29
2/25/82
RB

①

I-1604

256715

SERI/TR-9-8325-1

November 1981

Solar Decomposition of Cadmium Oxide for Hydrogen Production

Final Subcontract Report

James D. Schreiber
Bernard D. Yudow
Ronald H. Carty
Thomas P. Whaley
Jon B. Pangborn

Institute of Gas Technology
IIT Center
Chicago, Illinois

Prepared under Subcontract No. XP-9-8325-1

SERI

Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

MASTER

Operated for the
U.S. Department of Energy
under Contract No. EG-77-C-01-4042

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price:
 Microfiche \$3.00
 Printed Copy \$ 6.50

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

SERI/TR-9-8325-1
UC CATEGORY: 62

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SOLAR DECOMPOSITION OF CADMIUM
OXIDE FOR HYDROGEN PRODUCTION

J. D. SCHREIBER
B. D. YUDOW
R. H. CARTY
T. P. WHALEY
J. B. PANGBORN

SERI/TR--9-8325-1

DE82 011092

NOVEMBER 1981

INSTITUTE OF GAS TECHNOLOGY
3424 SOUTH STATE STREET
CHICAGO, IL 60616

PREPARED UNDER SUBCONTRACT
No. XP-9-8325-1

FOR THE

Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

Prepared for the
U.S. Department of Energy
Contract No. EG-77-C-01-4042

SERI TECHNICAL MONITOR

JAMES LEFFERDO

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

PREFACE

The decomposition of cadmium oxide to produce cadmium metal and oxygen in a solar furnace was accomplished in a series of experiments performed at the White Sands Solar Facility at White Sands Missile Range, N.M. This decomposition is the high-temperature step in the Institute of Gas Technology's hybrid thermoelectrochemical cadmium-cadmium oxide water-splitting cycle. A batch-type solar reactor that directly exposed the cadmium oxide to the horizontal solar flux of the White Sands Facility was constructed and used. A stream of argon carrier gas was used to sweep the decomposition products—cadmium vapor and oxygen—from the reaction site to a water cooled heat exchanger where the cadmium vapor was quenched to produce solid cadmium. The effluent stream was then analyzed for oxygen concentration. Due to high winds and rain during much of the time scheduled for the tests, it was not possible to perform the number of experiments that were planned. However, the experiments that were completed demonstrated the functionality of the solar reactor and the technical feasibility of performing the decomposition in a solar furnace. The cadmium collected on the quench heat exchanger ranged in purity from 67% to 84%. The successful completion of these experiments completed the demonstration of the cadmium-cadmium oxide cycle which has a potential thermal efficiency of 60%.

The authors gratefully acknowledge the contributions to this research effort made by Stephen Foh, Mono Mazumder, and Robert Curtis of the Institute of Gas Technology and by W. P. Key and James M. Lefferdo of SERI.

This report was prepared by the Institute of Gas Technology under SERI subcontract XP-9-8325-1.

James M. Lefferdo
SERI Project Manager

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

SUMMARY

OBJECTIVE/BACKGROUND

Hydrogen production by thermochemical water-splitting has been proposed as an energy conversion process for using heat to produce a chemical fuel (hydrogen) from a renewable resource (water). One such cyclic process that is experimentally workable and that exhibits many desirable characteristics — hydrogen pressure capability, high energy efficiency, and relatively noncorrosive chemicals — is based on the high-temperature thermal decomposition of cadmium oxide. This Institute of Gas Technology (IGT) hybrid cycle, requiring a relatively small electrical energy input to drive the first step, is —

To be very efficient, this chemically simple cycle requires about 75% of its total energy input as nearly isothermal heat above 1200°C to drive the CdO decomposition step. Thus, it appears ideal for coupling with a solar heat source capable of supplying nearly isothermal heat. The purpose of this investigation was to study the decomposition of CdO using a solar flux — to determine operating conditions that promise high process efficiencies and good yields, to obtain an approximate measure of the rate of the decomposition reaction, and to design and construct an experimental reactor in which CdO is directly irradiated and from which metallic cadmium is recoverable. This work is also a demonstration of a water-splitting cycle in which the thermal energy source is the same as would be used in actual practice rather than a simulated heat source.

DISCUSSION/CONCLUSIONS

Overall, the reactor designed for the cadmium oxide dissociation experiment functioned successfully. Problems encountered were associated with materials, transient effects of clouds, effects of argon flow on reaction, temperature measurement, and nonuniformity of the concentrated solar flux.

The ability to characterize mass and energy balances around a reactor is essential for process evaluation. Although the thermal conductivity cell used to detect oxygen evolution suggested the presence of oxygen, the concentration was usually not sufficiently above the baseline to give unequivocal answers on reaction rate. A more sensitive instrument must be used. Although not required in this study, reactor energy balance must be developed to characterize process efficiency as this cycle progresses in development.

The reactor developed for this study performed satisfactorily in establishing the feasibility of cadmium oxide decomposition under the realistic conditions of the solar-furnace environment. The solar-furnace environment is very appropriate for the evaluation of design concepts. However, the solar furnace probably cannot give precise rate data. The flux is too nonuniform, so temperatures of reactant and corresponding reaction rates are also nonuniform.

One of the most important results of this project was the recovery of samples from the quench heat exchanger that contained a surprisingly large amount of metallic cadmium. The fact that the sample taken from the quench heat exchanger was metallic in appearance and contained between 67% and 84% metallic cadmium would tend to indicate recombination of cadmium vapor and oxygen can be effectively prevented by the quenching operation. It would also tend to confirm recent studies that show cadmium oxide does not sublime appreciably.

Determination of the decomposition rate of cadmium oxide was severely limited by fluctuating and nonuniform reactant temperatures and baseline drift in the oxygen sensor. However, the estimated rate based on a single run seemed to follow a typical solid decomposition rate pattern with an initial acceleratory period, followed by a longer deceleratory period.

From a preliminary flowsheet analysis of the cadmium-cadmium oxide cycle, it was determined that at a cadmium oxide decomposition temperature of 1400°C and a requirement of 0.2 V in the electrolyzer the efficiency was 41%, assuming total quenching of the cadmium oxide decomposition products. This efficiency could increase to a maximum of 59% if total recovery of the latent heats of vaporization and fusion of the decomposition products is possible.

Feasibility of cadmium oxide decomposition has been established. Problems in reactor design have been identified and the process of finding solutions started. Further development work to precisely measure reaction rates needs to be undertaken and the development of continuous experimental reactors for solids begun.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION AND BACKGROUND	1
Discussion of CdO Cycle	1
Reaction 1: The Electrochemical Oxidation of Cadmium	1
Reaction 2: The Thermal Decomposition of Cadmium Hydroxide	3
Reaction 3: The Thermal Decomposition of Cadmium Oxide	3
OBJECTIVE	6
WORK STATEMENT	7
Task 1. Design of the STTFUA Experiment for CdO Decomposition	7
Task 2. Operation of the Experiment at the Solar Thermal Test Facility	7
Task 3. Data Analysis and Cycle Efficiency Determination	8
Task 4. Documentation and Reporting	8
TASK 1. EXPERIMENTAL DESIGN	9
White Sands Solar Furnace	9
Reactor Design	11
Design Approach	11
Final Design of CdO Dissociation Reactor	17
Gas Analysis System	17
Preparation of CdO Reactant	21
Reactor Testing at IGT	23
Experimental Plan	24
TASK 2. OPERATION OF THE EXPERIMENT AT WHITE SANDS SOLAR FACILITY	26
Setup of Experiment	26
Solar Furnace Preparation	28
Experiment 1	31
Experiment 2	35
Experiment 3	41
Experiment 4	47
TASK 3. DATA ANALYSIS	56
Chemical Analyses	56
Analysis of TCD Output — Experiment 4	58

TABLE OF CONTENTS, Cont.

	<u>Page</u>
Engineering Analysis of Cycle L-2	59
DISCUSSION AND CONCLUSION	63
Reactor Design	63
Field Testing of Solar Experiments	65
Decomposition of Cadmium Oxide	66
Cycle Efficiency	67
FUTURE WORK	68
REFERENCES	69
APPENDIX A. Functional Description of Cadmium Oxide Reactor Components	A-1
APPENDIX B. Experimental Plan	B-1

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
1	Equilibrium Partial Pressure of Cd and CdO From Simultaneous Reactions	5
2	White Sands Solar Facility (WSSF)	10
3	WSSF Irrandiance Profile at Focal Plane	12
4	Side View of Reactant Bed and Supports	14
5	CdO Reactor Components	18
6	Longitudinal Cross-Section of CdO Reactor	19
7	Assembled Solar Reactor — Front View	20
8	Assembled Solar Reactor — Rear View	20
9	Argon and Argon/Oxygen Gas Flows in Cadmium Oxide Dissociation Experiment	29
10	Reactor Installed on the 3-Axis Table in the Furnace Control Room	30
11	Reactant Temperature History — Experiment 1	32
12	Reactant Temperature History — Experiment 2	38
13	Reactant Temperature History — Experiment 2, (Cont.)	39
14	Reactant Temperature History — Experiment 3	44
15	Thermal Conductivity Detector (TCD) Millivolt Output — Experiment 3	45
16	Interior of Reactor After Completion of Experiment 3	46
17	Reactant Temperature History — Experiment 4	50
18	Thermal Conductivity Detector (TCD) (Oxygen Analyzer) Output — Experiment 4	51
19	View of Reactant Bed, Experiment in Progress, Prior to Shifting of Reactant Bed Supports	52
20	View of Reactant Bed, Experiment in Progress, Shortly After Shifting of Reactant Bed That Dumped Reactant From Third Channel From Top	53

LIST OF FIGURES, Cont.

