flows, also shown in Figure 12, were constant from about 24 to 42 minutes); and the test period was from approximately 7.6 to 8.3 hours (prior to the time of window sealant failure).

Figure 12. Insolation and Feed Gas Flow Histories for Test 1L.B34

Temperature histories at seven depths within the central portion of the absorber are shown in Figure 13 for test 1L.B34. Since the insolation during test 1L.B34 was essentially constant, these temperature histories reflect the changes in the feed gas flow rates shown in Figure 12. Generally speaking, the temperature is highest toward the front of the absorber and decreases through the absorber. For comparison purposes, the product gas temperature history measured 0.5 cm downstream of the center of the absorber is also included in the figure.

Axial and radial absorber temperature variations at 40 minutes of test 1L.B34 are given in Figures 14 and 15, respectively. Also included are the associated product gas temperatures 0.5 cm downstream of the absorber. Figure 14 shows the axial temperature variation near the absorber center ($r = 0$ and 2.5 cm) and product gas temperatures at the center and at four azimuthal locations ($r = 5.0$ cm). For the region where absorber data were obtained ($0.6 < z < 4.4$ cm), the temperature generally decreases with increasing distance from the front (exposed) surface.

The predicted solid and gas temperature variations for test 1L.B34 [15] suggest that the solid temperature increases from its value at the front

Figure 13. Time Variations in Center-of-Absorber Temperatures (7 Axial Locations at $r = 0$ and 2.5 cm) and Product Gas Temperature (at $r = 0$ cm) for Test 1L.B34

surface, reaches a maximum somewhere between roughly 0.3 and 2.3 cm, and then either remains about the same or decreases to a lower value at the back of the absorber. The temperature of the gas, which is near ambient initially, increases rapidly over the first centimeter and equilibrates with the solid temperature between approximately 1.4 & 2.3 cm from the front surface. From this point, the gas temperature is either the same as, or slightly greater than (up to 20°C) the solid temperature.

Because of the bias in the data from the forward-most thermocouple (discussed in Appendix C) only the data for $z > 2.3$ cm are representative of the solid and gas temperatures within the absorber [15]. Thus, it is not expected that the predicted solid and gas temperature variations occurring for $z < 2.3$ cm (see Appendix C) will be exhibited by the data.

If the general slope of the data were extrapolated to the back of the absorber ($z = 5.0$ cm), the resulting estimated "absorber exit temperature" would be reasonably close to the measured product gas temperatures (at $z = 5.5$ cm). These trends are exhibited by the data for many but not all of the tests and there is considerably more scatter in some of the data.

Figure 14. Center-of-Absorber Temperatures (versus z at $r = 0$ and 2.5 cm) and Product Gas Temperatures (at $r = 0$ and 5.0 cm) for Test 1L.B34, 40 Minutes

Figure 15. Radial Absorber and Product Gas Temperature Variations for Test 1L.B34, 40 Minutes

The radial temperature variation near the back of the absorber ($z = 4$ cm in Figure 15) has a maximum value at the center ($r = 0$) and exhibits two different trends with increasing radius. To the left ($r < 0$, $\theta = 180^\circ$), the absorber temperature generally decreases to the outer rim. To the right ($r > 0$, $\theta = 0^\circ$), on the other hand, the temperature initially decreases, then rises to a second peak, and subsequently decreases again to the rim. That these two trends are possible can be seen by examining the HERMES solar flux distribution results in Figure 7. One or both of these trends are exhibited in the radial variations of all tests analyzed. As a result of covering specific portions of the dish to decrease the solar flux at the center, the temperatures at the off-center peaks were sometimes larger than those at the center.

It is noteworthy that temperatures near the outer rim of the absorber, $r > 20$ cm, are significantly lower than those for the central region. Based on the data at $r = 27.5$ cm, outer rim temperatures can range from 200 to almost 500°C below the highest peak temperature. As discussed below, these low temperature regions can significantly reduce the overall methane conversion.

The temporal and radial variations in product gas temperature 0.5 cm downstream of the absorber are similar to the respective absorber temperature variations in Figures 13-15. The product gas temperatures are generally lower than the absorber temperatures at $z = 4$ cm; the greatest differences occur at the radial locations of the peaks in the absorber temperatures (Figure 15). However, as mentioned in the discussion of the axial temperature data (Figure 14), extrapolation of the absorber temperature variation to the back of the absorber yields an "absorber exit temperature" that is comparable to the measured gas temperatures.

Substrate Performance. During tests with the radially uniform absorber, the maximum recorded temperature, measured near the front-center of the absorber, exceeded 1200°C . Visual observations between tests revealed considerable discoloration of the front surface (from white to gray) and cracks of random lengths and directions in all pieces of the absorber. Eventually, separation of a portion of the front (5 PPI) layer of the central disk, allowing it to fall forward toward the window, resulted in the test series being terminated. During its removal from the receiver, the absorber remained intact as long as the spring-loaded clamping ring was holding it together. Once the ring was removed, many of the cracked pieces fell apart and/or pieces of the front layer separated.

Extensive post-test analyses were performed on this absorber to examine its structural integrity and determine whether there had been chemical, microstructural, or phase changes during the tests that might have contributed to the cracking. These included examination of the substrate

macro- and micro-structures using optical and electron microscopy to determine how fracture stress was generated, crack origins, and crack propagation directions; X-ray diffraction for chemical analysis of the discoloration of the front surface; and web strength measurements. For comparison purposes, some analyses were also performed on an untested absorber piece (spare piece B). The results of these studies are summarized below. Detailed results are presented in Appendix E.

Multiple cracks in both radial and circumferential directions occurred in most absorber pieces. This was accompanied by considerable separation of the front layer from the middle & back layers which generally remained together. The crack patterns on the front and back of the absorber were generally different (see Figures 16 and 17). Many fractures, however, appeared to originate in the back layer (some were believed to be associated with the drilled thermocouple holes). The apparent cause of the fractures is high thermal stresses.

The amount of cracking and extent of degradation varied considerably among the different absorber pieces. The most severe fracturing and layer separation occurred in the central disk, which was broken into at least twenty-one pieces. For the most part, this piece experienced the highest temperatures during the tests. Degradation of the outer ring pieces was not uniform around the absorber, which is not surprising in view of the solar flux distribution and the likely nonuniform distribution in the gas flow entering the absorber. Generally speaking, pieces in the lower right quadrant exhibit the greatest degradation, almost as much as the central disk, while those in the upper left quadrant exhibit the least, by a significant amount.

Absorber structural analyses revealed significant weakening of the matrix material (degraded strut strength), especially in the middle (10 PPI) and back (20 PPI) layers, as a result of the tests. Further, temperature gradients in the absorber produced thermal stresses that exceeded the bulk strength of the material and contributed significantly to the extensive cracking and front layer separation observed.

The nature of the cracking, material loss, layer separation, and physical appearance of the interior of the central disk are shown in Figure 18. The whiteness of the interior (primarily the middle and back layers) was initially believed to indicate a loss of rhodium catalyst during the tests. However, a similar whiteness of the interior was observed in an untested absorber piece upon breaking it. This question was addressed in post-test analyses of both tested and untested pieces aimed at determining catalyst content and dispersion, the results of which are discussed below.

Figure 16. Post-Test Crack Pattern on Front of Radially Uniform Absorber

Figure 1.7. Post-Test Crack Pattern on Back of Radially Uniform Absorber

Figure 18. Post-Test View of Central Disk (Radially Uniform Absorber) Showing Front Layer Separation and Interior Degradation

Figure 19, a magnification of the center region of the central disk shown in Figure 18, gives more detail of the absorber structure. Fractured struts are visible along the fracture surfaces of the front (5 PPI) layer. Additional details of the reticulated alumina foam structure are shown in the photograph (6X) and micrograph (40X) presented in Figure 20. The former illustrates the appearance of the substrate material as it was received from the manufacturer (prior to catalyst loading), while the latter shows details of a fractured strut and the washcoat of an untested, rhodium-coated absorber piece. Note in particular, the triangular hollow center of the fractured strut left by the urethane foam used in the manufacturing process, and the mud-flat-cracked appearance of the alumina washcoat, which was prevalent on both untested and tested pieces.

X-ray diffraction was performed on samples of washcoat and strut materials from untested absorber pieces (with and without Rh catalyst), and of washcoat material from the exposed surface (with the white residue) of a tested piece. Results indicate that there is no γ -alumina in the washcoat of either the tested or untested pieces. Since the γ -alumina washcoat was applied specifically to provide a much higher surface area for the Rh catalyst, its absence may have had a detrimental effect on the catalytic performance of the absorber.

The surface discoloration and some of the cracking and material loss are visible in the photograph shown in Figure 21. The degree of surface discoloration varied over the absorber surface, possibly the result of nonuniformities in the solar flux and feed-gas mass-flux distributions. Examination of the front surface in the discolored regions using optical microscopy revealed the presence of white deposits on the outermost webs. Additional post-test photos of the radially uniform absorber are presented in Figures A11 - A13, Appendix A.

Examination of the absorber, using scanning electron microscopy (SEM) and energy dispersive analysis by x-ray (EDAX) revealed that the white deposits on the absorber surface had a high silicon content. Possible sources of silicon include: the ceramic fiber gaskets between the absorber pieces, the ceramic felt around the periphery of the absorber, and the high-temperature silicone window sealant which overheated and decomposed during the tests. In support of the latter, the white deposits on the absorber surface appeared at the same time the silicone window sealant failed.

Regions of the absorber surface were examined using scanning electron microscopy (SEM). At 1000 X magnification, the white residue appears fibrous in nature. This is illustrated in the SEM micrographs of Figure 22 which provide a comparison of the absorber surface with and without the white deposit.

Photograph of 10 PPI Alumina
 Fabricated Surface w o Catalyst
 Magnification 6 X

SEM Micrograph of Spare Piece B
 Fractured Strut
 Magnification = 40 X

Figure 11. Post-Test View of Radially Uniform Absorber

**SEM Micrograph of Exposed Surface
In Region Having White Residue
Magnification = 1000 X**

**SEM Micrograph of Top of 3rd
Layer (20 PPI) of Piece 9
Magnification = 1000 X**

Figure 22. SEM Micrographs of Absorber Surface with and without the white Deposit

Catalyst Performance. Post-test absorber surface characterization studies were performed on the radially uniform absorber to determine catalyst content, dispersion, crystallite size, and activity; surface area; and the presence of carbon and hydrogen. The analyses, which were also performed on an untested absorber piece (spare piece B) to provide a basis for comparison, utilized the following techniques: atomic absorption (AA) analysis, X-ray fluorescence spectroscopy (XRF), and transmission electron Microscopy (TEM). The results of these studies are summarized below and presented in detail in Appendix F.

The Rh dispersion was found to be very nonuniform in depth through the absorber. The Rh content was higher in the front and back layers (2-3 times the design value), even higher on the exposed front and back surfaces, and lower in the middle layer. An untested absorber piece was similar indicating that the nonuniform dispersion is a consequence of the catalyst loading procedure and not operational history. The Rh was dispersed as individual crystallites that ranged in size from 2-6 nm on the untested piece. Post-test measurements showed larger Rh crystallites on the front surface (8-28 nm) than on the back (4-14 nm). These results are shown rather dramatically in the TEM photomicrographs (495,000 X magnification) in Figures F2 - F4 of Appendix F. High temperatures experienced during the tests are believed to have contributed to the sintering of the Rh particles.

Catalyst deactivation due to loss of Rh surface area on the front surface was seven times greater than on the back, which is consistent with the measured absorber temperature profiles and sintering behavior during the tests. Substantial sintering of the alumina washcoat also occurred on the front surface of the absorber (a factor of two reduction in surface area), which could have resulted in catalyst deactivation due to Rh encapsulation. The surface area of the back of the absorber was the same as that on both surfaces of the untested absorber.

Of particular importance to the success of this concept for CH₄ reforming, no carbon was detected on the absorber indicating that coking of the Rh catalyst did not occur. Post-test examination of the receiver revealed significant carbon deposition on non-catalytic, metallic surfaces downstream of the absorber.

Receiver Performance

The primary performance metric for the CAESAR receiver/reactor is the percent methane conversion (the percent of CH₄ entering the receiver that is converted in the reactor). The CH₄ feed gas flow history for test 1L.B34 of the radially uniform absorber, shown as mass flow in Figure 12, is shown again in Figure 23, in volume flow units, along with the CH₄ and CO product

Figure 23. Methane Feed Flow Rate and Product Mole Fraction Histories for Test 1L.B34

mole fraction histories. Variations in the product mole fractions reflect the step changes in the CH_4 feed flow rate. As the reactant flow rates were decreased, the reactor temperatures increased (see Figure 13) and the methane conversion increased, as indicated by the increase in the CO and decrease in the CH_4 product mole fractions.

Receiver operation with the radially uniform absorber is shown in Figure 24 during a cloud transient, where the insolation fell from $\approx 600 \text{ W/m}^2$ to almost zero on two different occasions, and the reactant flow rates were held essentially constant. Absorber temperatures, measured near its center, decreased from $780 - 950^\circ\text{C}$ at 28 minutes to as low as 500°C at 33 minutes and then increased again to $750 - 900^\circ\text{C}$ following the cloud passage. Methane conversion exhibited a similar excursion with the reduction in incident solar energy during this time period. The reactor responded satisfactorily to the changing insolation, returning to steady-state operation within minutes of returning to full sun.

The methane conversion and receiver thermal and chemical efficiencies were determined by applying conservation of mass and energy for the receiver, using the measured feed gas flow rates, product CH_4 , CO_2 and CO mole fractions, and incident solar power. The available measurements were insufficient to confirm material balances. Receiver thermal efficiency is the

Figure 24. Transient Operation during a Cloud Passage

percent of incident solar energy transferred to the gas phase as the total enthalpy change (both chemical and sensible) of the mixture. Chemical efficiency is the percent of incident solar energy transferred to the gas mixture as chemical enthalpy change.

CAESAR overall performance parameters were evaluated at nine times (at approximately steady-state conditions) during the seven tests selected for analysis (as described previously). The results, at six times for the radially uniform absorber and three for the nonuniform absorber, are summarized in Table I. In a viable design, the receiver must be both energy efficient and convert most of the available methane. For the radially uniform absorber, the methane conversion increases as both the solar power and the gas feed flow decrease. However, the thermal and chemical efficiencies generally decrease, indicating an increasing fraction of the incident energy is lost as the solar power and feed flow are reduced. Chemical performance is a nonlinear function of the incident solar power, feed gas flow, and catalyst activity. Since each varied during the tests, it is difficult to identify the specific causes of the performance trends.

Performance differences between the radially uniform and nonuniform absorbers, however, can be identified. For example, compare the results for tests 1L.B42 (27 min.) and 2C.B08, which both have the same feed gas flow.

Table I: CAESAR Performance Summary

test number	time (minutes)	solar power (kW)	feed flow (kg/hr)	thermal efficiency (%)	chemical efficiency (%)	methane conversion (%)
Radially uniform absorber (first absorber)						
1L.B33	22	115.7	145	85.6	54.4	39.1
1L.B34	40	105.7	110	79.3	50.7	45.9
1L.B42	16	88.8	52.3	44.0	29.0	45.6
1L.B42	27	86.3	42.0	39.7	25.2	48.8
1L.B44	25	78.7	40.1	43.8	28.5	51.6
1L.B44	39	74.8	26.7	31.7	20.8	60.0
Radially nonuniform absorber (second absorber)						
2C.B08	90	64.1	42.0	67.3	46.3	66.0
2C.B13	40	72.1	50.5	65.9	44.9	68.5
2C.B17	60	97.3	73.4	68.7	45.3	52.4

Although the solar power for the radially nonuniform absorber is 25% less than the power for the uniform absorber, the thermal efficiency is 70% higher, the chemical efficiency is 84% higher and the methane conversion is 35% higher. Comparing tests 1L.B44 (39 min.) and 2C.B13 for similar solar powers, the performance of the radially nonuniform absorber is again superior. The improved performance of the radially nonuniform absorber could be due to a one or more of the following factors: greater catalyst activity (catalyst deactivation of the radially uniform absorber was previously discussed), an improvement in the distribution of reactant gas flow through the absorber, or a more uniform incident solar flux.

The overall methane conversion for both absorbers is less than expected. It is clear that neither the design nor the operating conditions were optimum. Lower temperatures in the outer portions of the absorber, $r > 20$ cm, which comprises $\approx 60\%$ of the absorber area, resulted in less methane conversion in these regions, significantly reducing the total methane conversion for the receiver. Reference [15] shows that as the solar fluxes increase from 100 to 600 kW/m², the product CH₄ mole fraction decreases by over an order of magnitude and the gas temperature increases by 250°C. Clearly, lower temperature regions must be eliminated to achieve acceptable methane conversions and receiver efficiencies.