<u>Figure No.</u>		<u>Page</u>
21	Quench Heat Exchanger, Following Experiment 4	54
22	Edge View of Deposit From Quench Heat Exchanger From Experiment 4, Showing Dendritic Crystals on Metallic Cadmium (Magnification: 23X)	54
23	Effect of Cadmium Oxide Decomposition Temperature on Process Efficiency	61
B-1	Schedule of Tasks -- Maximum Time to Carry Out a Single Experiment in One Day	B-8
B-2	Schedule of Tasks -- Minimum Time to Carry Out a Single Experiment in One Day	B-9
B-3	Schedule of Tasks -- Time to Carry Out Two Experiments in One Day	B-10

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
1	WSSF Exposure Characteristics	11
2	Log of Experiments at WSSF	27
3	Loading of Reactant on Channels	33
4	Chemical Analyses of Residue Recovered From Cadmium Oxide Decomposition Experiments	56
5	Estimated Minimum Conversion of CdO to Cd	58
6	CdO Decomposition Reaction Rates in Experiment 4	59
B-1	Alternative Experimental Plans	B-4

INTRODUCTION AND BACKGROUND

Hydrogen production by thermochemical water-splitting has been proposed as an energy conversion process for using heat to produce a chemical fuel (hydrogen) from a renewable resource (water). One such cyclic process that is experimentally workable and that exhibits many desirable characteristics — hydrogen pressure capability, high energy efficiency, and relatively noncorrosive chemicals — is based on the high-temperature thermal decomposition of cadmium oxide.¹ This Institute of Gas Technology (IGT) hybrid cycle (U.S. Patent 3,907,980), requiring a relatively small electrical energy input to drive the first step, is —

To be very efficient, this chemically simple cycle requires about 75% of its total energy input as nearly isothermal heat above 1200°C to drive the CdO decomposition step. Thus, it appears ideal for coupling with a solar heat source capable of supplying nearly isothermal heat. The purpose of this investigation was to study the decomposition of CdO using a solar flux — to determine operating conditions that promise high process efficiencies and good yields, to obtain an approximate measure of the rate of the decomposition reaction, and to design and construct an experimental reactor in which CdO is directly irradiated and from which metallic cadmium is recoverable. This work is also a demonstration of a water-splitting cycle in which the thermal energy source is the same as would be used in actual practice rather than a simulated heat source.

The following is a discussion of the cycle steps and their operating parameters that affect the method of solar energy input to the process.

Discussion of CdO Cycle

Reaction 1: The Electrochemical Oxidation of Cadmium

Reaction 1 is an electrochemical step capable of operation at very low potentials at room temperature. In early experiments,² a cadmium anode and platinum cathode were used in a stirred 1.0N sodium hydroxide electrolyte to confirm that this reaction does occur as written. However, cadmium hydroxide,

being insoluble in aqueous sodium or potassium hydroxide electrolyte, deposits as it forms on the cadmium metal surface, resulting in high anodic overpotentials. Two solutions to this problem of anodic passivation have been investigated^{3,4}: 1) the use of an electrolyte in which oxidized cadmium is soluble, and 2) the use of a stirred mercury-cadmium anode.

Cadmium hydroxide is soluble in aqueous ammonia as $\text{Cd}(\text{NH}_3)_4^{2+} (\text{OH})_2^{2-}$. Because of the low conductivity of $\text{NH}_3(\text{aq})$ solution, it is necessary to add a small amount of NaOH as a supporting electrolyte. This results in a small degree of passivation, which can probably be eliminated entirely in a properly designed cell. The recovery of $\text{Cd}(\text{OH})_2$ from aqueous ammonia solutions should be possible by simply heating the solution to drive off ammonia. However, this idea has not been confirmed experimentally, and the impact of such a step on the overall process efficiency has not been assessed.

Aqueous sodium chloride electrolyte gives very satisfactory results and is currently the preferred electrolyte for this process. The cadmium species formed at the anode is a soluble ion, probably CdCl_3^- . The product anolyte, containing CdCl_3^- , and catholyte, containing sodium hydroxide, can be mixed in a separate vessel to yield the desired solid cadmium hydroxide and a regenerated sodium chloride solution for recycle back to the electrochemical cell. One possible problem with using sodium chloride is the occurrence of an undesirable side reaction forming a stable oxychloride, $\text{CdO}(\text{HCl})$, which could cause materials problems in the CdO decomposition step. This will be explained more fully later, under Task 1, where the production of "recycled" CdO is discussed.

A stirred cadmium amalgam should provide a constantly renewed anode surface, thus preventing the buildup of a passivating layer of cadmium hydroxide. Initially, a rapidly stirred aqueous KOH electrolyte was used. However, this results in the formation of a precipitate consisting of small droplets of amalgam coated with a layer of solid $\text{Cd}(\text{OH})_2$ that prevents the droplets from coalescing back into the amalgam. This problem can probably be solved; however, because very satisfactory results have been obtained using an amalgam anode containing 13 weight percent Cd and a 5 N NaCl anolyte at temperatures between 55° and 20°C, use of an aqueous KOH electrolyte has not been pursued. Anode overpotentials of 0.09 V at current densities of 33 mA/cm² have been measured. It has been estimated that current densities of

200 mA/cm² at voltages less than 0.3 V are achievable.³ Amalgams having a higher Cd content can be prepared by using higher temperatures, up to 321°C, the melting point of cadmium.

Because two anode designs — solid Cd and an amalgam — are feasible, at some point a decision will have to be made as to which design will be used in a production process. The choice will depend largely on the form and purity of the cadmium that is recovered from the CdO decomposition step. A solid cadmium electrode might be the choice if the condensed cadmium product of Reaction 3 is very pure and dense so that it can be used directly or reformed as an electrode. If the cadmium product is not pure, containing large amounts of CdO, for example, or has a fragile structure that will not stand up as an electrode, then the amalgam may be preferable. Although this project was not intended to resolve these questions, some preliminary information was sought that would point the way for further research.

Reaction 2: The Thermal Decomposition of Cadmium Hydroxide

The literature reports that Cd(OH) decomposes readily above 375°C; however, experiments⁵ have shown that decomposition will occur as low as 200°C and proceeds rapidly above 350°C. This reaction appears to be quite simple and straightforward and should cause no problems in the further development of the CdO cycle.

Reaction 3: The Thermal Decomposition of Cadmium Oxide

This reaction has been proved experimentally at IGT at 1125°C in a stream of inert (carrier) gas flow at 101 kPa (1 atm) pressure.² This reaction is documented in the literature^{6,7} as occurring at 900° to 1000°C, and it is so listed in the Handbook of Chemistry and Physics,⁸ but the results of IGT laboratory tests in a partial vacuum system showed the decomposition to be questionable at 750° to 950°C.²

A representative of Battelle Geneva (Switzerland) reported that the thermal decomposition of CdO was also tried at the Odeillo, France solar facility by the Centre National de La Recherche Scientifique (CNRS). This was reported to us by private communication after we presented this CdO cycle to hydrogen researchers at the 1976 Miami Hydrogen Energy Conference. Reportedly, scientists affiliated with the CNRS achieved decomposition of CdO at about 1100°C; however, the results of these experiments have not yet been published.

There is still some uncertainty whether the decomposing species is solid or gaseous CdO (or both) and whether CdO(s) sublimates to any significant extent. Early studies^{9,10} of CdO sublimation reported fairly high vapor pressures of gaseous CdO over solid CdO, reaching 101 kPa (1 atm) at about 1555°C, although it is not clear whether those investigators measured only CdO vapor pressure or total gas pressure (including Cd and O₂) over CdO. More recent studies^{11,12,13} at temperatures up to 1125°C indicate the vapor pressure of CdO(g) is too low to be measured and CdO is completely dissociated in the vapor phase. Studies recently completed at Los Alamos Scientific Laboratory¹⁴ (LASL) also show negligibly low vapor pressures of CdO. Clearly, sublimation and subsequent condensation and recycling of CdO would have a deleterious effect on the efficiency of the overall process. We consider the more recent studies and the work performed at LASL to be correct. However, in our flow sheet calculations (described in Task 3), we used the results of the earlier studies showing CdO to have a vapor pressure (Figure 1). This should result in conservative (worst case) estimates of process efficiency. In designing the CdO decomposition reactor for this project, we again assumed we would have to contend with CdO vaporization and condensation. This had an impact on the design of the inert gas flow system and the reactor window, as described below in Task 1.

The laboratory setup for CdO decomposition experiments at IGT usually consisted of a combustion boat containing CdO placed inside a horizontal tube heated in an electrical furnace. A flow of inert gas (argon) acted as a carrier for the gaseous Cd and O₂ and as a diluent to inhibit recombination in cold zones. Cadmium was condensed and crystallized on a water-cooled quartz cold finger inserted just downstream of the boat of CdO.

In general, we have found this reaction occurs very slowly and nonquantitatively at temperatures below 1100°C. The reaction has been experimentally proved at 1125° and 1200°C in a stream of inert (carrier) gas flow at 1 atm. Several trials at 1000°C under the same conditions resulted in unsatisfactory yields.

A81051033

Figure 1. EQUILIBRIUM PARTIAL PRESSURE OF Cd AND CdO FROM THE SIMULTANEOUS REACTIONS —

DATA FOR REACTION B FROM AN ANALYSIS OF HINCKE'S¹⁰
DATA BY KELLEY¹⁵

OBJECTIVE

The next step in developing the cadmium oxide cycle into a water-splitting process is to resolve, by measurement, the all-important but undefined conditions for operating the high-temperature endothermic step where anhydrous CdO is decomposed into 1) O₂ for separation and release from the cycle, and 2) Cd for recycle to the electrochemical hydrogen-producing step. In fact, the value of this cycle, relative to other candidate cycles for water-splitting and our plans for its development, depends on the real conditions of CdO decomposition.

Specifically, the objective of the work performed in this program was to obtain needed information on the following:

1. Testing of a reactor configuration interfacing a solar flux directly with the chemical reaction for decomposing a metal oxide into two gases.
2. The measured temperature (of the CdO) for effective CdO decomposition in a solar flux. The minimum temperature for reasonable rates was expected to be in the region of 1100° to 1200°C, although higher temperatures would be predicted from thermodynamic data.
3. Approximate rate determinations to discover if the decomposition is limited by solar flux, heat transfer, or reaction kinetics.
4. Measured data from which a realistic estimate of energy efficiency can be calculated for this water-splitting cycle when powered by solar energy. From this we can evaluate its merit and further development efforts.