Although the thermal and chemical performance of the radially nonuniform absorber is encouraging, the methane conversion obtained is below levels desired for most applications. Thermochemical energy transport, for example, requires methane conversions of 90% or greater [4]. Improved design and operating conditions are expected to significantly increase conversion. Additionally, a recuperator can be used between the reactant and product streams to improve the performance of a thermochemical transport system. It can provide a significant portion of the 10-30% of the incident solar power that is currently used for sensible heating of the reactants.

The conversion levels shown here are not appropriate for the destruction of hazardous waste, although the potential of this technology to hazardous waste destruction has been shown [18]. Since complete destruction is paramount and receiver efficiencies are of secondary concern, the reactor design and operating conditions may differ from a reforming application. Utilizing the knowledge gained during this investigation, receivers can be designed with significantly improved performance.

MODELING AND ANALYSIS

SANDIA ABSORBER MODEL

Introduction

The CAESAR reactor (see Figure 4) is an integrated solar receiver and chemical reactor uniquely suited to high-temperature/high-flux environments. This type of chemical reactor volumetrically absorbs concentrated solar energy throughout a catalytic porous absorber matrix volume, promoting heterogeneous reactions with fluid-phase reactant species flowing through the absorber.

A numerical model was previously developed to provide guidance in the design of the absorber and it is discussed in detail in Ref. [9]. Scoping calculations for the thermal and chemical performance of the reactor were presented in Ref. [10] for a range of absorber parameters and operating conditions. Predicted performance was based on a prototype absorber and anticipated operating conditions. These predictions were used to assist the final absorber design for CAESAR. At that time, however, some information (such as absorber radiative, convective and catalytic properties) necessary to model and evaluate the final design was not available.

The following sections discuss improvements of the numerical model described in Ref. [9], compare model predictions with test data, and indicate the predicted performance potential of these types of reactors under more ideal conditions.

Model Description

The numerical model and solution procedure used to predict reactor performance is described in detail in Ref. [9]. Improvements of the model and improved properties are presented here. In particular, the radiative transfer model has been improved, a spatially varying catalyst loading has been incorporated, convective and radiative properties for each layer in the multi-layer absorber have been determined, and more realistic boundary conditions have been applied. The model, in general, remains the same as presented in Ref. [9].

Briefly, the one-dimensional, planar, steady-state model of the absorber incorporates the following axial energy transfer mechanisms: solar and infrared radiation, heterogeneous chemical reaction, conduction in the solid phase, convection between the fluid and solid phases, and interaction with the quartz reactor window. Energy transfer at the microscale is not explicitly modeled. A continuum (rather than a discrete) approach has been taken. To account for radial variations in incident solar flux and mass flux, several one-dimensional and radially uncoupled problems are solved independently. For each problem, the model provides axial distributions (through the absorber) of: solid, fluid and thermocouple temperature, fluid composition, and energy fluxes. These are used to determine reactor (global) efficiencies, losses and conversion.

Radiative Transfer. The three-flux technique, as developed in Ref. [19] to more accurately account for the refractive effect at air-water interfaces, is used in this analysis to model radiative transfer in the solar band. It more accurately accounts for the typically conical solar flux distribution from dish concentrators. Volumetric absorption and radiative flux predictions from the three-flux technique compare well to those obtained from both the more detailed discrete ordinate method and experiments [19], particularly for conical incidence and anisotropic scattering. The three-flux technique offers a good compromise between accuracy, operational convenience and computation time. The two-flux technique is used for the infrared radiative transfer, which is typically diffuse.

The porous absorber matrix is modeled as a quasi-continuous, nonisothermal, homogeneous medium with transparent boundaries. It is assumed to be an absorbing, emitting, and isotropically scattering medium. Isotropic scattering is assumed since there is a lack of phase function information for radiative transfer within the reticulated material. (Anisotropic phase functions can be incorporated in both techniques.) As discussed below, any actual anisotropy is accounted for in the way the radiative properties are determined. The fluid phase is assumed to be radiatively nonparticipating.

The three-flux technique approximates radiative transfer by grouping the noncollimated radiant energy into three isotropic components in the three regions indicated in Figure 25. The positive-directed hemispherical flux is comprised of two fluxes, q_{s1}^+ and q_{s2}^+ , with the boundary between each isotropic region specified by μ_c ($\cos(\theta_c)$). The negative-directed hemispherical flux is represented by q_s^- . Additionally, a collimated flux ($q_{s, \text{coll}}$) can be included, which is used primarily when analyzing reflectance/transmittance experimental data. For the solar band, the radiative transfer is represented by,

$$\begin{aligned} \frac{dq_{s1}^+}{dz} = & \beta_s \frac{\omega_s (1 - \mu_c) - 2}{1 + \mu_c} q_{s1}^+ + \beta_s \frac{\omega_s (1 - \mu_c)}{\mu_c} q_{s2}^+ \\ & + \beta_s \omega_s (1 - \mu_c) q_s^- + \beta_s \frac{\omega_s}{2} (1 - \mu_c) q_{s, \text{coll}} \quad , \end{aligned} \quad (1)$$

$$\begin{aligned} \frac{dq_{s2}^+}{dz} = & \beta_s \frac{\omega_s \mu_c}{1 + \mu_c} q_{s1}^+ + \beta_s \frac{\omega_s \mu_c - 2}{\mu_c} q_{s2}^+ + \beta_s \omega_s \mu_c q_s^- \\ & + \beta_s \frac{\omega_s \mu_c}{2} q_{s, \text{coll}} \quad , \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{dq_s^-}{dz} = & \beta_s \frac{\omega_s}{1 + \mu_c} q_{s1}^+ - \beta_s \frac{\omega_s}{\mu_c} q_{s2}^+ + \beta_s (2 - \omega_s) q_s^- \\ & - \frac{\beta_s \omega_s}{2} q_{s, \text{coll}} \quad , \end{aligned} \quad (3)$$

$$\frac{dq_{s, \text{coll}}}{dz} = - \frac{\beta_s}{\mu_{\text{coll}}} q_{s, \text{coll}, \text{inc}} e^{-\beta_s z / \mu_{\text{coll}}} \quad . \quad (4)$$

Figure 25. Parameters for Three-Flux Radiative Transfer Technique

For the infrared band,

$$\frac{dq_r^+}{dz} = -\beta_r(2 - \omega_r)q_r^+ + \beta_r\omega_r q_r^- + 2\sigma\beta_r(1 - \omega_r)T_s^4, \quad (5)$$

$$\frac{dq_r^-}{dz} = -\beta_r\omega_r q_r^+ + \beta_r(2 - \omega_r)q_r^- - 2\sigma\beta_r(1 - \omega_r)T_s^4. \quad (6)$$

At the absorber inlet (sunlit side), the solar and infrared fluxes are specified by considering the interaction with the quartz window. The solar flux from the concentrator (having a rim angle of 32° ($\mu_c = 0.848$)) that exits the quartz window and is incident on the absorber is defined as $q_{s1, inc}^+$. For these simulations, both $q_{s, coll, inc}$ and $q_{s2, inc}^+$ are zero. The incident solar flux is assumed uniform over the frontal area being modeled. The boundary conditions at the absorber inlet are,

$$q_{s1}^+(0) = q_{s1, inc}^+ + \rho_{s, w}(1 - \mu_c)q_s^-(0), \quad (7)$$

$$q_{s2}^+(0) = \rho_{s, w}\mu_c q_s^-(0). \quad (8)$$

$$q_r^+(0) = \rho_{r,w} q_r^-(0) + \epsilon_{r,w} \sigma T_w^4 \quad (9)$$

Since the reactor (absorber and housing) is expected to be reasonably uniform in temperature near the rear of the absorber, and since no additional radiative data is available, adiabatic radiative boundary conditions are specified at the absorber exit,

$$q_{s1}^+(L) + q_{s2}^+(L) = q_s^-(L) \quad , \quad (10)$$

$$q_r^+(L) = q_r^-(L) \quad . \quad (11)$$

Radiative properties for this reticulated material are not well known. The scattering environment requires phase function and scattering cross-section information that, if the absorber was comprised of spheres or cylinders, could be determined using Mie Theory. However, the reticulated nature of the absorber precludes the use of Mie Theory. Additionally, dependent scattering may occur within the absorber, for which the standard radiative transfer equations do not directly apply. Consequently, an empirical approach is used to determine the effective solar and infrared properties for the porous absorber matrix.

Spectrally weighted data from both hemispherical and specular reflectance and transmittance experiments (see Ref. [10]) were obtained for various thicknesses of the rhodium-coated absorber illuminated with collimated incident flux. Predictions from the three-flux model with a collimated incident flux and isotropic scattering were made using different albedos and extinction coefficients and were compared to both the diffuse and specular measured data. The albedo and extinction coefficients for the best fit are taken as the effective radiative properties. These properties include any effects of anisotropic and dependent scattering.

Heterogeneous Chemistry and Mass Conservation. The reaction rate expressions and mass conservation equations are presented in Refs. [9,10]. The carbon dioxide reforming reaction is,

and the associated water-shift reaction is,

The reaction rates in Ref. [9] are presented in terms of variable weight percent rhodium. Predictions in that reference were presented for an anticipated catalyst loading of 0.2%. Analyses of the absorbers installed in the CAESAR tests indicated higher average loadings that were not uniform. The pretest rhodium loadings are presented in Table II under "Solution Procedure" below.

Energy Conservation. Energy conservation for the solid phase depends on the effective radiative properties, chemical reaction rates, enthalpies of reaction, porosity of the alumina matrix, specific heat transfer area for the alumina matrix, and convective heat transfer coefficient between the solid and fluid phases. For the solid phase,

$$-k(1-\phi)\frac{d^2T_s}{dz^2} = -\left[\frac{dq_{s1}^+}{dz} + \frac{dq_{s2}^+}{dz} - \frac{dq_s^-}{dz} + \mu_{coll}\frac{dq_{s,coll}}{dz} + \frac{dq_r^+}{dz} - \frac{dq_r^-}{dz}\right] - \left(R_1\Delta H_{R1} + R_2\Delta H_{R2}\right) - \alpha h_c(T_s - T_f) \quad (14)$$

The boundary conditions are,

$$-k\frac{dT_s(0)}{dz} = h_c(T_s(0) - T_f(0)) \quad , \quad (15)$$

$$-k\frac{dT_s(L)}{dz} = 0 \quad . \quad (16)$$

An energy balance on the fluid at $z = 0$ gives the additional boundary condition,

$$(m/A)C_{pm}(T_f(0) - T_{f,in}) - (1 - \phi)h_c(T_s(0) - T_f(0)) = 0, \quad (17)$$

where $T_{f,in}$ is the fluid temperature at the reactor inlet. These boundary conditions include only surface transfer mechanisms, similar to the approach taken in semitransparent media [20]. Boundary conditions for the radiative fluxes have been specified in Eqs. (7-11). The fluid-phase energy balance, thermophysical properties and enthalpic equations are given in Ref. [9]. The specific heat transfer surface area and the convective heat transfer coefficient for each layer were determined from estimations based on optical image analysis (see Ref. [10]) and physical data (porosity, web sizes, etc.).

Table II: Pretest Parameter Values

Absorber	Radially Uniform			Nonuniform*	
Layer	1	2	3	1	2
Pores/inch	5	10	20	10	30
Thickness (cm)	2.0	1.73	1.27	2.0	3.0
% Rh loading	0.6	0.3	0.4	0.6	0.4
Radiation					
$\beta_s(m^{-1})$	232.5	280.5	403.5	280.5	564.5
ω_s	0.331	0.286	0.319	0.286	0.524
$\beta_r(m^{-1})$	298.5	359.7	561.5	359.7	807.0
ω_r	0.537	0.540	0.644	0.540	0.771
Convection					
$\alpha(m^2/m^3)$	600	900	1400	900	1800
$k = 4.327 \text{ W/mK}$, $\phi = 0.85$ Inlet: $P_{mix} = 1.0 \text{ atm}$, $t_{f,in} = 300 \text{ K}$ Window: $\rho_{s,w} = 0.01$, $\rho_{r,w} = 0.05$, $\epsilon_{r,w} = 0.7$, $T_w = 800 \text{ K}$ * Outer ring (inner disk same as uniform absorber)					

Solution Procedure. The equations describing the thermal and chemical conditions in the volumetric solar absorption chemical reactor are formed as a system of fifteen coupled, nonlinear, first-order, ordinary differential equations. The radiative properties, specific heat transfer area, convective heat transfer coefficient and rhodium loading vary for each absorber layer (having different PPI). Table II presents a summary of all property values for each layer in both absorbers.

The radiative transfer and energy equations require the boundary conditions for this system of equations to be imposed at both the absorber inlet and the absorber exit. This nonlinear two-point boundary value problem is solved using the SUPOR Q computer code [21], which preserves relative accuracy by reorthonormalizing the solution vectors whenever they begin to lose their numerical linear independence and by the use of an adaptive solution point scheme. The absolute and relative error criteria are 1×10^{-3} .

Comparison With Test Data

Absorber temperatures were measured with unshielded thermocouples installed in holes drilled from the rear of the absorber. Due to the reticulated nature of the absorber and large radiative fluxes, data from

thermocouples located within the absorber may not directly represent either the solid absorber temperature or the gas temperature and, therefore, require interpretation. Assuming the thermocouples are not in direct contact with and are not directly shaded by an absorber web, the predicted thermocouple response (calculation of the thermocouple bead temperature in the predicted thermal environment) can be determined and can be compared with the measured data.

If the thermocouple bead had identical radiative and chemical properties as the solid absorber, its temperature would be the same as the solid temperature. However, since no catalytic chemistry occurs on the thermocouple and its radiative properties are different, the predicted thermocouple response differs. Since this correction is determined with the predicted thermal conditions from a continuum analysis, discrete effects around each thermocouple that are unknown (e.g., contact with the solid, total shading by a web, etc.) are not accounted for. These discrete effects can significantly affect the actual thermocouple response.

The thermocouple response is predicted by performing an energy balance on the thermocouple in the predicted thermal environment (local radiative, convective fluxes), assuming the thermocouples are not in direct contact with the absorber. The thermocouple temperature is given by the nonlinear transcendental equation,

$$\sigma \epsilon_{TC} T_{TC}^4 + h_c (T_{TC} - T_f) = \frac{\epsilon_{TC}}{2} \left(q_{s1}^+ + q_{s2}^+ + q_s^- + q_r^+ + q_r^- \right), \quad (18)$$

where ϵ_{TC} is the thermocouple emissivity and is assumed equivalent to the absorptivity. The thermocouple temperature is calculated using a Newton-Raphson approach.

Comparison with Axial Temperature Distributions. To compare model predictions with test thermocouple data, estimations of absorber properties during the test need to be specified. As discussed in the Thermal Performance section above, Test 1L.B34, one of the earliest tests of the radially uniform absorber for which good steady-state data were obtained, was selected in the hope that pretest parameter estimates for the absorber were applicable. However, since many tests had been conducted prior to this test (approximately 7.6 hours of testing out of a total of 11.5 hours of testing on this absorber), it is probable that the absorber had already been altered from pretest conditions.

Three parameter values are believed to have large uncertainties: the solar flux level (recall the nonuniform flux distribution shown in Figure 7), the

fluid mass flux (due to the annular ring flow entry technique indicated in Figure 4), and the rhodium activity (due to nonuniform loading and post-test indications of deactivation). The incident solar flux near the location of the axial thermocouples (center of the absorber) was determined by examining the HERMES flux data. For test 1L-B34 at 40 minutes, $q_{s1,inc}^+ = 525 \pm 15$ kW/m². For the absorber with a radially uniform flow resistance, the annular fluid inlet with no mixing region may produce a radially nonuniform flow field, with decreased flow toward the absorber centerline. At the centerline, the maximum fluid mass flux is that for uniform flow (0.1075 kg/m²s) with an estimation that the mass flux near the center could be decreased by up to 20%.

The rhodium activity in each of the three layers in the absorber could range from the pretest values specified in Table II to the measured post-test values. The measured post-test decrease in reaction rates is simulated in the model by decreasing the catalyst weight-percent loading levels to: 0.031 for the 5 PPI layer, 0.039 for the 10 PPI layer, and 0.084 for the 20 PPI layer (the degradation was not axially uniform -- compare with Table II). The thermocouple emittance during these tests was taken to be 0.85 ± 0.15 in Eq. (18).

The effect of these parameter uncertainties are considered when comparing the predicted thermocouple response with the thermocouple data. Parameter values that provide an upper bound, a lower bound and a best estimate for the predicted thermocouple response are listed in Table III. Parameter values are chosen to bound the response of the thermocouples located toward the front of the absorber. As discussed below, the parameter values that produce the lower temperature bound at the front of the absorber may not produce the lower temperature bound at the rear of the absorber.

Table III: Parameter Values for Test 1L-B34 (40 Minutes)

TTC Esti- mate	ϵ_{TC}	m/A*	Rhodium Loading (wt%)			$q_{s1,inc}^{**}$
			Layer 1	Layer 2	Layer 3	
Upper	1.0	0.0863	0.031	0.039	0.084	540
Best	0.85	0.1075	0.075	0.0375	0.05	525
Lower	0.7	0.1075	0.6	0.3	0.4	510
* (kg/m ² s); ** (kW/m ²)						

The upper-bound parameter values are: highest thermocouple emittance, lower fluid mass flux, highest solar flux near the absorber center, and post-test rhodium loading. The lower-bound parameter values are: lowest thermocouple emittance, uniform fluid mass flux, lowest solar flux near the absorber center, and pretest rhodium loading. The best-estimate parameter values are: average thermocouple emittance, uniform fluid mass flux, average solar flux near the absorber center, and a rhodium loading that gives a predicted exit temperature equal to the measured exit fluid temperatures. This last condition was imposed since the greatest confidence lies in the thermocouple data near the rear of the absorber and in the fluid temperature data (recall the previous discussion regarding discrete effects on the absorber thermocouple data). For layers 2 and 3, the best-estimate rhodium loading is slightly lower than the measured post-test values.

Figure 26 shows the comparison of the test data with the predicted values. The thermocouple data is generally bounded by these predictions and discrete effects may be apparent (e.g., the data point at 3.7 cm). The difference between the upper bound and lower bound is not constant with axial position in the absorber. Also, the thermocouple response for the best-estimate and lower-bound cases cross toward the rear of the absorber, corresponding to the solid/fluid temperatures in both cases. Figure 27 shows the corresponding predictions for the solid and fluid temperature distributions. Comparing Figures 26 and 27, there is a large difference between the predicted thermocouple response and the predicted solid and fluid temperatures toward the front of the absorber due to the solar flux. The predicted thermocouple, solid and fluid temperatures all coalesce toward the rear of the absorber, where the solar flux is small and the temperature is more uniform. For the lower-bound case, the temperature of the absorber toward the front results in decreased thermal losses and higher exit temperatures, relative to the best-estimate case. Consequently, the axial temperature distributions of the lower-bound and best-estimate cases cross. The effect of ϵ_{TC} on the thermocouple temperature decreases as the fluid and solid temperatures equilibrate (see Eq. (18)).

Methane Fraction and Volumetric Power Predictions. Figure 28 shows the corresponding methane mole fraction distributions, which are similar in magnitude. The volumetric power distributions for the terms in the solid-phase energy equation are shown in Figure 29 for the best-estimate parameters. The effect of decreasing the optical density toward the front (sunlit) side of the absorber is evident by the deeper penetration into the absorber of the solar energy (i.e., it is more volumetric), relative to that shown in Ref. [10] for the 20 PPI prototype CAESAR absorber. This effect is also shown by the solid temperature distributions (Figure 27). The discrete layer locations in the absorber can be observed in the chemical power distributions.

Figure 26. Comparison of Thermocouple Data with Predicted Thermocouple Response for Test 1L.B34, 40 Minutes

Figure 27. Predicted Axial Distributions of Solid and Fluid Temperatures for Test 1L.B34, 40 Minutes

Figure 28. Predicted Axial Distributions of Methane Mole Fraction for Test 1L.B34, 40 Minutes - Upper Bound, Best Estimate, and Lower Bound Cases Refer to Thermocouple Response

Figure 29. Predicted Axial Distributions of Volumetric Power for Test 1L.B34, 40 Minutes, with Best-Estimate Parameter Values (See Table III)

Comparison with Global Results. To provide global results using the one-dimensional model predictions, the nonuniform solar flux distribution is subdivided into solar flux contour bands. Model predictions are made for each flux band (using the average incident flux), which are then spatially integrated over the absorber cross-section. Area-averaging the solar flux is inappropriate because the thermal and chemical response is nonlinear with solar flux. The fluid mass flux is assumed uniform across the absorber. Once the fluid leaves the absorber, the fluid from each flux contour band mixes to produce a uniform exit mixture (no heterogeneous chemistry occurs). Conservation of mass and energy are used to obtain the mixture composition and temperature. The thermal and chemical efficiencies and methane conversion are calculated from the exit mixture conditions.

For test 1L.B34, the three-dimensional incident solar flux distribution is shown in Figure 7, indicating nonuniform illumination conditions. Figure 30 shows a grey-scale image of the 256 x 256 pixel HERMES data, with outlines of the inner disk and outer ring of the absorber. A very sharp drop-off in flux values is observed at the center of the image, which is believed to be caused by a flux meter located in the reflective surface used to obtain HERMES data. The affected area is small, so that the effect on this analysis is negligible.

Contours for specified flux levels are calculated and the contour lines are stored as polygon spline-fit paths. A flux-weighted centroid of the image is determined and is associated with the center of the absorber. By using an exclusion region, only the flux that illuminates the 0.3-m radius absorber is analyzed. The polygon areas within all contour paths are determined, from which the appropriate area for each flux band is determined. These areas are used when integrating across the absorber to calculate exit conditions. The contour bands for the flux illuminating the absorber are graphically indicated in Figure 31 as shaded contours.

Table IV shows the six flux bands, the area for each as a percentage of the total absorber area, and the predicted results for each flux band (the incident solar flux for each calculation is taken to be the average of the flux band contour levels). An order of magnitude variation in mole fractions and over 250°C difference in temperature are predicted at the exit. However, over 70% of the absorber is illuminated by flux levels between 250 and 450 kW/m², which is reflected in the mixture values.

Global reactor efficiencies are determined from these data. Thermal efficiency, η_{th} , is the percent of incident solar power transferred to the fluid as the total mixture enthalpy change (including both chemical and sensible enthalpy). Chemical efficiency, η_{ch} , is the percent of incident

Figure 30. Grey-Scale Image of Measured Solar Incident Flux Distribution for Test 1L.B34 - Inner Disk and Outer Ring Areas Identified

Figure 31. Contour Bands for Measured Solar Flux Incident on Absorber, Test 1L.B34

Table IV: Predicted Exit Conditions for Test 1L.B34
(40 minutes)

Flux (kW/m ²)	% Area	X _{CH₄}	X _{CO₂}	X _{CO₂}	X _{H₂}	X _{H₂O}	T _f (°C)
50 - 150	1.2	0.446	0.485	0.037	0.028	0.004	481.7
150 - 250	8.1	0.329	0.354	0.165	0.139	0.013	533.0
250 - 350	32.2	0.230	0.248	0.270	0.234	0.018	578.2
350 - 450	39.0	0.154	0.163	0.352	0.310	0.021	622.7
450 - 550	18.6	0.092	0.096	0.418	0.370	0.024	670.5
>550	0.9	0.047	0.045	0.468	0.412	0.028	743.7
Mixture Values:		0.177	0.188	0.328	0.287	0.020	610.0

solar power transferred to the fluid as chemical enthalpy change. Methane conversion is the percent of methane entering the reactor that is converted. For test 1L.B34, 40 minutes, the model predicts $\eta_{th} = 71.9\%$, $\eta_{ch} = 48.2\%$, and 46.5% of the methane is converted. This compares well to the test data for test 1L.B34 listed in Table I of Ref. [14], which specifies $\eta_{th} = 79.3\%$, $\eta_{ch} = 50.7\%$, and 45.9% methane conversion.

Predictions for Anticipated Conditions. To evaluate the radially tailored absorber (inner disk and outer ring) design under conditions that were anticipated for these tests, predictions were made for the solar flux levels and mass flux levels specified for Case 2B in Ref. [2]. For the inner disk, $q_{s1,inc} = 1912 \text{ kW/m}^2$, $\dot{m}/A = 0.2538 \text{ kg/m}^2\text{s}$; and for the outer ring, $q_{s1,inc} = 317 \text{ kW/m}^2$, $\dot{m}/A = 0.042 \text{ kg/m}^2\text{s}$. The pretest parameter values specified in Table II for the nonuniform absorber are used.

Figure 32 shows the predicted axial temperature and methane mole fraction distributions for both the inner disk and outer ring. Thermal and chemical conditions are more uniform between the inner disk and outer ring than predicted conditions for a non-tailored absorber (see Ref. [10]). The inner disk solid reaches an unacceptably high temperature, which is caused in part by the unexpectedly high rhodium loading for the first layer (indicated in Table II). The high catalyst loading both decreases the front surface temperature due to the endothermic chemical activity and causes a thermal maxima within the absorber due to rapid reactant depletion. This effect of increased catalyst loading was also observed in Ref. [10].

The effect of decreasing the optical density toward the front of the absorber relative to that in the prototype absorber in Ref. [10] is also evident in Figure 32. To reduce the temperature of the inner disk, the optical density should be further decreased, if practical, and either the mass flux increased or the rhodium loading decreased. Predicted reactor

Figure 32. Predicted Axial Distributions of Temperature and Methane Mole Fraction for Inner Disk and Outer Ring with Anticipated Operating Conditions

efficiencies are $\eta_{th} = 71.5\%$, $\eta_{ch} = 46.7\%$, and 99.1% of the methane is converted. Relative to the reactor efficiencies calculated for test 1L.B34, a significant increase in methane conversion is obtained with similar thermal and chemical efficiencies.

DLR RECEIVER MODEL

Description of the Simulation Model

The simulation model at DLR Stuttgart, as part of the CAESAR project, was developed to perform theoretical investigations of complete receiver-reactors. Emphasis was placed on the capability to calculate the thermodynamic and chemical behavior of receivers with complicated geometries which are expected as a result of optimization studies. Such a receiver will be composed of the following elements: absorber, window, fluid inlet (which might be built as an absorber too) and other zones (i.e. insulated receiver elements). A major issue of the model is the total radiative exchange in the receiver which is treated in a 3-dimensional way. The absorber is a sub-element of the complete receiver. A detailed description of the model can be found in Ref. [11]. The following sections outline the model.

Radiation Exchange in the Receiver. The calculation starts with the selection of the receiver geometry, and the definition of the receiver zones (which might be subdivisions of receiver parts). Then the distribution of the concentrated solar flux on all receiver elements is calculated, based on measured flux distributions or with theoretical methods (i.e. ray-tracing).

The net radiation exchange in the receiver is based on the so-called "zonal method." For the application to volumetric receivers with a quartz window covering the aperture it is essential to account for transmission and specular reflection. Therefore the zonal method was improved as described below.

Each of the N receiver zones has homogeneous material properties and thermodynamical data over the zone surface. These zones are divided into three different types, as follows:

- type 1: the zone temperature is prescribed,
- type 2: the heat flux of the zone is prescribed,
- type 3: the diffuse radiation leaving the zone is prescribed.

The radiative properties of the zones include specular and diffuse reflection, transmission and absorption. For each surface

$$\alpha + \tau + \rho_{\text{dif}} + \rho_{\text{sp}} = 1 \quad . \quad (1)$$

The radiation exchange could be formulated using a variable number of wavelength bands to account for spectral dependance of the properties (multi-band model).

For the calculation of radiation exchange the so-called exchange factors must be known. This exchange factor, $Y_{i,j}^k$, defines the part of the diffuse radiation emitted from element i in the wavelength band k which arrives on element j both directly and by all possible intermediate reflections and transmissions. In case that no transmission and specular reflection occurs the exchange factor is equal to the configuration factor.

The determination of the exchange factor matrix could be derived from configuration factor tables (for simple geometries) or calculated by suitable methods (e.g. ray-tracing procedures with Monte-Carlo techniques).

For the zones of type 1 or 2 the diffuse radiation leaving zone i is given by the sum of diffusely reflected irradiation and diffuse emission:

$$J_j^k = \rho_{\text{dif},i}^k (G_i^k + G_{s,i}^k) + E_i^k \quad (2)$$

The thermal emission in wavelength band k is defined by

$$E_{i_k}^k = \epsilon_i^k f_{\text{bb}}^k \sigma T_i^4 \quad (3)$$

with f_{bb} being the fraction of the black body radiation emitted in wavelength band k. Using the above definition of the exchange factors the diffuse irradiation of zone i is

$$G_i^k = \sum_{j=1}^N Y_{i,j}^k J_j^k \quad (4)$$

For the zones with prescribed heat flux (type 2) the temperature must be determined first. The heat flux into the zone is the difference between absorbed and emitted radiation:

$$q_{\text{ib}} = \sum_{k=1}^K \{ \alpha_{\text{ib}}^k (G_{\text{ib}}^k + G_{s,\text{ib}}^k) - E_{\text{ib}}^k \} \quad (5)$$

The index ib refers here to the ib-th zone of type 2. The prescription for the heat flux could include several terms as follows

$$q_{\text{ib}} = q_{0,\text{ib}} + \frac{\lambda_{\text{mat}}}{s} (T_{\text{ib}} - T)_{\text{ref}} \quad (6)$$

This allows to account for fixed heat fluxes and for fluxes which depend on the temperature of the calculated element. The latter term specifies the heat flux by thermal conduction (1-dimensional) through a material with thickness s. The temperature T_{ref} could be either fixed or variable. This is important to calculate the heat flux by conduction between the two surfaces of a window.

For the calculation of the total radiation exchange the absorber is simulated as a zone of type 3, i.e., with prescribed outgoing radiation J^k . The details of the absorber simulation are described in the next section. The described equations lead to a set of linear equations when no type 2 zones are included. If such zones are present a subset of nonlinear equations must be solved to determine the required zone temperatures.

Simulation of the Volumetric Absorber. The calculation of the steady-state thermal and chemical conditions within the volumetric absorber takes the following energy transfer mechanisms into account:

- radiation (absorption, scattering, emission),
- convection between absorber and fluid,
- sensible fluid heating,
- change in fluid composition by chemical reaction.

Heat conduction in the solid and the fluid is neglected since the mechanism of radiation transport is dominant at the temperatures existing in the absorber. The model allows one-dimensional calculation of all properties. The absorber could be composed of multiple layers with different characteristics, but the layer itself is treated as a continuum. The radiation transport is described by absorption and scattering coefficients with the same wavelength bands as in the receiver calculation. For the radiation a distinction is made between collimated and diffuse radiation. A modified two-flux-model is used to calculate the radiation distribution inside the absorber. The governing equations are described below. The index k (defining the wavelength band) is omitted here for convenience.

The collimated radiation impinging onto the absorber is separated into a number of N ranges with specific incidence angles μ relative to the absorber axis. The attenuation of this radiation is then given by

$$I_{c,n} = I_{c0,n} \cdot e^{-\frac{k_a + k_s}{\mu_n} z} \quad (7)$$

The two-flux equations could be derived as

$$\begin{aligned} \frac{dI^+}{dz} = & -2(k_a + (1-f)k_s)I^+ + 2bk_s I^- + 2k_a I_B \\ & + \sum_{n=1}^N \frac{k_s}{\mu_n} f I_{c,n} \end{aligned} \quad (8)$$

for the forward direction and

$$\begin{aligned} -\frac{dI^-}{dz} = & -2(k_a + (1-f)k_s)I^- + 2bk_s I^+ + 2k_a I_B \\ & + \sum_{n=1}^N \frac{k_s}{\mu_n} b I_{c,n} \end{aligned} \quad (9)$$

for the backward directed radiation. The emissive power is given by

$$I_B = f_{bb} \sigma T_a^4 \quad (10)$$

The boundary condition on the irradiated side of the absorber ($z=0$) is

$$I^+ = I_0^+ \quad (11)$$

which is the sum of all diffuse irradiation parts. The boundary condition at the opposite side ($z=L$) is given by

$$I^- = \rho(I_L^+ + \sum_{n=1}^N I_{c,n}) + I_{BL} \quad (12)$$

assuming that the surroundings behind the absorber has an effective reflection of ρ .

The energy balance is based on two chemical reactions and sensible heating of the fluid. The main reaction is methane reforming with carbon dioxide (index $j=1$)

This reaction is accompanied by the watergas shift reaction (index $j=2$)

Other possible reactions are neglected.