With further developmental work, we hope to demonstrate the CdO cycle through operation with completely recycled materials at conditions that promise high process efficiencies. These conditions, however, depend on the energy source, and we hope that a suitable solar-heat apparatus interfaced with this or similar cycles will make thermochemical hydrogen production more diversified with respect to energy supply (and less dependent on nuclear reactor development).

WORK STATEMENT

To perform this project, the tasks outlined below were presented in the project proposal (1979).

Task 1. Design of the STTFUA Experiment for CdO Decomposition

IGT will design and fabricate a reactor configuration that will provide for —

- a. Direct admittance of focused sunlight onto a bed of CdO
- b. Containment of CdO(s), Cd(g), and O₂(g)
- c. CdO bed temperatures in the (controllable) range of 1000° to 1500°C
- d. Removal and collection of the produced Cd and O₂, and flow of inert carrier gas as desired
- e. Measurement of temperatures, pressures, flow rates, and sample collection so that analyses of CdO, Cd, and O₂ will provide conversion data from which decomposition rates can be calculated.

To complete the design of the decomposition reactor, IGT chemical engineering personnel will visit the solar thermal test facility (STTF) to determine what supporting structures and fixtures are needed for mounting and operation of the reactor and instrumentation. We will also prepare quantities of recycled CdO from Cd(OH)₂ by first forming Cd(OH)₂ and then dehydrating this material to anhydrous CdO, which will provide a CdO morphology appropriate for this experiment. This material is preferred over purchased reagent-grade CdO for this investigation.

Prior to taking the equipment to the STTF, we will determine the sequence of experiments and test conditions including temperature, pressure, flow rate, and duration of exposure to solar flux. The equipment will also be checked out under laboratory conditions to further assure readiness for the STTFUA tests.

Task 2. Operation of the Experiment at the Solar Thermal Test Facility

IGT Engineering Research staff will transport the decomposition reactor, instrumentation, reactant materials, and auxiliary equipment to the STTF, set up the equipment, and test it for readiness. Next, the experiments will be conducted to gather the requisite data; and after the testing period, the reactor and equipment will be returned to IGT. Several sequential tests will

be performed at varying carrier gas flow rates, system pressures, and CdO bed temperatures (1000° to 1500°C) to ensure inclusion of the effective range of operating conditions for CdO decomposition.

Task 3. Data Analysis and Cycle Efficiency Determination

After operation of the experiment at the STTF and return of the equipment to IGT, the principal investigator and staff of the IGT Thermochemical Hydrogen Research Program will analyze the data and identify appropriate operating conditions for practical and effective decomposition in a solar flux. This will include an analysis of the decomposition rates and will identify the rate-limiting factors that we observed. Using the decomposition results and conditions, we will calculate the maximum attainable cycle efficiency, using established procedures.

Task 4. Documentation and Reporting

At the completion of each task, a letter report describing the progress and findings will be submitted. A detailed technical final report will also be submitted 2 months after the conclusion of Task 3.

TASK 1. EXPERIMENTAL DESIGN

White Sands Solar Furnace

The White Sands Solar Facility (WSSF) is operated by the Nuclear Weapon Effects Branch of the Applied Sciences Division, Army Material Test and Evaluation, an element of the U.S. Army Test and Evaluation Command.

The WSSF was originally constructed in 1958 and operated by the Quarter-master Research and Engineering Center at Natick, Massachusetts. In 1973, the WSSF was moved to the White Sands Missile Range, New Mexico, to provide for more effective use of the facility. The primary mission of the WSSF is to provide high intensity thermal radiation pulses that simulate the thermal pulse from a nuclear weapon detonation. The WSSF is also used for conducting investigations in the area of solar energy development.

The WSSF shown in Figure 2, is a focusing-type solar facility using a double reflecting system. The facility consists of four main components: 1) heliostat, 2) attenuator, 3) concentrator, and 4) a control chamber.

The heliostat consists of 356 flat plate mirrors, each 2 feet by 2 feet (61 x 61 cm) mounted on a steel frame 40-feet (12.2-m) wide and 36-feet (11.0-m) high for a total area of 1424 feet² (132.3 m²). In operation, the heliostat reflects the thermal energy from the sun to the concentrator. The heliostat automatically tracks the sun during the day, or the moon at night, thus keeping the concentrated thermal energy located at the focal plane in a fixed position during the course of experimentation. The concentrator consists of 180 spherical mirrors, each approximately 2 feet by 2 feet (61 x 61 cm) and mounted on a steel frame 30 feet by 30 feet (9.1 x 9.1 m) located 96 feet (29 m) south of the heliostat. Each mirror comprising the concentrator is individually positioned to concentrate the thermal energy at the focal plane, 36 feet (11.0 m) away, located inside the test and control chamber. Most, but not all, of the mirrors in both the heliostat and the concentrator are second-surface mirrors.

The WSSF can provide up to about 30 kW_{th} at the focal plane with a maximum heat flux of about 89 cal/cm²-s in a 5-cm diameter area at the center of the beam. Larger exposure areas up to approximately 12 inches (30 cm) in diameter can be obtained at lower flux levels by moving behind the focal plane of the facility. Maximum flux levels with a uniformity of 10% are

P81051081

Figure 2. WHITE SANDS SOLAR FACILITY

obtained over an exposure diameter of 2 inches (5 cm). The basic flux profile is a skewed Gaussian distribution with the 50% flux points occurring at a 2-inch (5-cm) radius from the center of the solar image as shown in Figure 3. Table 1 gives some of the important exposure characteristics of the WSSF.

Table 1. WSSF EXPOSURE CHARACTERISTICS

<u>Diameter, in.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>6.5</u>
Diameter, cm	2.5	5.1	7.6	10.2	12.7	15.2	16.5
% Total Power	6.5	24.6	49.5	74.5	91.5	99.1	100
Power Kilowatts	1.89	7.21	14.56	21.91	26.97	29.17	29.47
Min Flux cal/cm ² -s	88.2	79.2	59.4	38.7	14.4	4.5	0
Mean Flux cal/cm ² -s	89.1	83.7	69.3	49.1	26.6	9.4	2.2

The black body temperature corresponding to the maximum flux according to the Steffen Boltzman law is 2541°C.

The attenuator, which is located between the test and control chamber and the concentrator, consists of a louvered structure whose blades can be positioned in such a way as to regulate the amount of thermal energy reaching the concentrator. The test and control chamber is 8 feet by 8 feet (2.4 x 2.4 m) in cross section presented to the reflected thermal energy from the heliostat and 16 feet (4.9 m) in length. It contains the experimental test area, the controls for operation of the facility, and shutter systems for modulating the thermal energy.

Reactor Design

Design Approach

An initial decision was made to design a reactor that would be directly coupled to the solar flux; that is, one that would allow direct admittance of focused sunlight onto a bed of CdO. Direct coupling seemed preferable to indirect coupling, where concentrated sunlight is used to heat some heat transfer medium — an inert gas, for example — which, in turn, is used to heat the CdO. First, direct coupling is capable of supplying heat to the reaction at a constant flux and, under steady-state operation, at constant temperature. The reaction rate will be highest under these conditions.

A81051032

Figure 3. WSSF IRRADIANCE PROFILE AT FOCAL PLANE

Second, a directly coupled reactor can be designed to have a higher thermal efficiency because there will be none of the losses associated with heat exchangers. Third, because the spectral emissivity of CdO is quite high (about 0.75 at wavelengths of 1 to 4 μm),¹⁸ the CdO should be a very effective absorber of solar radiation, better than most ceramic heat exchanger materials that would be used in an indirectly coupled reactor.

Arguments can be made for using an indirectly coupled reactor. For example, heat storage would allow continuous operation, even when the sun is not shining. Also, such a system would act as a buffer against transients, such as an occasional cloud passing over. Nevertheless, for this project, a directly coupled reactor seemed more suitable.

Although establishment of the feasibility of CdO decomposition using solar energy and identification of appropriate operating conditions to carry out that reaction were the primary goals of this project, it was the need to measure the reaction rate, together with the need to interface the solid reactant with a horizontal solar beam, that had the greatest impact on the design of the solar reactor. To measure the decomposition rate, it is necessary to monitor, more or less continuously, either the changing weight of the reactant, or some property of the gaseous products. It was impractical to weigh the reactant in the solar furnace, so a gas property was to be measured. In concept, the simplest measurement would be of the oxygen content of a stream of inert sweep or carrier gas. The gaseous coproduct (cadmium vapor) could be readily condensed and solidified and separated from the gases leaving a simple mixture of two gases whose composition could be easily determined. This general concept was adopted. The details of the design follow.

For the oxygen analysis of the carrier gas to accurately reflect the reaction occurring in the reactant bed, it is essential that backmixing and lag time between oxygen evolution and analysis be minimized. This can be done by keeping the internal reactor volume and the distance between reactant bed and analyzer as small as possible. Ideally, the oxygen should not flow across the width of the bed, but straight through it, and the bed should be very thin, so there will not be temperature gradients through it. Because the solar beam is horizontal, its focal plane is vertical, so the reactant bed has to be vertical. Therefore, the ideal reactant bed would be a thin vertical

porous disk. However, the cadmium oxide we were to use was a powder. Although it could be pressed into a disk, the result would not be highly porous and would not be very stable. As it decomposed, it would collapse. The reactant-bed design that was adopted consisted of a set of "shelves" onto which the CdO was loaded. The shelves were made from ceramic tubes slit in half, lengthwise, to form a trough or channel. The channels were supported in a vertical array and separated from each other by a small gap to allow a carrier gas to sweep the O₂ and Cd vapor away from the reaction zone. (See Figure 4.) Each channel was tipped forward toward the direction of the flux so as to expose more of the CdO surface to the concentrated sunlight. The channels were made of zirconium oxide stabilized with 3% magnesium oxide, a material chosen for its superior resistance to thermal shock. This property was necessary because, as the CdO disappeared, the channels themselves would have to bear the full brunt of the solar flux.

A81051031

Figure 4. SIDE VIEW OF REACTANT BED AND SUPPORTS

The high temperature required for CdO dissociation necessitated the use of refractory materials for the hot areas of the reactor, particularly in the vicinity of the reactant bed. The oxidizing atmosphere inside the reactor precluded the use of refractory metals, all of which, except for the noble metals, readily oxidize at high temperatures. The rings and pegs that support the zirconia channels were made of alumina, as was the spacer ring. Another alumina ring of the same diameter as the spacer ring was positioned in front

of the reactant bed support; this inner liner served both to help locate the reactant-bed assembly inside the containment vessel and to shield the vessel from radiation. The reactant bed and inner liner were enclosed in a mullite outer liner, another radiation shield. (See Figures 5 and 6.) This assembly of ceramic parts was contained within a shell of Type 304 Stainless Steel. Although the shell was shielded from the high temperatures within, additional protection was provided by a water-cooled jacket around the portion of the reactor exposed to the high solar flux.

A window at the front of the reactor was necessary to keep air out and to keep toxic cadmium and cadmium oxide fumes in, while admitting concentrated sunlight into the reactor. A quartz window was used because of its high transmissivity for solar radiation and its resistance to thermal shock and chemical attack. However, despite its toughness, the window was the weakest point in the containment vessel; and because its strength decreases as it becomes hotter, it was essential to keep the window cool. This was accomplished by injecting inert gas (argon) through ports arrayed around the window perimeter. Inert gas injection served several purposes. First, it cooled the window by simple convective heat transfer. Second, it prevented cadmium and cadmium oxide vapors and particulates from accumulating near the window. If these substances condensed or settled onto the window, clouding it, the window would quickly absorb radiant heat that it would normally transmit if clear, possibly resulting in failure. Third, the inert gas swept the decomposition products away from the reaction zone, as pointed out earlier, and carried them to a cold-quench area at the rear of the reactor, where cadmium and CdO were condensed. Finally, the inert gas carried the oxygen out of the reactor to an analyzer.

A quench heat exchanger was located in the rear of the reactor to provide a cold surface for condensation of the product vapors and for rapid cooling of the products to prevent back reaction. It also prevented condensable reaction products from being carried out of the reactor, where they could plug gas lines or interfere with the gas analysis. It should be pointed out that heat recovery at high temperatures is an absolute necessity for a viable water-splitting cycle. However, it was beyond the scope of this project to investigate heat recovery from the reaction products.

The gases exiting the reactor flowed through a simple water-cooled countercurrent heat exchanger to cool them to room temperature before they entered the gas analyzer. The gas temperature at the reactor outlet was measured and recorded using a thermocouple.

An essential element in determination of reaction rates is characterization of reaction temperature. Determining temperatures and corresponding reaction rates is difficult in the solar furnace because the flux is not uniform, and temperature gradients exist through the bed of solid reactant, so the reactant will undergo various rates of decomposition depending on local temperatures. Pyrometry can be used to measure surface temperatures, but the emissivity of CdO is not accurately known, partly because it varies, depending on the thermal history of the sample. Furthermore, even a micro-optical pyrometer sees a spot of finite size, so the pyrometer would have to be continually reaimed as the experiment proceeded to prevent it from seeing a bare channel. Given the configuration of the White Sands furnace, it is not possible to adjust or even to take measurements manually once an experiment has begun.

Thermocouples buried in the bed of reactant measure local temperature only. Thus, it is difficult to tie temperature measurements unequivocally to reaction rates, at least without extensive development of instrumentation to characterize the detailed temperature distribution within the reactant. Recognizing this limitation on the validity of methods of temperature measurement, the reactant bed was instrumented with Type R (platinum/platinum-13% rhodium) thermocouples.

The design of the reactor was influenced somewhat by a flux map of the WSSF presented in a SERI report.²⁰ This map showed that a more uniform flux (at less-than-peak flux levels), and, therefore, more uniform temperatures across a 7-cm spot, could be found about 6 to 9 cm beyond the focus of the beam. The reactor was thus designed so the window occupied the focal plane, and the reactant bed was located 7 cm beyond the focal plane, so temperatures across the bed would be uniform. We subsequently learned that the published flux map was purely theoretical. The flux distribution at the WSSF has never been mapped.²¹ Although the flux across a 7-cm spot may in fact be more uniform at a point 7 cm beyond the focal plane than at the focus, it was far from uniform, as will be seen later. As a result, accurate reaction-rate

measurements were far more difficult to achieve than we anticipated when we were designing the reactor.

The design of an efficient receiver for solar radiation was not the intention of this work. With a holdup of less than 30 g of reactant and power levels of 30 kW_{th}, there was no need to consider designing an efficient reactor. The experiment called for reaction rate determination at elevated temperatures, but not for evaluation of reactor energy balances. The resultant reactor design is clearly not the most efficient. The reactor has large radiant losses from a large aperture, and the uninsulated shell is cooled by water jackets and an air blower. The sensible and latent heats of reaction products and sensible heat of the argon are recovered at low temperatures and are essentially wasted. However, the final design was quite reliable and provided data useful in the evaluation of CdO dissociation rates.

Final Design of CdO Dissociation Reactor

The final design of the CdO dissociation reactor was based on the considerations outlined in the previous section. Figures 5 through 8 show the various components of the reactor. Appendix A identifies the components of the reactor and explains their functions. The final configuration was a stainless steel shell lined with alumina ceramics, with a flange-mounted 0.5-inch (1.27 cm) thick quartz window to admit solar radiation to a vertical bed of reactant and a quench heat exchanger to condense cadmium and cadmium oxide. The result was a batch reactor that could be easily disassembled and cleaned, with an accessible interior that simplified loading with CdO. Argon injected through ports arrayed around the window provides window cooling and keeps the window clean. Thermocouples are inserted in the bed of the reactant to monitor temperatures.

Gas Analysis System

The progress of the reaction in our reactor was monitored by measuring the oxygen content of the gas stream leaving the reactor. Some means of continuous measurement was essential, not only for reaction-rate determination, but also more fundamentally for telling us when or if the reaction was taking place. The instrument used for these measurements was a thermal conductivity detector (TCD). The TCD met our requirements for portability; relatively rugged construction; easy setup, calibration, and operation; and fast response.

P80061660

Figure 5. CdO REACTOR COMPONENTS

A81051029

Figure 6. LONGITUDINAL CROSS-SECTION OF CdO REACTOR

Figure 7. ASSEMBLED SOLAR REACTOR — FRONT VIEW

Figure 8. ASSEMBLED SOLAR REACTOR — REAR VIEW

The TCD was calibrated by recording the millivolt output of the instrument as a sample of argon with known oxygen content flowed through it. The resulting calibration curve was nearly linear in emf:

$$x_{O_2} = 0.04924 (\text{emf}) 1.0123 \quad (1)$$

In this equation, x_{O_2} is oxygen mole fraction in argon, and emf is in millivolts. Oxygen concentrations as low as 0.0001 mole fraction (100 parts per million) could be detected.

Argon was chosen as the carrier gas because it was used extensively in our lab; therefore, all our metering equipment had already been calibrated. Unfortunately, the thermal conductivity of argon is only slightly less than that of oxygen, so the TCD is not the most sensitive indicator of oxygen in argon. Although helium, which has a much higher thermal conductivity than oxygen, would seem to be a better choice of carrier gas, the one lab test we made using helium gave erratic results. Lacking time to investigate this unexpected behavior, we decided to stay with argon.

The use of the TCD was not without problems. One that plagued us frequently, but unpredictably, was baseline drift. Another was electrical noise picked up by the chart recorder, although this was largely overcome by disconnecting an unused meter on the TCD, by proper grounding of the instruments, and by using a constant voltage transformer on power lines to the TCD and the recorder. One problem we did not have to contend with was careful regulation of gas-flow rates. The TCD was quite insensitive to changes in flow rates. Several weeks prior to the White Sands tests, the TCD was used in an unrelated project in which the oxygen-evolution rate from decomposing copper (II) oxide was measured. The instrument performed very reliably in those tests.

Preparation of CdO Reactant

To simulate more closely the conditions that would be found in a production-scale process, it was desirable in these experiments to use a reactant whose morphology is similar to that found in a process where the material is being continuously recycled. Therefore, we prepared "recycled" CdO in the lab by going through the steps of the CdO cycle, beginning with a simulation of Reaction 1.

Cadmium hydroxide was formed by reacting reagent grade cadmium chloride, the expected product of the anodic reaction when an aqueous sodium chloride electrolyte is used, with aqueous sodium hydroxide, the expected product of the cathodic reaction. The solid cadmium hydroxide was recovered by filtration.

The precipitate was washed many times with deionized water, a task made difficult by the cold-cream-like consistency of wet cadmium hydroxide. Despite this, the solid product had an unexpectedly high total chloride content — about 1 to 2 weight percent. Further water washes, including several in an ultrasonic bath to break up chunks of precipitate, failed to reduce the chloride content. After the product was dried in a packed-bed reactor with inert gas flow for 16 hours at 400°C, the total chloride content of the product cadmium oxide was 1.53 weight percent in one batch, and 2.38 weight percent in a second batch.

Subsequently, it was learned that a compound, cadmium hydroxychloride, CdOHCl , can be formed when cadmium hydroxide is precipitated in the presence of chloride ions,^{16,17} precisely the conditions under which cadmium hydroxide was produced here. The compound is apparently stable up to at least 400°C, but little more is known about it. The fact that it does form at all is significant because the most promising electrolyte for the electrochemical production of cadmium hydroxide is aqueous sodium chloride. Therefore, this substance can be expected to form in a side reaction under what otherwise are the most favorable operating conditions for the low-temperature end of the CdO cycle. On the other hand, aside from materials problems at high temperatures, the occurrence of this side reaction should pose no major difficulties because the desired electrochemical oxidation of cadmium will already have taken place, and the cadmium hydroxychloride will surely decompose at or below the temperatures at which cadmium oxide decomposes. Furthermore, the fact that different amounts of cadmium hydroxychloride were formed in the two separate batches implies that its formation can be minimized, if not prevented altogether. Further research will be required to resolve this problem.