The energy balance over the fluid leads to the differential equation

$$\frac{dT_f}{dz} = \frac{hA_{cV}}{(m/A)c_p} (T_a - T_f) \quad (15)$$

The specific heat capacity is dependent on chemical composition and temperature of the fluid. The boundary condition for the fluid temperature is

$$T_{f,z(0)} = T_{\text{fluid,in}} \quad (16)$$

For the absorber temperature no boundary condition is required. The energy balance for the solid is given by

$$\sum_{k=1}^K \{ 2k_a (I^+ + I^-) - 4k_a f_{bb} \sigma T_a^4 + \sum_{n=1}^N \frac{k_a}{\mu_n} I_{c,n} \} - hA_{cv} (T_a - T_f) \quad (17)$$

$$- \sum_{j=1}^2 \rho_{abs} \cdot r_j \cdot \Delta H_j = 0 \quad .$$

The reaction rates r_j for both reactions are given in Ref. [12]. The change in chemical composition for all participating species ($i=1,5$) can be expressed as

$$\frac{dn_i}{dz} = A \rho_{abs} \sum_{j=1}^2 \nu_{i,j} r_j \quad (18)$$

where $\nu_{i,j}$ is the stoichiometric factor of the species i in the reaction j . The boundary condition for the fluid composition is

$$n_{i,z(0)} = n_{inlet} \quad . \quad (19)$$

Calculation Procedure. The equations for the radiation distribution are solved separately using a finite difference scheme, whereas the equations for the fluid and absorber temperatures and chemical composition are solved with a Runge-Kutta procedure of fourth order.

The overall radiation exchange and the operation condition of the absorber and other elements are strongly dependent on each other. Therefore, various iteration levels are necessary to solve the complete system of equations. A FORTRAN-code called TOTCRR was developed at DLR Stuttgart to perform this task. The main steps of the calculation procedure are listed below. The solar flux distribution (calculated by a different code) is available as input data, as well as the exchange factor matrices for the given receiver geometry.

1. Read in all input data: definition of zones, collimated solar flux distribution, receiver operation conditions (i.e. mass flow, pressure, feed gas composition), exchange factors, radiative properties, etc.
2. Estimate initial values for radiation and absorber temperatures.
3. Calculate for all absorber elements:
 - a. distribution of radiation throughout the absorber;
 - b. fluid and catalyst temperature profiles in the absorber, change of chemical composition of the fluid;
 - c. check the results for convergence of fluid and absorber temperatures. If the convergence criterion is not reached, continue with step 3a).

As a result, the reradiation J from all absorber zones (type 3) is available for the enclosure calculations.

4. Calculate the temperature of zones having prescribed heat flux (type 2).
5. Calculate the total radiation exchange between all elements of the receiver (absorber elements, window elements, insulated sections, etc.). As a result, the (new) irradiation of all elements is obtained.
6. Check the results for convergence of the irradiation of each zone. If the convergence criterion is reached, continue; else go back to step 3.
7. Perform control calculations to ensure consistency of the results; store the results on file.

As an option, a desired methane conversion in the exit fluid could be specified. In this case, the mass flow is varied iteratively until the desired conversion is reached.

Comparison of Receiver Performance.

For the comparison of CAESAR test and simulation results, the receiver was modeled by 29 zones: 9 absorber elements (corresponding to the 9 absorber pieces), the annular fluid inlet ring, 18 window elements (front and back side, area division equal to absorber) and the aperture (necessary to form the enclosure for the modeling). Absorber properties were chosen as described in the section "Sandia absorber model". Catalyst activity was based on the data measured for the untested samples. The solar irradiation was determined from measurements taken with the HERMES system by averaging the local irradiation over each absorber piece.

During the first simulation runs, the receiver data were taken without additional modification of parameters. The corresponding results for the selected cases are given in Table V.

Table V: Comparison Between Test Data and Simulation Results (Values in Parentheses are the Absolute Differences)

test identifier	receiver efficiency			chemical efficiency			methane conversion		
	test / model (diff.) (%)	(%)	(%)	test / model (diff.) (%)	(%)	(%)	test / model (diff.) (%)	(%)	(%)
1L.34;40	79.3 / 80.9	(+1.6)		50.7 / 52.0	(+1.3)		45.9 / 45.1	(-0.8)	
1L.42;27	39.7 / 74.9	(+35.2)		25.2 / 50.7	(+25.5)		48.8 / 98.1	(+49.3)	
1L.44;25	43.4 / 76.0	(+32.6)		28.5 / 52.7	(+24.2)		51.6 / 96.1	(+44.5)	
1L.44;39	31.7 / 56.0	(+24.3)		20.8 / 33.2	(+12.4)		60.0 / 99.9	(+39.9)	
2C.07;18	76.1 / 75.3	(-0.8)		50.7 / 49.0	(-1.7)		50.9 / 48.2	(-2.7)	
2C.08T;90	67.3 / 72.5	(+5.2)		46.3 / 49.4	(+3.1)		66.0 / 70.3	(+4.3)	
2C.13T;40	65.9 / 72.2	(+6.3)		44.9 / 47.7	(+2.8)		68.5 / 71.5	(+3.0)	
2C.17T;60	68.7 / 75.1	(+6.4)		45.3 / 50.4	(+5.1)		52.4 / 58.7	(+6.3)	

Excluding the tests 1L.42 and 1L.44 (3 comparisons) the agreement between measurements and simulation is quite good. The excluded tests show extreme differences between test data and simulation. The reason for the poor agreement for these tests is quite clear. During the test 1L.39, the RTV (room temperature vulcanization) window sealant failed by partial decomposition. A white surface layer appeared on some regions of the absorber which was later determined to contain silicon (a main component of the RTV). This changed the optical properties (white spots increased the diffuse solar reflection losses) and could have affected the chemical activity of the catalyst, thus increasing absorber temperatures. Since it is hardly possible to account for these effects, all tests with the first absorber insert following 1L.39 were omitted from further examination. The data for subsequent tests also indicate that the receiver behavior changed drastically at that time. After installation of the second absorber insert (indicated by "2" as the first digit of the test identifier), the agreement between simulation and tests is again quite acceptable.

Comparison of Axial Temperature Distribution

Various temperature measurements were taken during the experiments. A set of thermocouples was installed in the inner disk within a radius of 2.5 cm around the center of the absorber at different depths. Thus, some information about the axial temperature distribution was obtained. The temperature readings of these thermocouples are compared to theoretical values. As discussed in previous sections, these readings do not really represent the absorber temperatures. The thermocouple near the front is expected to be quite sensitive to direct solar irradiation (due to the high local intensity), whereas the thermocouples deeper in the absorber (>2 cm) show only little measurement error (based on the data given in the section "Sandia Absorber Model", at a depth of 2 cm the error is about 10°C). Therefore, the elements towards the rear of the absorber are believed to give reasonable measurements.

The comparison of absorber temperatures was performed for five test cases (see previous section). First, the measured values were plotted versus the temperature distribution which resulted from the receiver calculation for the inner disk during the simulation of the overall receiver performance. All data for the receiver calculation were averaged over the specific receiver element (i.e., over the inner disk). Thus, it is clear that the calculated numbers represent also some kind of average temperatures. Since the solar flux distribution is quite inhomogeneous and the peak is located near the center where the thermocouples are installed, it is expected that the agreement between measured and calculated temperatures is poor. Nevertheless, the calculated data are included in Figure 33 as "inner disk".

To obtain more realistic data for the absorber center, additional calculations were performed with a simpler receiver configuration with only

Figure 33. Comparison of Measured and Predicted Axial Temperature Distributions for Test 2C.08T, 90 Minutes

one absorber element, representing the situation in the center of the absorber. For the insolation the peak values as determined by the HERMES measurements in the center of the focal spot were used. This procedure led to somewhat higher temperatures thus reducing the discrepancy between measurements and calculations. These results are included in the figure as "center temperatures".

Skocypec et al. [15] propose to decrease the chemical activity of the catalyst by a factor of 8 to improve the agreement between their calculations and the measurements. This proposal is based on the post-test evaluation of the first absorber which showed significant catalyst deactivation. Runs were performed with the catalytic activity reduced to 1/8 the nominal value using the above "simplified" configuration to determine the center temperatures based on peak insolation level. These results are included in the figure as "center temperatures; reduced activity."

There exists another effect which might be very important for the temperature distribution of a volumetric absorber. The mass flow used in previous calculations was based on the assumption of homogeneous mass flux (mass flow per frontal area) for the first absorber insert and on two different but homogeneous mass fluxes in the inner and outer sections of the

second absorber insert, respectively. This assumption holds under conditions with constant fluid properties, but with changes in composition and temperature it is incorrect. As described in Ref. [22], the mass flow distribution over the absorber could be changed by inhomogeneous irradiation. The reason for this effect is the changing flow velocity (due to density changes) and dynamic viscosity of the fluid while passing through the absorber. This results in a variation of pressure drop over the absorber. The pressure drop between front and back is mainly determining the local mass flow, and with a variation of local pressure drop, induced by inhomogeneous irradiation, the local mass flow changes. For a case with operation conditions similar to the CAESAR test conditions, the variation of irradiation distribution onto two absorber zones resulted in a mass flow decrease of about 16% (compared to the case with equal irradiation) in one zone when the irradiation of this zone was increased to 120% of the value of the other zone. The results showed also that the change of mass flow distribution does not only depend on irradiation, but also on the operation conditions of the receiver.

To account for this effect, simulation runs were performed for the center temperatures with the simplified model and the peak insolation data. Various mass flow reductions were tested for their influence on the axial temperature distribution. It was found that with a local mass flux reduction to 70% the nominal value for the inner disk the agreement between measurements and calculation could be improved significantly. These calculations are given in the figure marked as "center temperatures; reduced mass flow."

As an example for the comparison, the axial temperature profiles for the test 2C.08T;90 are shown in Figure 33. For each case considered, fluid and catalyst temperatures are nearly the same for an axial position greater than 2 cm. In this region, the differences between real temperature and thermocouple readings should also be quite small. For the inner disk case (based on irradiation averaged over the entire inner disk) the deviations between simulation and measurements is very drastic. The case center temperatures, based on the irradiation peak in the absorber center, shows slightly higher calculated temperatures, but the deviation to the measurements is still significant. Assuming peak irradiation and a reduced catalyst activity (center temperatures; reduced activity) results in even bigger deviation to the measurements in the rear part of the absorber, compared to the last case. In this case, especially the calculated temperatures in the front part of the absorber are increased. With the assumption of peak irradiation and locally reduced mass flow (center temperatures; reduced mass flow), the agreement between measurement and calculated temperatures is improved significantly. This was the general trend for all performed test comparisons. Although the choice of the reduced mass flow was done arbitrarily, it must be stated that the effect could

explain the discrepancy between measurements and simulation results better than other effects. But of course a detailed evaluation is required to verify the influence of the described effect. For this evaluation, more data are required which are not available so far.

Further development of the simulation model should be supported by continued experimental efforts, especially on the evaluation of absorber properties (radiative, catalytic and fluid dynamic).

Performance Studies

In order to identify the points where improvement is most promising, or to identify critical parameters, a parameter variation was performed. A detailed description of this study is given in Ref. [12]. The "base case" which serves as reference for comparison was based on a simplified geometry as follows: The receiver has an aperture diameter of 600 mm and consists of 5 elements: absorber, ring wall (30 mm wide), window front and back side, aperture (necessary to form the enclosure). The gas mixture ($\text{CO}_2/\text{CH}_4 = 1.1$) enters at ambient temperature through the ring wall, with a mass flow of 0.0424 kg/s and at an absolute pressure of 1 bar. Concentrated solar irradiation is 1 MW/m^2 . The absorber is made of 5 PPI reticulated ceramic foam with 0.4% rhodium loading. This results in a total incident power of $P_{\text{inc}} = 282.7 \text{ kW}$, a receiver efficiency of 79.1%, a chemical efficiency of 55.7% with a methane conversion of 95%. The main loss mechanisms are: 8% due to specular reflection at the window, 4.4% due to diffuse reflection from the absorber, and 7.8% due to diffuse thermal reradiation.

The parameters considered in the performance study were: solar flux density, methane conversion, catalyst activity, absorber pore size and porosity (including multiple layer absorbers), radiative properties of the absorber, convective heat transfer coefficient, feed gas composition and pressure, operation with partial reaction and with a counterflow heat exchanger.

As an example, the influence of solar flux density is shown in Figure 34 (for more information, see Ref. [12]). With a fixed mass flow, there is very little conversion at low solar flux densities, keeping the chemical efficiency low. Nevertheless, the receiver efficiency is high since most of the radiation is transformed into sensible heat of the fluid. With increasing solar flux density, conversion increases almost linearly, until most of the methane is converted. At 1 MW/m^2 , 95% of the feed methane is reacted. When the solar flux density is further increased, the additional energy must be absorbed mainly by sensible gas heating, as indicated by a drastic rise in fluid exit temperature. This results in greater reradiation losses, thus reducing efficiencies. Chemical efficiency shows a peak at about 800 kW/m^2 , corresponding to a conversion level of about 85%. At lower

Figure 34. Influence of Varying Solar Flux Densities on Efficiencies (Mass Flow = 0.0424 kg/s)

flux densities, the energy absorbed as sensible heat in the fluid becomes more important, at higher flux densities the increased thermal reradiation losses reduce the chemical efficiency.

Other important results of the parameter variation are: the variation of methane conversion with constant irradiation does not result in a significant change of efficiencies, as long as the conversion is in a reasonable range (30% to 95%). On the other hand, less conversion means higher mass flow through the receiver, followed by higher losses in the piping and pumps of a complete system.

The variation of the catalyst activity also shows little influence on efficiencies, unless a certain minimum activity is ensured. Lower activity than this minimum value leads to a drastic increase of absorber temperatures, thus reducing efficiencies by higher thermal reradiation losses. The minimum value depends mainly on the operation conditions, and since the catalyst is very expensive, this value is important in terms of cost-effective design of the absorber.

The influence of absorber pore size and porosity depends strongly on the assumptions taken for the interactions between these properties, the catalyst

loading, and the radiative and convective properties. Further research work is required to evaluate these interactions.

Another significant improvement is the addition of a counterflow heat exchanger which utilizes the sensible heat content in the exiting mixture for preheating of the entering gas. A heat exchanger with 90% efficiency improves the chemical efficiency from 55.7% (without heat exchange) to 76.1% while preheating the entering mixture to 780°C.

Further improvement could be achieved by changing the receiver geometry. The use of domed windows can minimize the specular reflection losses, and a cavity-like absorber geometry is expected to result in better performance.

CONCLUSIONS AND RECOMMENDATIONS

The CAESAR tests have successfully demonstrated the concept of solar reforming of methane with carbon dioxide in a commercial-scale direct absorption receiver/reactor on a parabolic dish. The volumetric chemical reactor, consisting of a porous alumina absorber coated with rhodium catalyst, operated successfully during both steady-state and solar transient (cloud passage) conditions.

The focus of this test was to demonstrate "proof-of-concept" and determine global performance such as reactor efficiencies and overall methane conversion. An important and pressing need is to conduct laboratory-scale experiments under relatively well-controlled conditions with sufficient diagnostics so that comparisons can be made with code predictions. Code-validation experiments need to be conducted to provide greater confidence in our predictive capability for larger-scale reactors. This test (and previous tests [23]) were not intended to provide data for code validation.

The absorber is the critical component in a receiver/reactor of this type and its performance is key to the success of the system. In the CAESAR reactor, the performance of the Rh catalyst is encouraging because it promoted the reforming reaction throughout the tests and avoided carbon formation, despite some deactivation due to sintering and possible encapsulation by alumina.

Other aspects of the absorber, however, must be improved to achieve long-term operation and eventual commercialization. Principal among these are:

- absorber matrix characteristics such as:
 - substrate material,

- microstructure (including web surface characteristics and washcoat),
- macrostructure (including pore and web geometry),
- layer thickness, and
- layer separation;
- catalyst crystallite size;
- catalyst loading technique; and
- overall geometry (including the effects of receiver cavity geometry).

Attention should also be given to improving operating conditions such as incident solar flux and reactant gas mass flux distribution over the absorber surface. Likewise, modified operating procedures, particularly during startup, could reduce absorber degradation and improve absorber performance.

Modifications to the receiver design, such as the window (domed window for lower reflection and mounting design), the reactant flow passages, and the addition of a recuperator, could also improve receiver performance. Clearly, the CAESAR tests are only the first step in the development of an optimal receiver/reactor system and commercialization of the technology.