The final analysis of the reactant used in this project is: 94.7 wt % CdO , 0.7% Cd(OH)_2 , and 1.53 % Cl^- . The percentages do not add up to 100 because only the weight of the chloride ion was accounted for; the cations associated with Cl^- were not determined.

Reactor Testing at IGT

The reactors were leak tested at IGT before being taken to the WSSF. Compatibility of the platinum thermocouples and zirconia channels with cadmium oxide was also evaluated. In the reactor pressure test, the reactor was assembled with window in place, but with all gas inlet/outlet and thermocouple ports sealed; the quench heat exchanger was also in place in the reactor. The reactor under test was instrumented with a pressure gauge and a pressure relief valve was provided to avoid excessive pressure buildup. The first reactor was pressurized to 30 psig (308 kPa). The reactor was equipped with a 3/16-inch (0.48-cm) thick quartz window, rather than the 0.5-inch (1.27-cm) thick window used in the tests at the WSSF. At 30 psig, the 3/16-inch window blew out. While awaiting delivery of 0.5-inch windows, leak testing was conducted by substituting an aluminum plate for the window. The criteria subsequently developed for a successful leak test was a pressure loss not to exceed 2 psi (14 kPa) in five minutes from an initial pressure of 20 psig (239 kPa). The first reactor performed acceptably both with an aluminum disc and with the 0.5-inch window. Care was taken to torque the window-retaining ring evenly and to minimum torque to ensure sealing. However, the second reactor showed a significant leak down rate; the leak was found to be coming from where the thermocouple assemblies, used to sense reactant temperature, screwed into the reactor body. The thermocouple fittings were welded into the body of the reactor (the second reactor only, the first reactor was leak free). However, when assembled at the WSSF, the reactor still leaked. It was rewelded by WSSF personnel, but has never been leak tested again because the risk of missing an opportunity to run an experiment was too great if the leak still existed. The underlying problem was that the curved shell of the reactor did not allow sufficient "bite" to assure good sealing for a threaded fitting. Further, welding was difficult because the fittings were spaced very closely. The problem was not insurmountable. WSSF personnel welded the fittings on the inside of the shell, and this cured the problem.

The platinum thermocouples were evaluated for compatibility with cadmium oxide and reaction products by immersing the thermocouple in CdO and heating to 1500°C in a laboratory box furnace. Microscopic inspection of the thermocouple showed very fine surface cracks indicating grain growth, the result of exposure to high temperatures.¹⁹ The thermocouple was clean, not

embrittled, and gave identical temperature readings to a brand new thermocouple. This was considered a satisfactory result.

Cadmium oxide was loaded onto a zirconia channel and heated to 1500°C in the laboratory box furnace. No interaction of the materials was observed. This test validated the selection of zirconia as the reactant support material.

Experimental Plan

An experimental plan was drawn up to formalize the planning of the CdO dissociation experiment at the WSSF. The plan was submitted to the WSSF personnel and also to SERI. A copy of the plan appears in this report as Appendix B. The experimental plan described the ten experiments planned at the WSSF to identify the reaction rate of cadmium oxide dissociation. Several runs were planned at reactant temperatures of 1200°, 1300°, 1400°, and 1500°C. Three scenarios were identified that defined the time to complete experimental runs, based on the time to complete critical tasks. The tasks identified in accomplishing an experimental run were: reaction setup, system leak test, bringing the reactor up to an initial temperature of 800° to 1100°C, heating the reactor to the reaction temperature, taking data during the reaction, cooling the reactor, reactor removal, cleanup, and data reduction. The scenarios projected the time to complete an experiment ranging from completion of one experiment in a 15-hour day to completing two experiments in a 9-hour day. Because the times required for reactor heat-up, cooldown, assembly and disassembly, and oxygen detector stabilization were not known, it was difficult to anticipate the precise number of runs accomplishable per day.

Plan no. 1 was the most conservative: It allowed for only one run per day.

Plan no. 2 was more optimistic: It allowed one run each on the first and second days, followed by two runs the third day, one the fourth, two the fifth day, etc. This allowed sufficient time on the first two days to gain complete familiarity with the solar furnace and the experimental procedure. After the first two days, the alternation of one run and two runs per day assured sufficient time to setup the experiment for the two-run days.

Plan no. 3 was the most optimistic: It provided for two runs per day for five days.

Of course, the experimental plan was tentative. The actual operation of each experiment followed closely the steps of the plan and the scenario of completing one experiment in a 9-hour day.

117(3000)/65030Tas1

TASK 2. OPERATION OF THE EXPERIMENT AT WHITE SANDS SOLAR FACILITY

Experimental work was scheduled for 10 days during the period from August 23 to September 6, 1980. Work actually carried out is summarized in Table 2; the four experiments completed are detailed below. Because of clouds and rain, it was possible to operate the solar furnace on only five of the days reserved for our use.

The first three experiments were essentially shakedown tests, where we learned how the reactor would behave in a high solar flux — what reactant temperatures to expect from a given attenuator setting, how fast the reactor heated up and cooled down, some feel for the rate of oxygen evolution, how to assemble and disassemble the reactor as quickly as possible, and how the instrumentation behaved. The fourth experiment was the most successful from the standpoint of yielding quantitative data. Nonetheless, all but the first experiment provided useful qualitative results that establish the feasibility of decomposing cadmium oxide in a solar flux.

Setup of Experiment

The first step in setting up an experiment was the cleaning of the reactor to remove the residues from the previous run. All new ceramic parts and thermocouples were used for each run. The inner asbestos window gasket was replaced to guarantee a good seal of the window to the flange. A new O-ring was also used. While still in the laboratory, a new quartz wool plug was inserted in the rear of the reactor, the quench heat exchanger was inserted and sealed, and platinum thermocouple assemblies were made up.

The reactor was then carried to the furnace room where final assembly of the experiment was completed. The ceramic parts were inserted in the reactor. The thermocouples used to sense reactant temperature and outlet gas temperature were fitted to the reactor. Using face masks to avoid inhalation of CdO dust and surgical gloves to avoid contact with reactant, a beaker was filled with CdO and each reactant support channel was loaded. The weight of reactant on each channel was determined and recorded. After loading the reactant onto the channels, the reactor was sealed by fastening the window flange to its mating flange on the body of the reactor. The quartz window had been cleaned and reused or replaced by a spare in the laboratory. The reactor was bolted to the three axis table. Subsequently, argon lines, water inlet and drain

Table 2. LOG OF EXPERIMENTS AT WSSF

Experiment No.	Date	Experiment Plan	Accomplishments
1	Sat., Aug. 23	None	Equipment setup
	Sun., Aug. 24	None	Equipment setup
	Mon., Aug. 25	--	Cloudy, no tests
	Tues., Aug. 26	--	Cloudy, no tests
	Wed., Aug. 27	Heat reactor slowly to reach 1200°C in about 3 hrs	Aborted after 85 min due to gasket problems and clouds; max temp = 817°C
	Thurs., Aug. 28	--	Leaky reactor, no experiment despite clear skies
2	Fri., Aug. 29	Heat reactor slowly to reach 1200°C in about 3 hrs	Cd produced, but no O ₂ detected; reached 1350°C before test terminated due to clouds
	Sat., Aug. 30	--	Cloudy, no tests
	Sun., Aug. 31	None	WSSF closed
	Mon., Sept. 1	None	WSSF closed
3	Tues., Sept. 2	Heat to 1000°C in about 1 hr, then raise temperature quickly	Cd produced; O ₂ detected, but in meager amounts; bulk of reactant consumed before high temperatures were reached; max temp = 1610°C
4	Wed., Sept. 3	Heat to 550°C for 20 min, then open attenuator to maximum opening in Experiment 3	Cd produced; O ₂ production rate measured; fairly constant temperature of 1400°C maintained for 20 min
	Thurs., Sept. 4	--	Cloudy, no tests
	Fri., Sept. 5	--	Cloudy, rain, no tests
	Sat., Sept. 6	--	Cloudy, no tests

lines, thermocouples, and the effluent heat exchanger were connected. A schematic of the argon flow and the flow path of gases exiting the reactor is shown in Figure 9. Figure 10 shows the reactor as installed in the furnace room.

Having completed plumbing and instrument connections to the reactor, a leak test was performed to ensure the integrity of the system. In the leak test, the reactor and gas plumbing were pressurized to 20 psig (239 kPa) with argon. Valves on the rotameter to the oxygen analyzer, control valve, and positive shutoff valve were closed. Thus, the pressure test proved the system was "leak free" as far as the inlets of these valves downstream of the reactor. The pressure in the reactor was monitored and the reactor was deemed leak free if the pressure in the reactor took longer than five minutes to decay to 18 psig (225 kPa). The pressure in the reactor consistently took five minutes or longer to decay to 18 psig.

Upon successful completion of the leak down test, the positive shutoff valve was opened fully, the inlet rotameters were set to give 10 liters per minute of argon flow, inlet rotameter to the oxygen analyzer was set to flow 0.5 liter per minute, the control valve was opened fully, and the positive shutoff valve was closed. The purge valve on the pressure relief valve was opened to purge this line of air and then was closed. After gas had flowed for several minutes, the baseline on the oxygen analyzer stabilized, indicating the reactor was oxygen free and the oxygen analyzer was ready. Cooling water was turned on to cool the water-cooled aperture, window flange, body of the reactor, quench heat exchanger, and the effluent heat exchanger. The setup procedure took approximately two hours for the first run and decreased in subsequent experiments as greater familiarity with the system was gained.