Based on information gained during these experiments, the following recommendations are offered to assist in the next phase of this development:

- Select an absorber substrate material that is more resistant to thermal stress (lower Young's modulus and thermal expansion coefficient) and will reduce catalyst sintering and encapsulation. Partially or fully stabilized zirconia offers the possibility of improved performance in all three respects.
- Investigate different web thicknesses, thinner layers of different pore sizes, elimination of bonding between layers, and other substrate microstructures beside reticulated foams (e.g., fiber matrix), to reduce the effects of thermomechanical stress and to improve mechanical durability.
- Investigate varying the absorber geometry (number of layers and layer thicknesses) and the absorber structure (pore size, porosity, and microstructure) to:
 1. improve thermodynamic behavior of the absorber, for example deeper penetration of solar radiation, which would lower surface temperatures and temperature gradients (and hence reduce radiation losses and thermal stresses), and
 2. adapt the local mass flow to the local irradiation to avoid overheating of the absorber (which contributes to catalyst deactivation and efficiency reduction).
- Investigate the interactions between varying web thickness, pore size, catalyst loading, optical properties, and convective heat transfer.
- Evaluate alternative catalyst loading techniques to improve catalyst dispersion through the absorber, produce smaller crystallites, and

increase surface area (eliminating the need for a washcoat). For example, a thin-film catalyst ion exchange deposition process appears to have good potential to achieve improved loadings.

- Optimize absorber geometry, utilizing the effect of receiver cavity shape on incident solar flux distribution, to provide a suitable distribution over the absorber surface.
- Include a counterflow heat exchanger between the reactant and the product gas streams to improve the chemical efficiency of the system.
- Modify operational procedures to significantly reduce thermal shock and thermal gradients in the absorber (hence thermal stresses) during system startup (going on-sun).

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APPENDIX A

CAESAR Absorber, Receiver, and Dish Photographs

Figure A1. Central Disk of Radially Uniform Absorber Showing the "V" Groove around its Periphery and the Variation in Pore Size (5/10/20 PPI Front to Back - Top to Bottom in Photo)

Figure A2. Outer Ring Piece of Radially Uniform Absorber Showing the "V" Tongue and Groove on Two of its Edges (Front Surface is up in Photo)

Figure A3. Front View of Radially Uniform Absorber Assembled without Fiber Gaskets in Joints Between Pieces

Figure A4. Rear View of Central Disk of Radially Uniform Absorber Showing Thermocouple Holes Drilled in Back Surface

Figure A5. CAESAR Receiver During Assembly

Figure A6. CAESAR Receiver (A) Mounted Inside a Moveable Test Bed on the PAN Dish. The Receiver Aperture is Facing up toward the Reflector Surface, a Portion of which is Visible in the Upper Right Corner of the Photo. Also Visible in the Photo are the Roll-Up Shutter (B) Covering the Receiver Aperture, the Product Gas Exhaust Duct (C), the Box Containing the Gas Analysis System (D), and the OPTILOG Unit (E)

Figure A7. Front of the CAESAR Receiver, as Reflected in the PAN Dish Mirrors, Showing the Aperture (A) Surrounded by a Thermal Protection Plate (B)

Figure A8. CAESAR Receiver on the PAN Dish in a Raised Position (Not On-Sun)

Figure A9. On-Sun Testing of the CAESAR Receiver

Figure A10. Close-Up Photo of CAESAR Receiver During On-Sun Testing

Figure A11. Post-Test Photo of Radially Uniform Absorber Showing Numbering System of the Absorber Pieces.
Post-Test Analyses Were Performed on Specimens Taken from Pieces 6 and 9 (See Appendices E & F)

Figure A12. Post-Test View of Piece #8 of the Radially Uniform Absorber

Figure A13. Post-Test View of Piece #8 of the Radially Uniform Absorber Showing Front Layer Separation and Interior Degradation

APPENDIX B

Gas Supply and Analysis Systems

Gas Storage Facilities

Gas storage facilities were installed by DLR at the PAN site to provide the nitrogen (N_2), carbon dioxide (CO_2), and methane (CH_4) required for the CAESAR tests. The nitrogen was stored in a liquid storage tank (supplier: Messer-Griesheim, type KV 27) with a maximum nitrogen content of 2000 kg. The pressure in the tank was set to 20 bar. After leaving the tank, the liquid N_2 passed through three evaporizer units to ensure that it was all vaporized and near ambient temperature when it entering the gas supply system provided by Sandia.

The CO_2 was also stored as a liquid in a tank (supplier: BUSE, type 1W2300) having a maximum capacity of 2300 kg. The pressure inside the tank, which was determined by the liquid temperature, could not exceed 80 bars. As the liquid evaporated in the tank, CO_2 gas passed out through a back pressure regulator which was set to 17 bars.

The CH_4 feed gas was stored in gaseous form in two sets of high pressure bottles, each consisting of 3 bottles (200 liters, 200 bar max.) connected in parallel. While operating on one set of bottles, the other set could be exchanged without interruption of testing. Before entering the gas supply system, the methane passed through a back pressure regulator set to 17 bar. A separate CH_4 bottle with its own regulator was used for the pilot light on the flare system.

Gas Supply System

The gas supply system is used for controlling and measuring the flow of CO_2 , CH_4 and N_2 to the catalytic matrix in the Catalytically Enhanced Solar Absorption Receiver (CAESAR) experiment. The system consists of shut off and regulating valves for the CO_2 and CH_4 gases, a regulating valve and bypass valve for the N_2 system, along with flow measuring equipment and sample bottles (Figure B1).

Figure B2 shows a pictorial view of the front and back sides of the equipment rack that contains the supply system. The flow meter displays are located at the top of the rack and the nitrogen controls, with on/off switch and pressure gage, in the middle. The control valves for the carbon dioxide and methane gases are located at the bottom-most position. The display units are all in english units: pounds per square inch (psi) for pressure and standard cubic feet per minute (scfm) for the mass flow rate (14.7 psi=1 atmosphere, standard conditions for flow are 25°C and 760 mm Hg(mercury)).

Figure B1. Schematic of Gas Supply, Calibration, and Analysis Systems

Figure B2. Front and Back Views of the Gas Supply Rack

Installation. The gas supply system requires several gas and electrical connections. The air-actuated valves require 24 volts for power and 100 psig (psig=gauge pressure which is absolute pressure + 14.7 psi, in this case 100 psig = 7.8 bar absolute) for operation. The flow meters require 110 volts/60 hertz power. A strip of screw-type wiring connections is mounted at the back of the equipment rack. In addition to the 24 volt power connections, the connections from the flow meters to a data acquisition system are on the same wiring strip. The output from the flow meters is 0 to 5 volts full scale and is linearly proportional to the flow rate.

Gas connections are shown in the back view of Figure B2. The N₂ inlet connection is 25 mm and the CO₂ and CH₄ connections are 12 mm outside diameter. The 100 psig air connection for the valves is 6 mm. All gases discharge through a 25 mm outlet connection at the bottom of the equipment rack. The metric fittings have been installed on all inlet locations, but the outlet fitting was removed for shipping and should be installed before use. It is a compression fitting which requires 1 and 1/4 turns on the nut after a finger tight fit has been achieved. After initial installation, during which the compression fitting is swaged (deformed) on to the tubing, only 1/4 turn after a finger tight fit is required.

On the back side of the rack, near the bottom, 5 gas sample bottles must be installed before applying pressure to the gas supply system. The quick disconnect fittings have a pressure limit of 250 psig (18.2 bar absolute) when no bottle is attached and over 1000 psig (70 bar) when one is attached.

Operation. Before using the gas supply system, 110 and 24 volt power must be turned on and 100 psig air pressure must be supplied to the air-actuated valves. The N₂ electrical switch should be set to OFF, and the shut off valves for all three gases should be off (the white handle should be turned fully clockwise and both shut off valves for CO₂ and CH₄ should point to the right). The on/off switches for the flow meters should be up (on) and displaying zero.

The flow of nitrogen may be started by rotating the white-handled valve counterclockwise until the flow meter shows the desired flow rate. The flow of CO₂ and CH₄ may be started by opening the shut off valves (rotating them 1/4 turn counterclockwise (pointing up)) and rotating the regulating valves counterclockwise until the desired flow is obtained.

If the full flow of nitrogen is desired, turning the N₂ electrical switch ON will open the bypass valve and close the CH₄ valve. The flow of CO₂ will not be affected. Turning the switch OFF returns the system to normal operation.

Disconnecting the Gas Supply System. It is possible to trap high pressure gas in the piping of the gas supply system. Before disconnecting the inlet piping, be sure to open the regulating valves (N₂, CO₂, and CH₄) and cycle the shut off valves and air-actuated valve for CH₄.

Calibration Data. Copies of the calibration sheets for the flow meters were provided for the tests. The "Output Voltage" is the value that would be recorded by the data acquisition system for the given flow rate.

2 of 2

Gas Calibration and Analysis Systems

Two important components of the CAESAR support equipment are the gas calibration system and the gas analysis system. Schematics of these systems are shown in Figure B1. The gas calibration system is used to supply calibration gases to the infrared gas analyzer and to display the output of the analyzer during the daily calibration. The gas analysis system is used to monitor the concentrations of CH_4 , CO, and CO_2 in the exhaust gases from the CAESAR experiment.

Gas Calibration System. The gas calibration equipment is mounted in a mobile equipment rack which, during the calibration process, is positioned close to the metal box containing the gas analysis system mounted behind the receiver (see Figure 10). The layout and function of the equipment is straightforward. The panel meters that display the output from the gas analysis system are mounted next to each other near the top of the rack. Below them are located the flow meter, for controlling the flow of gas into the gas analysis system, a pressure gauge, and two valves: one for shutting off flow into the system and the other for selecting the particular gas for calibration. Connections between the gas bottles and the calibration system are made through 6 mm (outer diameter) Swagelock fittings at the back of the equipment rack. No electrical power is required.

Everyday, it is necessary to check the calibration of the infrared gas analyzer in the gas analysis system. First, connections between the calibration system and the analysis system are made using the electrical cable and gas tubing mounted in the back of the calibration equipment rack. These attach to the front panel in the gas analysis system. The gases used for calibration should have their bottle pressure regulators adjusted to less than 30 psig (3 bar absolute). After turning the Gas Selection valve to nitrogen, the flow valve is opened and the flow meter adjusted to read 50 or less. After the infrared gas analyzer is adjusted to read zero, the span of each channel is adjusted using the appropriate gas.

Gas Analysis System. The layout of the gas analysis system is shown in Figure B3. The principle components include: the infrared gas analyzer, main sample pump, vacuum pump, solenoids, sample bottles, dryers, filter, fan and strip heater. The pressure and vacuum levels are adjusted using metering valves and 2 pressure gauges. The front panel controls include: a connector for the calibration system panel meters, a quick-disconnect for the calibration gas tubing, a 3-way valve for controlling whether the gas to the gas analyzer comes from the calibration system or the main sample pump, 3-way and 4-way valves for supplying pressure or vacuum to the sample bottles, and switches for controlling power to the strip heater, gas analyzer, pumps, or fan, respectively.

The aluminum box that contains the analysis equipment has 12 holes drilled on the side and bottom at both ends. The hole diameters should allow the use of 12 mm diameter bolts for attaching the container to the framework. The container should be supported on the bottom, not just the side, and at both ends. The orientation of the aluminum box should be such that the end that contains the fan is toward the ground during operation. This affords the

CAESAR Gas Sampling System Layout

Sandia National Laboratories
Manufactured, Rev. March 8-82

Figure B3. Layout of Gas Analysis System

best protection against water intrusion. The analysis system must be covered when not in use as it is not water proof.

Outside connections to the gas analysis system include: the gas sample connection (6 mm outer diameter tubing), the thermocouple connection (type K, next to the gas sample inlet), 110 volt/60 hz power, analyzer output lines (0 to 1 volt), solenoid control lines (24 volt).

For the daily calibration, the electrical and gas connections are made to the gas calibration system, the 3 way valve turned to the "Calibrate" position, and the gas analyzer turned on. After the analyzer has warmed up for 15 minutes, the zero gas should be selected from the calibration system front panel. The zero adjustment is made using a flat-bladed screw driver with the zero control on the front of the gas analyzer. It may be necessary to remove several sample bottles for easy access to the controls. After each of the channels (CH_4 , CO, and CO_2) has been adjusted for zero, the span control should be checked by selecting the appropriate gas using the calibration system and observing the output of the gas analyzer on the panel meters.

If the analyzer shows little drift from day to day, it is possible to use the calibration switch on the front panel of the gas analyzer to check the span. Basically, the calibration switch causes a neutral density filter to move into the light path between the light source and the photo detector. The panel meters have been calibrated to display the proper span reading for the given output voltage when the filter is in place. If the panel meters show the proper value when the calibration switch is pressed, the electronics of the gas analyzer are probably close to being properly adjusted.

It is important to note that the panel meters themselves can drift from their proper calibration point and the overall calibration of the panel meters and gas analyzer should be checked periodically. To do this, a voltmeter should be connected to the output of the gas analyzer. As each gas is fed through the analyzer, the span should be adjusted so that the voltmeter shows 1 volt output. The panel meter should be checked and adjusted so that it displays the proper maximum value.

Conditions in Albuquerque, New Mexico, were warm and dry at the time of this writing, so it was not possible to check the effects of cold weather or moisture on the performance of the gas analyzer. Under wetter, colder conditions and when large temperature changes occur, it is expected that the gas analyzer will drift. Its sensitivity to those conditions will have to be determined in Germany.

Prior to testing, the main sample pump may be used to pull the pressure in the sample bottles down to 20 to 25 in. Hg. This is done by turning two valves to "Vacuum" and turning on the sample pump (the position of the remaining valve on the front panel is unimportant). Each bottle is evacuated by either activating each solenoid for several seconds (watch the pressure/vacuum gauge) or by manually opening each solenoid by using pliers on the manual bypass switch.

For operation, the valves are turned to "Run" and "Pressure", the calibration cable and tubing should be disconnected, and the switches labelled "IR", "Pumps", and "Fan" put in the up position. The pressure/vacuum gauge should read between 30 and 40 psig, and the vacuum gauge should show approximately 5 in. Hg. The metering valve that controls the flow of sample into the analyzer should be adjusted so that only a very low flow rate of gas (1 to 2 liters per minute) is possible.

At the end of the test period, power should be turned off to the gas analysis box, and the sample bottles removed for analysis. Overnight, the heater should be turned on to prevent condensation.

Some operating limits exist for the equipment in the gas analysis system. The temperature limits for the pumps, fan and gas analyzer are approximately 40° F (4° C) and 100° F (38° C). The heater is only 500 Watts and is not sufficient to keep the system warm when the fan is running. The maximum pressure for the main sample pump is 58 psig for continuous operation so it is necessary to check the pressure/vacuum gauge periodically.

If enough hydrogen leaks into the gas analysis box, a detonation could take place. The fan must be operating when the box is in use to insure that no buildup of hydrogen takes place.

APPENDIX C

Instrumentation and Measurement Uncertainties

Instrumentation

The instrumentation was selected to provide information on the global performance (methane conversion and efficiencies) of the receiver/reactor. The CH₄ and CO₂ feed gas flow rates were measured using Kurz mass flow meters (accurate to $\pm 2.25\%$ of the measured values) located in the gas supply system (see Appendix B). The product gas was sampled continuously through a water-cooled probe mounted in the exhaust duct sufficiently far downstream of the receiver exit to ensure that the gas was well mixed and the sample represented an area-averaged product composition. After filtering and drying, the sample stream passed through an Anarad infrared three-gas analyzer that provided continuous measurement of the CH₄, CO₂, and CO concentrations. Samples of both feed and product gases were periodically collected and analyzed using a gas chromatograph (accurate to $\pm 3\%$).

Absorber temperatures were measured using fifteen 1/16 in. diameter, stainless-steel sheathed, type K thermocouples inserted into holes drilled in the back of the absorbers at various radial-azimuthal ($r-\theta$) locations and at six axial (z) locations (see Figures 8 and 9).

Temperatures of the product gases were measured at two locations: just downstream of the absorber and at the exit of the receiver (see Figure 1). The former were measured using a cross-array of twenty-one 0.1-mm dia., unsheathed, Pt/Rh thermocouples mounted in a silica fabric net located 0.5 cm behind the absorber. Temperatures of the mixed product gases leaving the receiver were measured by a cross-array of 5 shielded, 1.5-mm dia., sheathed, Pt/Rh thermocouples mounted behind the mixing element. The stated accuracy of these thermocouples is $\pm 0.25\%$.