Solar Furnace Preparation

At this point, the reactor was positioned to the side of the focal plane and a calorimeter provided by WSSF was located at the focal plane. The first step in preparing the solar furnace for operation was to remove lines securing the heliostat. The furnace operator then brought the heliostat on track. Once the heliostat was on track, the attenuator was opened fully, with the fast shutter still closed. The shutter was opened, a calorimeter reading taken, and then the attenuator and fast shutter were closed. In conjunction with a measurement of the direct normal insolation and solar time, the

A81051030

Figure 9. ARGON AND ARGON/OXYGEN GAS FLOWS IN CADMIUM OXIDE DISSOCIATION EXPERIMENT.

P81051087

Figure 10. REACTOR INSTALLED ON THE 3-AXIS TABLE
IN THE FURNACE CONTROL ROOM
[The Calorimeter (Circular Object to the Right of the Reactor)
is in Place Behind the Fast Shutter, Ready to Take a Reading]

facility operator could determine the flux at the center of the focal plane at any other attenuator position and solar time. The reactor was then moved into position behind the water-cooled aperture and the shutter was opened.

Preparation of the solar furnace took about one hour.

Experiment 1

In the first experiment, we had planned to measure the reaction rate at 1200°C. Because we expected the ceramic components to be very susceptible to thermal shock, we intended to heat the reactor to 1200°C over a period of about three hours, then hold the temperature steady at 1200°C.

It immediately became apparent that the flux was not uniform across the reactant bed as we had hoped. This can be seen in the plot of reactant temperatures versus time (Figure 11) where the reactant bed temperature in the top channel was as much as 150°C lower than the temperature in the next channel down. The thermocouples in the two lowest channels were inoperative. The thermocouples proved to be quite delicate; much greater care in assembling and handling was used in subsequent experiments.

The experiment began with a total argon flow rate of 10 l/min with 3.3 psig (124 kPa) pressure and 29.73 g of reactant (Table 3) inside the reactor. The water flow rate through the quench heat exchanger was 6.6 l/min. Cooling water temperature was 28° to 29°C. In all four experiments, the quench heat exchanger outlet water temperature was never more than 2°C higher than the inlet temperature. Also, in all the experiments, the gas temperature at the outlet of the effluent heat exchanger was never more than 28°C.

At twenty minutes into the experiment, the internal reactor pressure had increased to 10 psig (170 kPa), and the argon flow rate had dropped to about 5 l/min. Apparently, the quartz wool plug was becoming clogged. Thin wisps of white smoke could frequently be seen coming from the reactant, which appeared to blacken as it was exposed to the solar flux. Within 25 minutes the reactor pressure had increased to 17 psig (219 kPa). As a safety precaution, the pressure regulator at the argon tank was set at about 18 psig (225 kPa), so neither the reactor pressure, nor the argon flow rate, which was now down to 4.5 l/min, could be increased. At 63 minutes, a strong smell of burning rubber was coming from the reactor. Because there were no rubber materials in contact with the reactor, which was still cool enough to touch,

Figure 11. REACTANT TEMPERATURE HISTORY — EXPERIMENT 1

Table 3. LOADING OF REACTANT ON CHANNELS

Channel No.	Experiment No.			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
	g			
1 (Top)	6.69	4.79	4.35	4.04
2	9.32	6.88	6.40	6.93
3	7.79	6.12	6.71	6.30
4 (Bottom)	<u>5.93</u>	<u>5.13</u>	<u>4.05</u>	<u>3.54</u>
Total	29.73	22.92	21.51	20.81

we concluded that the asbestos gasket must be deteriorating. It was presumed, though not yet known then, that the asbestos contained some organic binder that was being driven off as the window heated up. There was immediate concern that the gasket might fail, allowing toxic fumes to be leaked from the reactor. At 73 minutes, we observed that the window was partially clouded by some white material, and even the vent lines 15 feet (5 m) downstream were becoming cloudy. The argon flow rate had dropped to 2.5 l/min. When smoke began evolving from the front of the reactor at 82 minutes, we decided to abort the experiment so we could determine what was causing the smoke and what was happening to the asbestos gaskets. The attenuator was closed at 84 minutes and shutdown at 85 minutes. At that moment, clouds began passing over White Sands Solar Facility, so the experiment would have ended then even without the other problems. From a maximum reactant temperature of 817°C, the reactor cooled to room temperature in less than 100 minutes with cooling water still flowing.

A postexperiment leak test showed the reactor leaked at a lower rate than before the experiment. Though the gasket material may have begun to deteriorate, it still provided an adequate seal.

The surface of the brown CdO on the channels had turned blackish brown. The material seemed to have settled, or compacted, considerably, because no oxygen was detected by the TCD, and little, if any, of the CdO could have decomposed.

A section of the inside of the window, about 1/4 of its area, was clouded with a white substance, easily removed by wiping. The clouding was reduced near an argon injection port, indicating that the clouding might not have occurred at all if the argon flow rate had not been reduced to a quarter of the design flow rate because of clogging of the quartz wool plug.

There was a significant buildup of some black substance around the inside edges of the front flange and around the rear flange just outside the ceramics. The composition of this black substance is unknown. It may have been carbon if organic binder from the gasket was thermally cracked inside the reactor. Or, it could have been finely-divided cadmium or cadmium oxide, which would explain why it was easily wiped off using dilute nitric acid.

The inner window gasket was yellow-green around its perimeter except at one point where a broken alumina peg sat at the bottom of the flange next to the window. The discoloration appeared to be the result of thermal decomposition of the gasket or, more likely, its organic binder. The peg seemed to have blocked reradiation from inside the reactor and kept the edge of the gasket relatively cool at that spot.

The window itself apparently devitrified somewhat. It was cloudy in the central portion below the surface of the quartz on the reactor side. Although the maximum temperature measured inside the reactor was about 800°C — below the devitrification temperature — the window may have been hotter. This could have resulted because the gas flow rate was too low, or because once the window became clouded it was absorbing instead of transmitting much of the flux.

The ceramic components were completely unscathed.

The top front tube of the quench heat exchanger was thickly coated with what appeared to be the same white substance found on the window. The rest of the heat exchanger was coated nonuniformly with material with colors ranging from brown to grey to black. The walls of the reactor surrounding the heat exchanger were also coated, with the heaviest coating at the top. As much of this material was scraped off the heat exchanger and walls as was possible and saved for chemical analysis later. The amount recovered was approximately 1.5 g.

The quartz wool plug, as expected, was completely filled with more of the unknown white substance.

The heat exchanger and reactor interior were easily cleaned using nitric acid. This solvent was used because it very readily dissolves both cadmium and cadmium oxide but generally does not affect 304 stainless steel. We had planned to use new ceramic parts in each subsequent experiment until it became necessary to reuse some part. Because only four experiments were completed, new ceramics were used in all.

Experiment 2

Two measures were taken to prevent further problems with the gaskets. First, the 4.75-in. (2-cm) water-cooled aperture was replaced with a 3-in. (7.6-cm) aperture. By increasing the distance from the flux-heated portion of

the window to the gasket edge from 0.5 in. (1.3 cm) to 1.4 in. (3.6 cm) the gasket was expected to remain cooler. From our experience in Experiment 1, we felt the smaller aperture should still provide much more flux than we would need. Second, a ring of Fiberfrax ceramic felt was placed inside the front flange next to the window to shield the gasket from heat radiated from the reactor interior. We had no further problems with the inner gasket. The outer gasket, which did not seal anything, but rather served only as a cushioning material, continued to decompose and emit gases that smelled like burnt rubber in each experiment. But the unpleasant odor was the only problem encountered.

The second experiment was to be conducted on the day following the first experiment. However, after setting up and loading the second of our two reactors, we found it leaked badly around two welded fittings that we had presumed were leak-tight. It took the rest of the day to prepare the first reactor for another test. The one reactor was used in all four experiments.

The plan for the second experiment was the same as for the first: heat the reactor up to 1200°C slowly over about 3 hours to avoid thermally shocking the ceramics, then hold the temperature steady at 1200°C to measure the oxygen evolution rate.

In this and the next two experiments, thermocouples were attached to the outside surface of the reactor shell using worm-drive clamps, so the surface temperature would be accurately known.

Argon and water flow rates were established as in Experiment 1. The temperature record of this experiment, which lasted 3-1/2 hours, is shown in Figures 12 and 13. Very steady temperatures were attained in this experiment, but again they varied greatly from one channel to the next, this time by as much as 250°C. The small step-changes in temperature, especially noticeable in the latter half of the experiment, occurred each time the attenuator opening was increased.

A log of Experiment 2 follows:

- 30 min — Light gassing or smoking from the reactant was first observed. Such gassing was seen periodically up to about 85 minutes.
- 73 min — The ceramic front support ring was cracked through, although the channels and reactant still seemed well supported and in no danger of collapsing. The cracking occurred after a step change in attenuator position.

Before the change, temperatures ranged from 565° to 700°C; after the change, they ranged from 730° to 815°C. The high rate of change in temperature apparently shocked the ceramics. At this time, we began to smell gasket degradation.

- 88 min — Reactor pressure had increased only slightly, from 3.8 psig (128 kPa) at the start to 4.65 psig (133 kPa). The window was still clear. The gas temperature at the reactor outlet was up to 107°C; the highest reactor surface temperature was 137°C at the top of the shell just above the quench heat exchanger.
- 93 min — Temperatures were fluctuating because of manual heliostat tracking adjustments, but otherwise were holding steady.
- 107 min — Attenuator was opened another 0.5 degree. The reactant appeared to be darkening a bit, although the extreme brightness and consequent use of dark glasses or welding goggles made color judgements unreliable.
- 125 min — The attenuator was opened another 0.3 degrees. This marked the beginning of a slightly more rapid run-up to reaction temperature.
- 135 min — The attenuator was opened another 0.3 degrees.
- 145 min — The attenuator was opened another 0.4 degrees.
- 147 min — The reactant appeared to be dark brown, with a texture more like coral than powdery.
- 157 min — The attenuator was opened another 0.4 degrees.
- 166 min — The attenuator was opened another 0.3 degrees. The reactant seemed to have settled somewhat. The reactor pressure had increased slightly to 5.2 psig (137 kPa).
- 173 min — The attenuator was opened another 0.4 degrees.
- 174 min — The reactant temperature in channel number 3 reached 1200°C. There was no noticeable change in oxygen evolution. The TCD had been reading a fairly uniform 0.04 to 0.06 mV since 20 minutes into the experiment, but because we had had trouble establishing a smooth baseline before the experiment began, this upscale reading was discounted as baseline drift.
- 182 min — The attenuator was opened another 0.3 degrees to 13.0 degrees.
- 192 min — The attenuator was opened another 0.3 degrees.
- 200 min — The attenuator was opened another 0.3 degrees. The reactant appeared compacted. The reactor interior looked dirty, possibly because of condensing cadmium oxide.
- 211 min — The attenuator was opened to 14.0 degrees.

Figure 12. REACTANT TEMPERATURE HISTORY — EXPERIMENT 2

Figure 13. REACTANT TEMPERATURE HISTORY — EXPERIMENT 2

- 217 min — Clouds. Reactant temperatures dropped precipitously from 1385°C down to about 830°C in the first minute. The experiment was terminated. The gas temperature at the reactor outlet reached 289°C before the clouds arrived. The temperatures on the surface of the reactor shell ranged from 169°C above the reactant channels to 263°C above the quench heat exchanger.
- 217.5 to 218 min — The TCD reading dropped from 0.033 to 0.016 mV. This drop is miniscule, only 1% of full scale, but nevertheless the only significant change in TCD output that occurred during the entire experiment. That this change occurred immediately following the sudden drop in reactant temperatures strongly suggests that the upscale reading during most of the experiment was caused by the presence of oxygen and not simply baseline drift. Within 7 minutes, the TCD reading appeared to have settled to a new baseline that ranged from 0.0004 to 0.015 mV during the next 75 minutes.

At the end of the experiment, the reactant was black. All four channel thermocouples were exposed, though we do not know for how long because that part of the reactor could not be seen while the experiment was in progress. It appeared that a substantial amount of reactant had either vaporized or reacted.

The window was still clear, and we could see no evidence of devitrification. The inner gasket appears to have degraded somewhat, judging from the yellow-green discoloration around its inside edge and on the Fiberfrax, where it contacted the gasket. However, it appeared none of the gasket decomposition products passed the Fiberfrax.

The ceramic front support ring was cracked in two places. The second crack, on the side of the thermocouple leads, could not be seen while the experiment was in progress. The rear support ring was cracked in three places. The mullite outer liner was cracked in half circumferentially, forming two shorter tubes. The crack was in the plane of the front surface of the front support ring and was probably not caused by thermal shock, but by simple thermal stress resulting from the two ends of the liner being kept at different temperatures. The front half of the liner was just inside the shell cooling jacket, the coolest point in the reactor, whereas the rear half was just outside the reactant bed, the hottest point in the reactor. The thin Fiberfrax mat between the outer liner and the steel shell may have helped alleviate the temperature gradient, but not enough to fully protect the mullite liner.

The quench heat exchanger was well coated with materials showing a wide range of colors. The top front tube was coated with shiny beads, generally

light gray. The roof of the reactor above the heat exchanger was coated with the same material. The next two tubes down were coated with a greenish-yellow substance, slightly granular in texture. The fourth tube had a smooth light-green coating, and the bottom tube was dark green with streaks of different shades. The fronts of the manifolds, especially the bottom half, showed striking variations in color — black, brown, green, yellow, and gray.

Chemical analyses were not available to us at the solar facility. However, we did use a simple, qualitative test to differentiate between cadmium and cadmium oxide based on the reaction of these substances in nitric acid, Reactions 4 and 5.

Cadmium metal reacts vigorously with nitric acid, releasing hydrogen, whereas CdO simply dissolves. Using this "fizz test," we determined that the shiny, beady material on the quench heat exchanger was metallic cadmium. Apparently, cadmium and oxygen were being produced throughout the experiment, but at very low rates.

The quartz wool plug, though well filled with variously colored and textured materials, obviously did not significantly impede the flow of gases through it. This was probably because a much larger plug (about the size of a fist before packing into the reactor) was used in this experiment. The plug used in the first experiment was only about an inch across.

The materials coating the heat exchanger and reactor walls were scraped off and saved for subsequent chemical analyses.

Experiment 3

It was apparent in Experiment 2 that some oxygen was produced, but at a barely detectable rate. The plan for Experiment 3 was to flux the reactant with energy at a rate sufficiently high to produce amounts of oxygen that would drive the TCD reading well up-scale. Our immediate goal now was to simply establish conclusively that cadmium oxide could be decomposed in our reactor; the proof would be an undisputable output of oxygen.

Only one significant change was made in the experimental setup. A blower was arranged to blow air on the rear-shell area of the side of the reactor,

opposite the channel thermocouples to keep the surface temperatures lower. This would augment the cooling of the gases to condense the cadmium and help prevent recombination with oxygen. (Because an air conditioner was kept running whenever the furnace was operated, ambient temperatures inside the control room never exceeded 24°C.)

In this experiment, we again planned to heat the reactor slowly, but to no more than 1000°C, then to open the attenuator 4 to 5 degrees at a time to raise the reactant temperature quickly to where the reaction rate would be high. The experiment began at 9:16 am with the attenuator initially opened 3.3 degrees. After 10 minutes, the temperature in the top channel, the highest, (Figure 14) had leveled off at about 595°C. The attenuator was opened another 0.2 degrees then, and again at 14 minutes, then another 0.1 degrees at 18.6 minutes, 23.4 minutes, 43.4 minutes, 47.7 minutes, 53.3 minutes, 54.4 minutes, 61.3 minutes, 64.2 minutes, 65.9 minutes, and 68.0 minutes. Very few changes were observed in the reactant in the first 70 minutes. At about 35 minutes, it was apparent that some settling or compaction of reactant had occurred because the bases (but not the tips) of the thermocouple sheaths were now exposed. The burnt-rubber odor from the gaskets was first noticed at 42 minutes.

The TCD output (Figure 15) at zero minutes was 0.005 mV (0.02% O₂), the nonzero reading caused either by baseline drift or traces of oxygen (air) that was not purged from the reactor. When the attenuator was first opened, a small hump appeared in the TCD output, reaching a maximum of 0.037 mV (0.17% O₂) at about 3.5 minutes, and lasting until 7 minutes, where it leveled off at 0.023 mV (0.11% O₂). Between 30 minutes and 70 minutes the reading increased very slowly, but quite steadily, to 0.05 mV (0.02% O₂).

At 71.1 minutes, the attenuator was opened another 3.7 degrees, and at 71.5 minutes the TCD output began a comparatively steep rise. When this seemed to be leveling off at about 0.08 mV (0.4% O₂) after 2 minutes, the attenuator was opened another 4.9 degrees, at 73.3 minutes. This resulted in an immediate rise in the TCD output, which reached a peak of 0.17 mV (0.82% O₂) at 74.3 minutes. Reactant temperatures at this time ranged from 1170° to 1380°C. When the attenuator was opened another 5 degrees at 75.8 minutes, the TCD output quickly rose to 0.25 mV, the highest value reached in any of our experiments. This reading corresponds to an oxygen concentration of about 1.2%. Reactant temperatures reached 1610°C at about 77 minutes.

The quartz window seemed to begin fogging at about 76 minutes, although the fogging was only on the cooler portions of the window; the center remained clear.

By 77 minutes, it appeared the center and bottom channels were almost out of reactant; the rapid and steady decline in the TCD output seemed to substantiate this. At 78 minutes, the attenuator was closed 5.6 degrees to begin a slow cooldown of the reactor. The TCD output leveled off at about 0.07 to 0.08 mV until 85 minutes when, after the attenuator was closed another 3.6 degrees, it leveled off again at 0.06 mV. It remained there for the next 23 minutes, despite the closing of the attenuator after only 15 minutes. At about 108 minutes, with the reactant now down to 330°C, the TCD output began to rise slowly, eventually reaching 0.22 mV at 185 minutes, long after the reactor had cooled to room temperature, and only pure argon was flowing through the system. Although the peaks observed earlier were without doubt the result of oxygen presence, the unpredictable behavior of the TCD leaves the data essentially useless from a quantitative standpoint.

The blower worked well, keeping the reactor shell cool. The maximum surface temperature in this experiment was 141°C, compared with 263°C in the previous experiment.

Once the reactor had cooled, it was found that fogging on the window seen earlier was a brown discoloration, possibly CdO, and occurred only at the relatively cool edges of the window. The center of the window, where the high flux levels were, was clear. The Fiberfrax insulation that protected the gasket was stained lightly with black on the window side; next to the gasket it was stained yellow-green because of some gasket decomposition. The alumina inner liner was stained brown, nonuniformly with most of the stain at the top. (See Figure 16.) The front support ring was cracked in two places. The zirconia channels, as always, were undamaged, but had changed color, from orange to off-white, where they were exposed to the solar flux. The tips of the thermocouple sheaths were significantly degraded, appearing corroded or decomposed, although the thermocouples themselves functioned throughout the entire experiment. The middle two sheaths seemed to be fused to the zirconia, though the zirconia was unaffected. The ends of the channels, which were shadowed by the front support ring, were coated with a hard, crystalline, sparkling, black substance that did not fizz in nitric acid, but did appear

Figure 14. REACTANT TEMPERATURE HISTORY — EXPERIMENT 3

Figure 15. THERMAL CONDUCTIVITY DETECTOR (TCD) (Oxygen Analyzer)
MILLIVOLT OUTPUT — EXPERIMENT 3

P81051082

Figure 16. INTERIOR OF REACTOR AFTER COMPLETION OF EXPERIMENT 3

more brownish, like CdO , as it dissolved. The black material was found mostly on surfaces that originally held no reactant. The rear support ring was cracked in three places and coated with more of the sparkling, black substance, though the color tended more toward brownish gray than on the channels. The mullite liner had a hairline crack through its middle, but remained in one piece.