Measurement Uncertainties

To assess the uncertainty of the measured data, consideration must be given to both the accuracy of the instrument (previously stated) and the conditions under which the measurements were made. Experience in calibrating the IR analyzer suggested that the actual uncertainty was greater than anticipated. Appreciable drift in the zero settings (and to a lesser degree in the span settings) was noted from one calibration to the next, especially for the CO₂ sensor. Based on several calibrations, errors ranged up to approximately 8% and were random in nature. Furthermore, poor performance of the gas dryers in the sample conditioning line introduced additional uncertainties of unknown magnitude.

Since the HERMES measurements were made after the tests were completed, and the receiver removed from the dish, differences between target positions and actual receiver locations introduce additional uncertainties. Lateral

shifts of the receiver of 2-4 cm caused changes in absorber temperatures of 200-300°C as a result of the sharp peaks in the flux distribution (see Figure 7).

Because of the reticulated nature of the porous absorber, large radiative fluxes, and noncatalytic thermocouples, the measured absorber temperatures may be significantly higher than the solid matrix or gas temperatures. This phenomenon has been examined in detail using the Sandia absorber numerical model (see section on the comparison of model predictions with axial temperature distributions). The thermocouple measurement at the most forward location ($z = 0.7$ cm) is approximately 70-130°C above the solid temperatures. This difference is negligible for the remaining thermocouples, so the uncertainty in these data approaches the quoted accuracy of the sensors. The uncertainty in the product gas temperatures, which are the most accurate data obtained during the tests, is expected to be close to the quoted accuracy of the thermocouples. Because Pt and Rh are catalysts, data from the product gas thermocouples could be affected by any heterogeneous chemical reactions that might occur. However, since the product gas is essentially at equilibrium as it leaves the absorber, this effect is believed to be negligible.

Other factors which undoubtedly introduced uncertainties in the absorber temperatures and product gas measurements are azimuthal and radial variations in the gas mass flux entering the absorber, deactivation of the catalyst with time, and discoloration of the front surface of the absorber (and its effect on optical properties and catalyst activity).

APPENDIX D

CAESAR Test Data

Table D-I: Overview of all CAESAR Tests in 1989

EXT	SCAN	DATE	COV	POS.	INSOL	TMAX	NCH4	NP	REMARKS
0A.B01	(250+	08/06 14:14	-	-	-	-	-	6	DELAY TIME TEST
0A.B02	(369	08/06 15:13	-	-	-	-	-	10	FLOW TESTING
0C.B02	(		-	-	-	-	-		NO DESCRIPTION
0C.B03	(?	05/07 8:35	-	-	-	-	-		NO DESCRIPTION
0C.B07	(?	20/07 15:41	-	-	-	-	-		CONTROL FOR 1K.B03
0C.B08		? 17/08 11:..	-	-	-	-	-		INSTRUMENT CHECK
0C.B09		? 17/08 11:45	-	-	-	-	-		INSTRUMENT CHECK
0C.B10		? 17/08 12:35	-	-	-	-	-		INSTRUMENT CHECK

1E.B01 *	? 30/05	13:..	-	13.22				0	DISH CONTROL
PROBLEMS									
1E.B02 *	152	30/05 13:25	-	13.22			0		DISH TEST
1E.B03 *	190	30/05 13:54	-	13.40	560		0		CLOUDY
1F.B01 *	145+	30/05 14:37	-	13.40	670		0		CLOUDY
1F.B02	(136+	30/05 15:08	-	13.40			0		DISTURB. TEST
1G.B01 *	165	14/06 10:33	-	13.29	750		0		CLOUDY
1G.B02 *	82	14/06 10:53	-	13.41			0		CLOUDY
1G.B03 *	165	14/06 11:07	-	13.41			0		CLOUDY
1H.B01 *	58	14/06 11:38	-	13.50			0		CLOUDY
1H.B02	(200	14/06 12:13	-	13.50			0		PYROMETER CHECK
1H.B03 *	66	15/06 15:08	-	13.60			0		CLOUDY
1H.B04	(300+	16/06 10:00	-	13.60			0		
1H.B05	(172	19/06 09:10	-	13.60		1000+	0		

BEGIN OF REACTION TESTS									
1I.B01	(410	19/06 11:23	-	13.40				4	N2/CO2/CH4TEST
1J.B01	(589+	27/06 10:52	-	13.40				11	N2-->0, IR-PROBLEMS
1J.B02	(373	05/07 13:15	-	13.40					N2MIN = 50SCFM
1J.B03	(430	06/07 10:13	-	13.40	500	520	24	6	N2 = 0
1K.B01	(447	06/07 15:20	-	13.40	600	500	22	4	FLOW STEPS
1K.B02 *	48+	20/07 14:40	-	13.40					CONTROL PROBLEMS
1K.B03	(308+	20/07 ..:..	-	13.40	830	500	28	3	N2 = 0
1K.B04	(473	21/07 10:47	-	13.40	820	500	24	7	
1L.B03	34+	11/08 10:59	1L.D03	13.60			0		COVER TEST
1L.B04	52	11/08 11:35	1L.D04	13.60			0		COVER TEST
1L.B05			1L.D05				0		COVER TEST
1L.B06									NO DESCRIPTION
1L.B08	47+	15/08 10:34					0		
1L.B09	149+	15/08 11:40					0		
1L.B11	(340	15/08 13:25			800		25	5	COVER TEST, UNSTEADY
1L.B15				13.40					COVER TEST
1L.B16				13.60					COVER TEST
1L.B17		14:38	1L.D17	13.50					COVER TEST

1L.B18			14.50	1L.D17	13.40					COVER TEST
1L.B19				1L.D17	13.60					COVER TEST
1L.B20		18/08 10:06		NO COV	13.50					COVER TEST
1L.B21		18/08		1L.D21						COVER TEST
1L.B22	118+	18/08 11:00		1L.D22	13.50					COVER TEST
1L.B23	105	18/08 13:30		1L.D22						COVER TEST
1L.B25	173+	24/08 10:30			13.50					COVER TEST
1L.B26	80+	24/08 11:00			13.60					COVER TEST
1L.B27	* 72	24/08			13.50					IR-PROBLEMS
1L.B28	* 385	24/08 13:15			13.50	650	450	20		UNSTEADY
1L.B29	*138+	24/08 14:53			13.50	700		23		W.-COOLER TEST
1L.B30	(113+	24/08 15:20			13.50	700	500	20		
1L.B31	* 99	30/08 11:30	1L.D31	13.50						COVER TEST
1L.B32	* 80	30/08 12:00	1L.D32	13.50						COVER TEST
1L.B33	/ 372	31/08 13:30		13.50	850	560	38	4		COVER TEST
1L.B34	/ 540	31/08 14:00		13.50	820	580	37	4		COVER TEST
1L.B35	(166	31/08 15:15		13.50	800	580	37			COVER TEST
1L.B36	173	07/09 11:30	1L.D36							COVER TEST
1L.B37	(162	07/09 13:30	1L.D36		700	500	36	1		COVER TEST
1L.B38	(140	07/09 14:00	1L.D36		700	510	34			COVER TEST
1L.B39	(128+	07/09 14:50			700	580	34	1		COVER TEST
----- 09/11/90: EXCHANGE OF WINDOW SEALING AFTER DESTRUCTION -----										
1L.B42	/ 400	18/09 14:00	1L.D42	13.50	700	620	34	2		COVER TEST
1L.B44	/ 563	15:20	1L.D42		620	660	39	2		COVER TEST
1M.B01	/ 593	20/09 12:50	1M.D01	13.50	600	610	36	0		CLOUD TRANSIENTS
----- BEGIN OF TESTS WITH SECOND INSERT -----										
EXT	SCAN	DATE	COV	POS.	INSOL	TMAX	NCH4	NP		REMARKS
2A.B01	* 294	16/10 11:00	2A.D01		820	590	37	2		SHORT, UNSTEADY
2B.B01	* 94	16/10 11:45	2A.D01	13.50				0		
2B.B02	* 287	16/10 12:45	2B.D02	13.50	750	550	34	2		SHORT, UNSTEADY
2C.B01	(547	17/10		13.40	800	580	37	4		TRANSIENTS
2C.B02	* 336	18/10 10:45		13.35	600	560	38	0		CLOUDY
2C.B03	* 133	18/10 11:30		13.60	600	490		0		POSITION CHANGED
2C.B04	(339	18/10 13:00	2C.D04	13.55	800	600	34	2		CLOUDS
2C.B05	* 304	23/10 10:40	2C.D05	13.40	600	500	0	0		PURE N2
2C.B06	* 549	23/10 11:00	2C.D06	13.34	700	580	37	2		HAZY
2C.B07	* 510	23/10 CONTI	2C.D06	13.34	700	600	33	2		HAZY
2C.B08T	/1301	25/10 11:30	2C.D08	13.40	550	670	38	5		GOOD TEST
2C.B11	(399	27/10		13.40	600	570	34	0		SHORT, FLOW VAR
2C.B12	(274	27/10	2C.D12	13.40	600	590	35	0		SHORT
2C.B13T	/ 731		2C.D13		600	650	36	2		GOOD TEST
2C.B15T	/1112	10/11 11:30	2C.D15		750	630	41	0		GOOD TEST
2C.B17T	/1305	17/11 11:45	2C.D17	13.40	800	670	42	3		GOOD TEST
----- CONTINUATION OF TESTS WITH SECOND INSERT (SECOND TEST PHASE) -----										
EXT	SCAN	DATE	COV	POS.	INSOL	TMAX	NCH4	NP		REMARKS
3A.B20T	774	22/10 ??:??	?	13.50	870	550	22	?		HIGH FLOWRATE
3A.B22		22/10		13.40	850	540	23	?		
3A.B23T	200	23/10		13.60				?		
3A.B26T	740	23/10		13.30	850	570	22	?		
3A.B28T	858	24/10		13.55	700	580	24	?		
3A.B30		24/10		13.50	650	530	22	?		
3A.B31T	519	??:??		13.65	+550	480	23	?		
3A.B33		26/11	3A.D33	CHNGD	+750	510	28	?		WINDOW CRACK?

3A.B34T	1734	27/11	3A.D34	CHNGD	700	670	32	?	
3A.B37T	1153	CONTI	3A.D34	CHNGD	650	680	34	?	END OF 3A.B34T
3A.B40T	808	30/11 12:40			750	590	30	?	
3A.B42T	1412	05/12 10:20			750	630	32	?	

DESCRIPTION OF COLUMNS:

EXT: EXTENSION OF THE DATA FILE (2C.B10 MEANS THE FILE 'CAESAR2C B10'

SCAN: TOTAL NUMBER OF SCANS IN THAT FILE

DATE: DATE OF TEST, DAY/MONTH HH:MIN (TESTS 1..&2...:1989; 3...: 1990)

COV: (- MEANS NO COVERS ON THE DISH, A NUMBER MEANS A COVERED DISH)

POS: FOCAL DISTANCE (M)

INSOL: AVERAGE INSOLATION LEVEL (W/M2)

TMAX: MAX. EXIT(!) TEMPERATURE (CENTIGRADES)

NCH4: CO-FRACTION IN IR-READING (%), 0 MEANS ONLY N2-FLOW

NP: NUMBER OF GAS-CHROMATOGRAPHY SAMPLES TAKEN

REMARKS: GENERAL REMARKS

+: MEANS 'MORE THAN'

+ -: MEANS 'UNSTABLE CONDITIONS'

CONTI: MEANS THAT THE PREVIOUS TEST IS CONTINUED

MARKS IN COLUMN 8: | --> DATA FILE IS NOT AVAILABLE ON VM-SYSTEM

{ --> DATA FILE IS AVAILABLE ON VM-SYSTEM

/ --> DATA FILE IS WORTH BEING EVALUATED AND
AVAILABLE ON VM-SYSTEM

* --> DATA FILE IS NOT WORTH BEING EVALUATED

UNDERLINE: DENOTES TESTS SELECTED FOR FURTHER ANALYSIS

Table D-II: Measured Data and Calculated Performance Parameters for the Nine Test Times Analyzed

	Radially Uniform Absorber						Radially Nonuniform Absorber		
test time (min)	11.B33 22	11.B34 40	11.B42 16	11.B42 27	11.B44 25	11.B44 39	2C.B08 90	2C.B13 40	2C.B17 60
insolation (W/m ²)	850	820	700	680	620	590	530	600	800
INLET DATA									
CO ₂ -flow (scfm)	35.9	27.0	12.9	10.4	9.9	6.8	10.4	13.0	17.8
CH ₄ -flow (scfm)	32.3	24.6	11.6	9.2	8.9	5.3	9.2	9.7	17.1
GC-analysis (%) CO ₂	51.0	-	57.5	-	-	-	-	-	51.7
CH ₄	49.0	-	42.5	-	-	-	-	-	48.3
CO ₂ /CH ₄ -ratio	1.11	1.10	1.11	1.13	1.11	1.28	1.13	1.34	1.04
EXIT DATA									
mean temperature (°C)	550	590	550	630	620	660	660	650	640
IR-analysis CO ₂	26.5	22.5	19.0	17.9	15.0	15.2	8.2	8.0	20.1
(%) CH ₄	24.0	19.7	15.7	13.6	12.9	8.9	8.2	6.8	15.7
CO	32.6	33.6	34.0	34.7	35.0	36.5	37.6	36.1	39.3
GC-analysis CO ₂	-	-	-	-	-	-	-	-	14.4
(%) CH ₄	-	-	-	-	-	-	-	-	15.8
CO	-	-	-	-	-	-	-	-	37.8
H ₂	-	-	-	-	-	-	-	-	32.0
correction method	IR-zero	IR-zero	GC	GC	GC	GC	GC	GC	GC
CO ₂	21.8	20.6	20.0	19.5	17.2	17.5	11.8	16.0	14.0
calculated CH ₄	21.6	18.3	17.9	16.5	15.3	11.5	9.7	8.4	15.4
composition CO	29.6	31.1	31.9	32.7	34.7	36.6	40.1	38.6	36.8
(%) H ₂	2.7	1.2	1.8	1.4	1.9	2.2	1.8	1.7	2.9
H ₂ O	24.3	28.8	28.3	29.9	30.8	32.1	36.5	35.1	31.0
POWER DATA									
incident power (kW)	115.7	105.7	88.8	86.3	78.7	74.8	64.1	72.1	97.3
sensible heat (kW)	36.3	30.2	13.2	12.5	11.8	8.2	13.5	15.2	22.8
reforming reaction (kW)	60.6	52.9	25.3	21.5	22.0	15.2	29.2	31.8	42.9
watergas reaction (kW)	2.0	0.7	0.5	0.3	0.4	0.3	0.5	0.5	1.2
total absorbed power (kW)	98.9	83.8	39.0	34.3	34.2	23.7	43.2	47.5	66.9
receiver efficiency (%)	85.6	79.3	44.0	39.7	43.8	31.7	67.3	65.9	68.7
chemical efficiency (%)	54.4	50.7	29.0	25.2	28.5	20.8	46.3	44.9	45.3
methane conversion (%)	39.1	45.9	45.6	48.8	51.6	60.0	66.0	68.5	52.4

Comments to the Test Data Tables

- receiver efficiency:

$$\eta_{rec} = \frac{\text{power absorbed as heat and by reactions}}{\text{solar radiation through aperture}} \quad (1)$$

- chemical efficiency:

$$\eta_{chem} = \frac{\text{power absorbed by reactions}}{\text{solar radiation through aperture}} \quad (2)$$

- methane conversion:

$$\chi_{CHA} = \frac{\text{amount of methane flow which is reformed}}{\text{total methane flow in feed gas}} \quad (3)$$

- CO₂/CH₄-ratio based on flow meter data
- mean temperature: average temperature of 5 thermocouples in the exit
- GC data included if available, otherwise a '-' is given
- correction method:
 - IR-zero: the IR-readings were corrected for the offset obtained with pure nitrogen flow
 - GC: the IR-readings were corrected for a gas chromatography sample taken short before or after the evaluation time
 - calculated composition: the exit composition was evaluated based on inlet composition and the corrected exit contents with a mass balance

APPENDIX E

Radially Uniform Absorber Substrate Post-Test Analysis

date: June 3, 1991

To: J. F. Muir, 7313

From: S. Jill Glass, 1845

Subject: Post-test Analyses of CAESAR Absorber No. 1.
Update on 2-6-91 memo.

This memo is the final version of the combined contents of two previous memos (Aug. 10 and Oct. 11, 1990) and summarizes post-test (solar tests) analyses of CAESAR absorber no. 1. Data for CAESAR absorber no. 1 were compared to data collected for untested spare piece B. Because of extensive cracking damage observed in CAESAR absorber no. 1 after solar testing, analyses focused on the mechanical integrity of the absorber. Scanning electron microscopy (SEM) and x-ray diffraction (XRD) were also conducted to ascertain whether there had been chemical, microstructural or phase (crystal structure) changes during solar testing that may have contributed to the cracking of the absorber.

Strength tests show statistically significant differences between strut strengths of the three layers of the absorber, and within different regions of individual layers of the absorber, but not between the solar-tested and untested material. This last result is contrary to expectations because, qualitatively, it appeared that the tested absorber had severely degraded in strength. The strength tests appear to have been inadequate for detecting these differences. According to the manufacturer (Hi-Tech Ceramics, Inc.), the starting material consists of α -alumina (92%) and mullite (8%) over which a wash-coat of γ -alumina is applied. X-ray diffraction indicates, however, that there probably is very little, or no γ -alumina in the washcoat. This may have a detrimental effect on the catalytic performance of the absorber.

Strength Characterization

CAESAR absorber no. 1 cracked extensively during solar testing as shown in the schematic in Figure E1. It also appeared, qualitatively, that the material, even in uncracked regions, had degraded in some manner and had a lower toughness than the untested material of spare piece B. This conclusion was based on the ease with which the struts of individual cells in the tested material could be broken with a fingernail. This apparent reduction in toughness made it difficult to handle pieces of the absorber without

CAESAR Absorber no 1.

Figure E1. Schematic of the Crack Pattern Observed on CAESAR Absorber No. 1 after Solar Testing

causing further damage. Strength tests, consisting of a comparison of the strength of the porous alumina in the three layers that make up the absorber disc, before and after solar testing, were conducted to confirm whether the toughness had decreased.

One explanation for the extensive cracking and strength degradation of the absorber was that it was exposed to excessive stresses during solar testing that led to the development of microcracks. Microcracks were observed on solar tested pieces of the absorber. These microcracks subsequently grew and/or linked with other microcracks to become macrocracks. Another explanation is that the absorber was initially tough enough to resist cracking under the applied thermal stresses; however, during solar testing it underwent degradation that reduced its toughness and thus made it susceptible to failure under the applied thermal stresses. Another possibility is that the absorber was exposed to excessive stresses and it underwent a chemical degradation that further reduced its toughness and its ability to resist cracking.

Thermal stresses existed in the absorber because of temperature differences in both the axial and radial directions. Temperature differences arise because the heat source is on one face and because there are areas of the absorber shielded from the heat (i.e., the rim and the backside of the absorber). Axial and radial temperature differences as high as 170°C and 440°C, respectively were measured.¹ Bulk thermal stresses, σ_{thermal} , can be estimated using the following equation and literature values of the appropriate parameters.

$$\sigma_{\text{thermal}} = \frac{E\alpha\Delta T}{(1 - \nu)} \quad (1)$$

where

E	=	Young's modulus or stiffness (3-6 GPa)
α	=	thermal expansion coefficient (6-7x10 ⁻⁶ in/in°C or m/m°C)
ΔT	=	temperature difference (°C)
ν	=	Poisson's ratio (0.25)

When σ_{thermal} exceeds the bulk failure strength,² σ_{failure} , the material cracks. Since the bulk failure strength of the alumina/mullite material is in the range of 2-3 MPa (290-434 psi),³ the highest bulk thermal stress the disc can experience without cracking is less than 2-3 MPa. The above equation was solved for σ_{thermal} using the measured temperature differences and the highest values of the other equation parameters. Thermal stresses in

1. J. F. Muir, R. E. Hogan, Jr., R. D. Skocypec and R. Buck, "Solar Reforming of Methane in a Direct Absorption Catalytic Reactor on a Parabolic Dish: I - Test and Analysis," 1991 ASME-JSME International Solar Energy Conference, Reno, Nevada (March 17-22, 1991).
2. Bulk strength is defined in terms of the stress required to initiate and propagate a crack through a macro-section of the material.
3. R. Brezny and D. J. Green, "Fracture Behavior of Open-Cell Ceramics," J. Am. Ceram. Soc., 72 [7] 1145-52 (1989).

the range of 10-25 MPa were calculated, which definitely exceed the bulk failure stress of the absorber material.

It should be noted that the bulk strengths used above were for specimens that contained no flaws other than the natural processing flaws (e.g., strut porosity, struts broken during handling, etc.). The absorber had many holes drilled into it and these appear to have acted as flaws that are much larger than the natural flaws. The expression, "appear to act as flaws," is used because much of the cracking appeared to have initiated at thermocouple holes; however, normally, for a flaw to act as a crack-initiating flaw, it must be a stress concentrator. Because the porous absorber material already contains numerous pores or holes with geometries similar to that of a thermocouple hole, these should give rise to the same stress concentration as a thermocouple hole. It is possible, during drilling of the thermocouple holes, that struts adjacent to the drilled thermocouple holes were cracked, or that macrocracks (cracks that ran through a series of struts) developed around the thermocouple hole. These flaws may have acted as the stress concentrators necessary for cracking.

The larger the stress-concentrating flaw, the weaker the body as demonstrated in the following equation

$$\sigma = \frac{K_{IC}}{Y\sqrt{\pi c}} \quad (2)$$

where K_{IC} = fracture toughness (MPa $\sqrt{m}$)
 σ = fracture strength (MPa)
 Y = geometrical constant
 c = flaw size (m)

If the fracture toughness remains constant, the strength will be lower for a body containing a larger stress-concentrating flaw. The intrinsic flaw size of cellular ceramic materials is on the order of the pore or cell size, which in the absorber is 1/5", 1/10" or 1/20", depending of whether the piece is 5, 10 or 20 pores per linear inch (PPI) respectively. If thermocouple holes act as stress-concentrating flaws, and these flaws are much larger than the intrinsic flaws, the strength will be greatly reduced from that of a body without thermocouple holes. For example if the thermocouple hole flaw size is four times the cell size, the strength will be halved.

If the fracture toughness, K_{IC} , has been reduced due to chemical or microstructural changes, the material will also be weaker (Equation 2). To determine whether the toughness was reduced during solar testing, strengths of untested spare piece B and solar-tested piece no. 9 were compared. Bulk strength measurements of this material are difficult because they require relatively large specimens with specific geometries. Since it has been shown both theoretically and experimentally that bulk strength scales with the strength of the struts which make up the individual cells,⁴ strength comparisons were conducted using strut strengths. Individual struts of 5 PPI as-received 92% α -Al₂O₃ can be seen in Figure E2.

4. R. Brezny, D. J. Green and C. Q. Dam, "Evaluation of Strut Strength in Open-Cell Ceramics," J. Am. Ceram. Soc., 72 [6] 885-889 (1989).

Figure E2. Optical Micrograph Showing the Individual Struts that Make Up the Absorber. Magnification = 6X

Strut strength has also been shown to be largely independent of cell size (as described by the number of pores per inch, PPI) and density. The absorber is composed of three separate layers. The first layer (the face of the absorber exposed to the sun) is 5 PPI, the second is 10 PPI and the third is 20 PPI. Note that although the strength of a strut may be independent of its size (strength is load per unit area required to cause failure) the load to break an individual strut will decrease with strut diameter. Hence, the individual struts that make up the pieces of the absorber with larger PPI (smaller cell size) may be damaged more easily during handling, leading to a greater degradation in the bulk strength of that particular layer.

Strut strength was determined by attaching a wire to a strut, measuring the strut dimensions and then pulling the wire and measuring the load required to break the strut. The following equation was used to calculate strut strength, σ_{ft} , from the breaking load and sample dimensions:⁵

$$\sigma_{ft} = \frac{36PLD}{9\pi D^4 - 16bh^3} \quad (3)$$

where P = fracture load (N)
 L = strut length (m)
 D = strut diameter (m)
 b = base of triangular hole within the strut (m)
 h = height of the triangular hole within the strut (m)

5. R. Brezny, D. J. Green and C. Q. Dam, "Evaluation of Strut Strength in Open-Cell Ceramics," J. Am. Ceram. Soc., 72 [6] 885-889 (1989).

The triangular hole dimensions, b and h , were assumed to be constant and a literature value of $150\text{ }\mu\text{m}$, for the same material with a similar density and cell size, was used.⁶ Considerable estimation occurs when strut dimensions are measured and the combined errors can lead to errors in the strut strength as high as 50%.

Comparisons of strut strengths between the same regions of untested spare piece B and piece no. 9 (central section of 9-section disc expected to be representative of solar-tested material) were made to test for a strength reduction due to solar testing. Because of the differences in processing and exposure various parts of the absorber received, the decision was made to compare tested and untested materials from several locations. For example, the sides of layers were fracture surfaces, whereas the top and bottom of layers were fabricated surfaces. Also extra material was deliberately added to the struts on the outer faces of the first and third layers to increase the strut damage resistance.

Extra material added to some regions made it impossible to test the struts on the bottom of the third layer (20 PPI) because struts were too close together to allow a wire to be threaded around them. It also was impossible to test the top of the second layer for spare piece B because it was still firmly attached to the bottom of the first layer. Similarly, it was not possible to test the bottoms of the second layer of spare piece B and piece no. 9, because they were also still attached to the top of the third layer.

The average strut strength, strut strength standard deviation and the number of struts tested for each sample are shown in Table E-I. Generally twenty or more struts were broken for each specimen; however, fewer data were obtained for the sides of the second and third layers of piece no. 9, because many of the selected struts broke during handling prior to the strength tests.

A schematic of the three layers of the absorber, along with the strut strengths measured on the top, side and bottom of each layer is shown in Figure E3.

Statistical comparisons were made of the mean strut strengths within specimens (to show which layers had experienced the most damage) and between specimens (to see if the strength had degraded due to solar testing). Using $\alpha=0.05$ as the level of significance for a student's t-test it was found that there were significant difference in the means of the strengths between the following strength test samples (numbered according to Table EI).

1 and 2	(B, top 1st layer and B, side 1st layer)
3 and 4	(B, side 2nd layer and B, side 3rd layer)
5 and 6	(9, top 1st layer and 9, side 1st layer)
5 and 7	(9, top 1st layer and 9, bottom 1st layer)
5 and 8	(9, top 1st layer and 9, top 2nd layer)

6. R. Brezny and D. J. Green, "Fracture Behavior of Open-Cell Ceramics," J. Am. Ceram. Soc., 72 [7] 1145-52 (1989).

Table E-I: Strut strength data

Sample, region tested, and no. of pores per inch	Mean strut strength (MPa)	Standard dev. (MPa)	No. of struts tested
1. B, top 1st, 5 ppi	107	61	24
2. B, side 1st, 5	12	14	22*
3. B, side 2nd, 10	14	18	25
4. B, side 3rd, 20	35	46	21
5. 9, top 1st, 5	79	44	25
6. 9, side 1st, 5	43	33	19
7. 9, bottom 1st, 5	21	18	17
8. 9, top 2nd, 10	20	23	19
9. 9, side 2nd, 10	14	13	13**
10. 9, side 3rd, 20	16	9	4**

* Data is suspect due to some discrepancies and will not be used for statistical comparisons.

** Too few data for statistical comparisons.

Spare Piece B

1st layer	top=	107±61 MPa
5 ppi	side=	12±14*
	bottom=	

XXXXXXXXXXXXXXXXXXXXXXXXXXXX

2nd layer	top=	
10 ppi	side=	14±18
	bottom=	

XXXXXXXXXXXXXXXXXXXXXXXXXXXX

3rd layer	top=	
20 ppi	side=	35±46
	bottom=	

Piece No. 9 of Solar Absorber No. 1

1st layer	top=	79±44
5 ppi	side=	43±33
	bottom=	21±18

2nd layer	top=	20±23
10 ppi	side=	14±13**
	bottom=	

XXXXXXXXXXXXXXXXXXXXXXXXXXXX

3rd layer	top=	
20 ppi	side=	16±9**
	bottom=	

Note: XXXX designates that these layers are joined; *** designates that the struts were too closely spaced to allow wire to be threaded around them.

Figure E3. Strut Strength (MPa) at Various Positions within a Specimen

Statistically the differences in mean strut strength between the top, side and bottom of the same layer, and the strength differences between layers are real. Therefore it is likely that some regions of the sample were damaged more than others due to smaller strut diameters (smaller struts break easier) or due to more extensive contact with other pieces during testing and handling.

There was no significant difference between the means of:

1 and 5 (B, top 1st layer and 9, top 1st layer).

Therefore we cannot conclude that there was a strength degradation due to solar testing, although qualitatively it appeared that there had been. If more data were collected, it might be possible to say that the mean strut strength of piece no. 9 is less than that of spare piece B. Large variability in the data is typical for these tests and hence many data must be collected to make valid comparisons and to distinguish between samples. Clearly the number of strut strength measurements should be greater than the number that were made. Another strong caution that must be applied when examining these data is that true strut strength distributions were not obtained because the weakest struts often broke before the test was conducted. Thus if one region had more weak struts than another, these may not have been seen. Unfortunately, the number of struts that broke prior to testing was not noted. This number might have served as an indication of strength degradation.

Based on the strut strength test results it cannot be concluded that there has been any kind of degradation that has caused the overall strength to be lower. Our qualitative observations, however, indicated otherwise. The discrepancies between our qualitative observations and our measurements can probably be accounted for by the fact that, during the strut strength tests, we measured only the strongest portion of the strut strength distribution. The weakest struts broke during wire tying and specimen handling prior to testing, and therefore any strength and hence fracture toughness degradations were masked by this.

X-ray Diffraction Analyses

X-ray diffraction was conducted to determine whether phase changes (changes in the crystal structure) had occurred which might have contributed to a degradation of the absorber's strength and catalytic capabilities. The absorber material was designed to consist of an α -alumina (α -Al₂O₃) and mullite (3Al₂O₃•2SiO₂) substrate with a washcoat of γ -alumina (γ -Al₂O₃). Rhodium catalyst is deposited on the γ -alumina washcoat. γ -alumina generally has a much higher surface area than α -alumina and is expected to enhance the catalytic performance of the absorber. If γ -alumina is exposed to too high a temperature it can be transformed to α -alumina. The absence of γ -alumina should not influence the mechanical integrity or performance of the disc, since the washcoat is not securely bonded to the α -alumina struts, but information on which alumina phase is present may be important in understanding the performance of the rhodium catalyst. If the alumina is no longer present in the γ -phase, the surface area may be much lower than

expected, and the rhodium may not be exposed sufficiently to perform efficiently as a catalyst.

The phase compositions (crystal structures) of four samples of absorber material were compared. These samples, labelled as Samples 1-4, are described in Table E-II. Washcoat from a piece of CAESAR absorber no. 1, which was covered with white residue, was included in this analysis in the hope that the residue could be identified. Washcoat samples were removed from the α -alumina and mullite substrate by gentle scraping with a scalpel. Sample 3 was prepared by scraping the washcoat off and grinding up what remained.

Since the strut or substrate material is a mixture of a α -alumina (α - Al_2O_3) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), both of these phases should be found in Samples 3 and 4. The washcoat is expected to be γ -alumina and hence γ -alumina should be found in Samples 1, 2 and 4. Rhodium was deposited over the washcoat and therefore is expected to be found on samples containing washcoat such as 1, 2 and 4. Sample 4, however, was never coated with rhodium and therefore this sample serves as a baseline against which the Samples 1 and 2 can be compared. Additionally, since it did not undergo the processing step in which the rhodium was added, it may help pinpoint when new phases may have appeared.

X-ray spectra for each sample are shown in Figures E4-E7 along with summaries of the results for each sample. Table E-III shows what phase each peak in the spectra corresponds to according to the d-spacings (distance between atom planes), which are displayed at the top of each spectrum. Major peaks seen on all four spectra at d-spacing's greater than 9.8 are instrument peaks and do not originate from the sample.

Major peaks for Sample 1 (Figure E4) were identified as α -alumina. This, by itself, is surprising since this sample should only be γ -alumina washcoat. This result, taken with the fact no major γ -alumina peaks were observed, strongly suggests that any γ -alumina, that might at some point have been present, has transformed to α -alumina. This sample also contains some mullite, which is not expected unless some of the substrate material was included, or any silica present in the system was able to migrate (perhaps via vapor transport) and then react with alumina to form mullite. Inexplicably, only one of the two major rhodium metal peaks could be located, and because it was located in the same region as a possible mullite peak (Rh and mullite peaks have similar d-spacings), it could not be confirmed as a rhodium metal peak.

The major peaks in Sample 2 (Figure E5) are α -alumina and the remaining are rhodium. It is not known why both major rhodium peaks are apparent in this sample, and not in Sample 1, since both are samples of washcoat with a rhodium coating. Because this sample did not produce any peaks that were not seen for the others, the spectrum gave no clue as to what the white residue might be. It is possible that it is one of the phases already identified, such as α -alumina, or another phase that is present in too small a quantity to appear as an identifiable peak. All peaks for Sample 3 (Figure E6) were identified as α -alumina or mullite.

All major peaks for α -alumina and mullite were detected in Sample 4 (Figure E7). As with Sample 1, the two major peaks for γ -alumina (at d-

Table EII. Samples Compared for Phase Composition using X-ray Diffraction.

1. Washcoat material of untested Spare Piece B.
 2. Washcoat material of solar-tested piece with white residue (from Piece No. 7).
 3. Strut material with no washcoat from Spare Piece B.
 4. Washcoat and strut material of uncoated material (no rhodium).
-

spacings of approximately 1.98 and 1.40) were not detected. Two minor γ -alumina peaks appear to be present but it is not possible to positively identify these because they are located in the same region as mullite peaks. The fact that the major γ -alumina peaks were not found strongly suggests that there is no γ -alumina in the specimen or that the γ -alumina present in the material has a preferred orientation. Based on the way in which the samples were processed, there is no reason to suspect that there would be a preferred orientation. Since the manufacturer coated the specimens with what was presumably γ -alumina, it is possible that during some subsequent heat treatment, the temperature at which γ -alumina is stable was exceeded and the γ -alumina transformed to α -alumina. Since this transformation normally occurs at temperatures greater than 1100°C it appears that the material may have been exposed to excessive temperatures at some point. Another possibility is that the γ -alumina comprises less than 5% of the total sample volume, putting it under the detectability limits of the x-ray equipment. Since the x-ray sample was ground up from α -alumina struts covered with a relatively thin washcoat, it is possible that this was the case.

It is possible that in some of the samples that were expected to contain γ -alumina, the amount of γ -alumina may have been below detectability limits. However, detectability limits are not an issue in samples that consisted only of washcoat. Since washcoat samples do not appear to contain γ -alumina, it is probably safe to assume that it is absent in all of the samples. Therefore the γ -alumina was either absent in the starting material, prior to coating with rhodium and solar testing, or it had transformed to α -alumina prior to both of these processes. The initial motivation behind adding the γ -alumina washcoat was to give the absorber material a high surface area. High surface area provides numerous sites for the rhodium catalyst, making it highly dispersed and therefore more active. A conversion to α -Al₂O₃ may be accompanied by a reduction in surface area if densification or grain growth occurs. In this case the absorber may no longer have the desired high surface area and may not be giving the expected catalytic performance.

Scanning electron microscopy (SEM)

In addition to a strength degradation due to thermal stresses and the subsequent cracking, strength degradation may have occurred due to some kind of chemical degradation during solar testing, as evidenced by discoloration observed on some regions of the absorber. Some regions were also covered with white deposits. Scanning electron microscopy (SEM), in conjunction with energy dispersive analysis by x-ray (EDAX), was conducted on various pieces

Figure E4. X-ray Sample 1. Washcoat Material of Untested Spare Piece B

Figure E5. X-ray Sample 2. Washcoat Material of Solar-Tested Piece with White Residue (from Piece No. 7)

Figure E6. X-ray Sample 3. Strut Material with no Washcoat from Spare Piece B

Figure E7. X-ray Sample 4. Washcoat and Strut Material of Uncoated Material (No Rhodium)

Table EIII. Major X-Ray Peaks and the Phase that each Corresponds to.

Approximate peak d-spacing (Å)	Phase
9.97	Instrument peak
9.82	Instrument peak
5.39	Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)
3.47	α -Alumina (Al_2O_3)
3.39	Mullite
2.88	Mullite
2.69	Mullite
2.55	α -Alumina
2.38	α -Alumina
2.20	Mullite and Rhodium
2.09	α -Alumina
1.90	Rhodium
1.74	α -Alumina
1.60	α -Alumina
1.55	α -Alumina
1.51	α -Alumina

of the absorber to determine if microstructural or chemical inhomogeneities were associated with differences in appearance.

Figure E8 shows the general appearance of the microstructure, including the cracked washcoat and a cross-section of a fractured strut. A triangular hole, characteristic of the way these materials are made, can be seen in this micrograph. An EDAX spectrum characteristic of the material in Figure E8 is shown in Figure E9. EDAX identifies which elements are present, and from the relative heights of peak in the spectrum, a qualitative picture of the relative amounts of these elements can be obtained. The spectrum in Figure E9 shows that Al, Si, Rh and Ca are present and that the last three elements are minor components.

Figure E10 is an SEM micrograph of one of the regions of solar-tested material covered with white residue. At the magnification of this micrograph, the residue is revealed as being fibrous in nature. An EDAX spectrum corresponding to this region is shown in Figure E11. There is a much larger amount of Si in this region relative to regions that did not contain these fibers. The Si found in this region could be present as SiO_2 , or may be an aluminosilicate such as mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The origin of this material is uncertain; however, there are several sources of Si in the system including the Fiberfrax, the grease used around the window, and the disc itself, since it originally contained mullite.

Figure E8. SEM (Scanning Electron Microscope) Micrograph of the 92% Al_2O_3 Cellular Ceramic Material used in the CAESAR Absorber No. 1. Magnification = 50 X

Figure E9. EDAX (Energy Dispersive Analysis by X-Ray) Spectrum Corresponding to Region in Figure E8

Figure E10. SEM Micrograph of CAESAR Absorber No. 1 in a Region Covered with a White Residue. Magnification = 1000 X

Figure E11. EDAX Spectrum Corresponding to Region in Figure E10

A specimen of piece no. 9, which had a region labelled as black area no. 1 on it (rainbow-type appearance when viewed up close with the unaided eye), was examined to determine whether it was chemically or microstructurally different than other regions. Part of this specimen, shown in Figure E12, was observed to have a microstructure different than other microstructures observed for the absorber. Preliminary EDAX measurements did not indicate chemical differences between this region and others that have been observed, but further examination is required to say this with more certainty. If this project is continued, it is recommended that further analyses of the deposits be conducted using an SEM with the capabilities to detect elements with low atomic numbers.

Summary

CAESAR absorber no. 1 cracked extensively during solar testing because stresses, due to thermal gradients in the disc, exceeded the bulk strength of the absorber material. It also appears that thermocouple holes drilled in the absorber may have acted as stress concentrators and reduced the bulk strength of the material according to Equation 2 (larger flaws). This caused the absorber material to break under smaller thermal gradients than an undamaged disc would have.

Qualitatively it appeared that the toughness and hence the strength of the solar-tested material had degraded, perhaps due to some kind of chemical degradation. Strut strength tests were not able to confirm this. It appears that the strut strength testing approach was flawed, because we were not able to obtain data for the weakest struts which broke before strength measurements were made. If the solar-tested material is truly weaker than the untested material, we were unable to detect this with this testing approach. More informative results could probably be obtained using the same approach if many more struts were tested. Better results could possibly also be obtained by using another testing approach that measures the bulk strength using large specimens.

X-ray diffraction results indicate that there is no γ -alumina in the washcoat. The absence of γ -alumina may have a negative effect on the catalytic performance of the absorber. Examination of the absorber, using scanning electron microscopy (SEM) and energy dispersive analysis by x-ray (EDAX) revealed that white deposits observed on some sections of the absorber had a high silica content. A discolored region of the absorber was not identified as being chemically different, however, more extensive chemical analyses are recommended if further testing is to be conducted.

Further testing should also include examination using optical and scanning electron microscopy to obtain information about where cracks originated in the disc, what types of flaws were present prior to testing, and what damage was introduced during handling and solar testing.

Figure E12. Scanning Electron Microscope (SEM) Micrograph of Discolored Region with Unusual Microstructure. Magnification = 200 X

APPENDIX F

Radially Uniform Absorber Catalyst Post-Test Analysis

Date: July 26, 1990

To: J. F. Muir, 6216

From: R. G. Dosch, 6212

Subject: Post-test Analysis of CAESAR Absorber No. 1

This memo summarizes the results of my contribution to the post-test analysis of the CAESAR Absorber No. 1. The work included examination of both pre- and post-test materials to determine Rh content, Rh distributions and crystallite size, catalytic activity of the dispersed Rh, analysis of carbonaceous material, and surface area analyses. All the results reported herein on post-test materials were obtained from analyses and tests done on materials from the portion of Piece #8 marked RD as shown in Figure F1. Samples of pre-test materials were obtained exclusively from a piece labeled "Spare B", which differed from Piece #8 only in that it had not been tested. The post-test and pre-test, or control materials, will subsequently be referred to as #8 and "B", respectively.

The CAESAR Absorber No. 1 consisted of three layers of reticulated mullite-containing alumina of differing pore structures which were bonded together to serve as a support for an alumina washcoat, which in turn was coated with Rh using a rhodium nitrate solution and incipient wetness techniques. Samples used in this work were pieces of the front and back layers with the largest surfaces being approximately 4 in² and thicknesses of about 0.5 in. They were prepared by sawing through the center layer of pieces containing equal amounts of all three layers and removing the remaining center layer via abrasion. The resulting pieces of the front and back layers weighed between 25 and 30 grams. When samples were taken for chemical and surface area analyses, I attempted make the samples representative of the entire thickness of the layer being sampled. Samples used for the catalytic activity tests were taken primarily from the exposed portion of the the front and back layers. This was intended to provide samples which had seen the most and least severe temperature conditions. The TEM samples consisted of small flakes of the Rh-impregnated washcoat which were scraped off the outermost or exposed portions of the front and back layers. The TEM analyses were intended to provide information concerning Rh distribution and crystallite size and changes therein which resulted from the test conditions.

CAESAR Absorber no 1.

Figure F1. Schematic of the Crack Pattern Observed on CAESAR Absorber No. 1 after Solar Testing

Samples used for the Rh analyses intended to provide an average Rh content in a given layer ranged from 8 to 15 grams. The descriptive chemistry of Rh suggests that the solubility of Rh in mineral acids is highly dependent on dispersion and thermal history. For example, Rh black may dissolve in aqua regia while Rh subjected to fire assay techniques may resist attack by all mineral acids or combinations thereof. After soaking the CAESAR samples overnight in hot aqua regia, it was apparent that only a small fraction of the Rh dissolved. Atomic absorption (AA) analysis of the aqua regia extract, given in Table F-I, represent only that part of the Rh which dissolved. The same samples that were soaked in aqua regia were then reduced to powder in a tungsten carbide ball mill and analyzed for Rh content using energy dispersive X-ray fluorescence (XRF) spectroscopy. These results are also given in Table F-I and represent that portion of the Rh which was insoluble in aqua regia.

In all cases, only a small fraction of the Rh was dissolved in aqua regia. However, the post-test samples contained much less aqua regia-soluble Rh relative to the total Rh content than did the control samples. This suggests that at least some of the Rh was altered during the testing, probably due to high temperature effects such as sintering. Sintering would reduce the Rh surface area, thus making it more difficult to dissolve. The results also show that the front layer contained a higher Rh content than did the back layer and that the test environment apparently did not cause any significant loss of Rh. The former is probably an artifact of the the Rh loading procedure. The latter is of interest in that the wash-coat containing the bulk of the Rh which could be removed very easily by light abrasion apparently remained in place under the conditions used in testing.

The Rh on all samples was also found to be impervious to boiling H_2SO_4 and to bisulfate fusion. This information is included for reference purposes should a similar analysis be done in the future.

Figures F2-F4 are transmission electron microscope(TEM) photomicrographs of Rh-impregnated washcoat taken from the front surface of #8, the back surface of #8, and from the front and back exposed surfaces of piece "B", respectively. It is readily apparent that the test conditions promoted Rh sintering or crystallite growth on both the front and back surfaces of the CAESAR absorber. A rigorous particle size determination would be superfluous for this analysis since there is no activity data to correlate with; however, qualitatively the Rh particles on the front of the post-test absorber generally fall in the range of 8-28 nm with an average size on the order of 18 nm and those on the back of the post-test absorber fall in the range of 4 to 14 nm with an average size of about 6.5 nm. The control sample, "B", had Rh particles in the 2 to 6nm range with the average particle being on the order of 4nm. The same trend can be observed in the size of the alumina grains in the washcoat which supports the Rh.

Catalytic activity tests were done with samples taken primarily from the front and back exposed surfaces of the post-test, #8, and the control piece, "B". As in the case of the TEM samples, this was done to provide samples which had been exposed to the most and least severe temperature conditions during testing. The samples were reduced to -100 mesh in a sapphire mortar and pestle and analyzed by X-ray fluorescence spectroscopy. The results,

Table F-I: Rh Content of CAESAR Absorbers ¹				
	#8 Front	#8 Back	"B" Front	"B" Back
Si	3.2	2.9	2.5	2.7
Al ₂ O ₃	96.3	96.8	97.0	97.0
Rh-aqua regia	0.0013	0.0045	0.055	0.063
Rh-total ²	0.60	0.40	0.56	0.36
Rh-XRF ³	0.60	0.70	0.70	0.70

- 1) Analytical results given in percent by weight.
- 2) Combined XRF and AA analysis of the analytical samples.
- 3) XRF analysis of surface samples used in activity tests.

given in Table F-I, show that the outer surfaces tend to have higher Rh content than the average Rh content in the layer as a whole. This result is most likely an artifact of the method used for Rh loading.

We do not have the capability in hand to test these catalysts under the temperature regimes, i.e., 1000°C, used in the CAESAR test. We do have considerable experience in testing the hydrogenation activity of noble metal catalysts, and typically use the rate of hydrogenation pyrene as a figure of merit in evaluating new catalyst materials. Since good hydrogenation catalysts tend to also perform well as dehydrogenation catalysts and reforming involves dehydrogenation steps, the pyrene hydrogenation test may provide a valid indication of catalyst deactivation.

Rate constants for the hydrogenation of pyrene using the four catalyst samples are given in Table F-II in units of milligrams of pyrene hydrogenated per sec per gram of Rh. The tests were done by heating a mixture of 1 gram of hexadecane, 100 mg of pyrene, and 40 mg of catalyst at 100°C under 100 psig H₂ for 15 minutes. The amount of pyrene hydrogenated was determined by gas chromatographic analysis. It is clear that the Rh on the post-test sample had undergone significant deactivation with respect to hydrogenation activity as compared to the control samples. The Rh on the front surface of the absorber (#8) showed more deactivation than that back surface. This correlates with the TEM data which shows the Rh on the front surface to have a lower surface area (larger grain size) than that on the rear surface. If catalyst deactivation is due solely to active metal sintering, a similar degree of deactivation probably took place in the CAESAR tests. No such extrapolation can be made if other deactivation mechanisms, which would be beyond the scope of this work, were involved.

The #8 and "B" samples used for the activity tests were analyzed for carbon and hydrogen to determine if coking had occurred during the test. Neither element was detected in any of the samples. Nitrogen BET analyses

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Figure F2. TEM Micrograph of Front Surface of Piece #8, Radially Uniform Absorber (495,000x Magnification)

Table F-II Pyrene Hydrogenation Rate Constants*			
#8 Front	#8 Back	"B" Front	"B" Back
0.5	3.4	9.7	16.3
* Rate constants in units of mg pyrene reacted/sec · g Rh			

were also performed to determine if surface area of the absorber had changed during the tests. A -10+20 mesh size fraction representative of the entire layer was used in the analysis. The results given in Table F-III show that testing resulted in an overall two-fold decrease in surface area of the front layer, which most likely had seen the highest temperatures during the test. This result would be consistent with a deactivation mechanism based on active metal encapsulation; however, there is not sufficient information available to draw this conclusion since the TEM results are inconclusive and the phenomena resulting in surface area change is unknown. With regard to the latter, the change could be the result of sintering of the reticulated alumina support, the wash coat, or both. The surface areas of the back surfaces of #8 and "B" agree within experimental error suggesting that the back surface of #8 was at a lower temperature than the front surface during the tests.

Table F-III BET Surface Areas*			
#8 Front	#8 Back	"B" Front	"B" Back
0.90	2.30	1.90	2.0
*Results given in m ² /g .			

The results of the work described above suggest other studies which could be undertaken to provide more insight into the properties of the CAESAR absorber. For example, chemisorption studies could be done which would determine if the catalyst deactivation we observed was directly proportional to active metal surface area. Further surface area and pore size distribution analyses could be done to separate the relative contributions of the reticulated alumina support and the washcoat to the changes in surface area.

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