The quench heat exchanger was thickly coated with a grayish material that fizzed strongly in nitric acid, indicating a high content of metallic cadmium. Part of the top tube was covered with an extremely fragile fibrous or weblike crystal growth of a black, sparkling material that did not fizz in nitric acid. This was the only occurrence of this black mold-like growth. A large quantity of material also condensed on the inside walls of the rear of the reactor, presumably because the blower had kept the reactor shell so cool.

Experiment 4

In Experiment 3, it appeared by the time the attenuator was opened widely, much of the CdO had reacted. Not only did this leave little material from which oxygen, and, therefore, rate data, could be obtained, but it also left thermocouples exposed. Once a thermocouple is exposed, it no longer measures the temperature of CdO , so it would be very difficult to associate a reaction rate with a temperature. Therefore, in Experiment 4, we planned to expose a nearly full load of reactant to a high flux. To do this, we would heat the reactant for only a short time to a relatively low temperature, about 500°C , to drive off any volatile impurities (such as water), and then pulse it at a flux level we knew would deliver the temperature desired. From Experiment 3, we knew an attenuator opening of about 17 degrees would heat our reactant to about 1500°C . The expected temperature rise of 1000°C in a minute or so would be sure to damage the ceramics; however, based on what happened in the first three experiments, we were confident that only three pieces would break — the two support rings and the mullite liner. — and that even if those pieces broke, they would continue to support the reactant channels in the flux.

The equipment was setup the same as in Experiment 3 except the blower was pointed down toward the top of the reactor where cooling was required most.

The experiment began at 10:20 am with the attenuator opened 7 degrees. Reactant temperatures (Figure 17) began to level-off after 5 minutes, reaching temperatures, after 20 minutes, ranging from 500° to 630°C. The TCD reading (Figure 18) began to rise just 1 minute after the experiment began, resulting in a hump of about 7 minutes duration, similar to, but a little sharper than the one obtained in Experiment 3. A baseline of 0.02 mV (0.09% O₂) had been established before the start of the experiment; after the hump, a steady reading of about 0.026 mV (0.12% O₂) was attained. At 14 minutes, despite a steady flux and nearly constant temperatures, the TCD output began to rise again, leveling off after 20 minutes at 0.075 mV (0.36% O₂). We do not know whether this was because of oxygen production or just more baseline drift.

At 21.4 minutes, the fast shutters were closed, while the attenuator was opened to 17 degrees. At 22 minutes, the fast shutters were reopened to begin the pulse of high flux. Reactant temperatures rose sharply — as much as 720°C in the first minute — as did the TCD output, which peaked after 2 minutes at 0.155 mV (0.75% O₂). Temperatures leveled off 10 minutes after the pulse began, with the highest temperature fluctuating between 1410° and 1440°C. The TCD reading decreased slowly.

During this experiment, photographs of the reactor were taken by a WSMR photographer stationed in the concentrator framework. At 23 minutes, one minute after the pulse began, the photographer reported that reactant was dumped from one of the channels. The channel apparently was jolted by the sudden expansion or cracking of some piece of ceramic; after dumping its load, the channel remained in place, still supported. However, all the channels had been tilted slightly out of horizontal, as though the front support ring had rotated a few degrees. Figures 19 and 20 show the reactant bed just before and just after the reactant was dumped from the No. 3 channel.

Although the window was reported to have begun to fog up just when the shutters were opened, it was clear a minute and a half later. At 26 minutes (4 minutes after the pulse began), the ceramics seemed to be getting darker, possibly because of CdO condensing on cooler surfaces. At 28 minutes, a loud pop of cracking ceramics was heard. Burning rubber was first smelled at 30 minutes.

At 54.3 minutes, it appeared there was little material remaining on the channels, so at 55 minutes, the shutters were closed to terminate the experi-

ment. A calorimeter reading was taken at 58.4 minutes, which showed the flux level during the pulse was 30.7% of the maximum flux, or about 21.5 cal/cm. When the shutters were closed, the TCD output began to decrease at a slightly higher rate, then leveled off at 0.05 mV, where it stayed until about 108 minutes, when it rose to, and stayed at, 0.06 mV. Once again, the accuracy of the TCD data was compromised by the baseline drift.

At the end of the experiment, the center of the window, where the flux passed through, was clear, but the area between the Fiberfrax and the edge of the flux was clouded by a brown substance, probably CdO. It was evident from the stain of condensed CdO on the front support ring that the focus was slightly to the right of center. The unreacted material at the bottom of the inner liner that was spilled from the third channel down was black on the surface, but the bulk of it was brown, the same color as the original reactant. The tips of the thermocouple sheaths in the second and fourth channels were eaten away or corroded like those in Experiment 3. The sheath in the third channel, which was not in contact with CdO during most of the experiment, but was exposed to the highest flux, was undamaged. The sheath in the top channel was also undamaged. Although this sheath was exposed to lower flux levels than the others, an important difference from the degraded sheaths was this one was not in contact with the zirconia channel. It appears there may be some reaction involving alumina when it is in contact with both CdO and MgO-stabilized ZrO.

As in the previous experiments, the only effect exposure to high solar flux and decomposing CdO had on the zirconia channels was to change their color from orange to off-white. Again, their cool ends were coated with black and sparkly black material, essentially the same as in Experiment 3. Both the front and rear support rings were cracked in one place, but still intact. The mullite liner was cracked in half and in somewhat worse shape than it had been after the previous experiments.

The quench heat exchanger, especially the top front tube, was coated with grayish metallic-looking crystals (Figure 21). The bottom tube was black, the second tube from the bottom was yellow-green on the upper half and partly black underneath, and the second and third tubes from the top more closely resembled the top tube. It seemed as one progressed from bottom to top, the more the product resembled metallic cadmium. Substantial amounts of metallic-like material were also condensed on the ceiling of the reactor above the quench heat exchanger where the shell was cooled by the blower. Although the gray dendritic crystals (Figure 22) had the obvious look of metal (and fizzed

Figure 17. REACTANT TEMPERATURE HISTORY — EXPERIMENT 4

Figure 18. THERMAL CONDUCTIVITY DETECTOR (TCD) (Oxygen Analyzer)
OUTPUT — EXPERIMENT 4

P81051083

Figure 19. VIEW OF REACTANT BED, EXPERIMENT IN PROGRESS,
PRIOR TO SHIFTING OF REACTANT BED SUPPORTS

P81051084

Figure 20. VIEW OF REACTANT BED, EXPERIMENT IN PROGRESS,
SHORTLY AFTER SHIFTING OF REACTANT BED THAT DUMPED
REACTANT FROM THIRD CHANNEL FROM TOP

P81051085

Figure 21. QUENCH HEAT EXCHANGER, FOLLOWING EXPERIMENT 4

P81051086

Figure 22. EDGE VIEW OF DEPOSIT FROM QUENCH HEAT EXCHANGER FROM EXPERIMENT 4, SHOWING DENDRITIC CRYSTALS OF METALLIC CADMIUM (Magnification: 23X)

vigorously in nitric acid), it may have not been the only form of metallic cadmium present on the heat exchanger. Some samples of soft powdery flat black material also fizzed in acid, indicating they may be finely divided metal.

117(3000)/65030Tas2

TASK 3. DATA ANALYSIS

Chemical Analyses

After each experiment, as much material as possible was scraped from the quench heat exchanger and the rear part of the reactor and brought back to IGT for analysis. Although substantial amounts of material were trapped in the quartz wool plug, no attempt was made to recover this material because there was no simple and effective way to physically separate it from the quartz. In Experiments 2, 3, and 4, two separate samples were recovered. The first was a small sample of material from the quench heat exchanger that had the physical appearance of metallic cadmium. The second sample consisted of the rest of the material recovered. Table 4 summarizes the analysis of each sample. Each sample was prepared for analysis by grinding it into a fine powder, and the analysis was made of a portion of this now homogeneous sample. The chloride content was determined because the reactant contained chloride. Substances other than Cd^0 , CdO , and Cl^- were not determined, so the percentages in Table 4 do not add up 100.

Table 4. CHEMICAL ANALYSES OF RESIDUE RECOVERED FROM
CADMIUM OXIDE DECOMPOSITION EXPERIMENTS

Experiment No.	Sample Source*	Weight of Sample, g	Composition, wt %		
			<u>Cd^0</u>	<u>CdO</u>	<u>Cl</u>
1	QHE, RR	~1.0	22.3	37.7	8.06
2	QHE	0.80	83.8	13.5	1.20
2	QHE, RR	4.25	62.4	31.6	2.17
3	QHE	1.39	66.8	30.2	0.97
3	QHE, RR	4.00	46.0	48.5	1.76
4	QHE	1.97	81.8	15.2	0.77
4	QHE, RR	1.35	50.6	43.4	1.91

* QHE = Quench Heat Exchanger, RR = Rear of Reactor.

The metallic cadmium content of the samples is surprisingly high. This indicates that Cd and O_2 do not recombine in the gaseous state to the extent feared. Cadmium vapors that were carried to the vicinity of the quench heat exchanger succeeded in condensing as a metal and were quite effectively quenched. It also implies that CdO does not sublime appreciably, tending to confirm the most recent studies on CdO vapor pressures. As reported earlier,

substantial amounts of CdO coated the ceramics that were near or downstream of the reactant bed and were neither actively heated by direct solar flux nor actively water-cooled. Apparently, cadmium condensed on these surfaces, but then oxidized. If cadmium oxide formed directly from cadmium vapor and oxygen, then the oxide content of the heat exchanger deposits should be much higher.

The high cadmium contents of samples from Experiments 1 and 2 are particularly noteworthy because the temperatures recorded in those experiments were quite modest. The most obvious explanation for this is that the reactant surface temperatures were considerably higher than the temperatures measured by the thermocouples buried in the reactant. On the other hand, there are no peaks or step changes in the temperature history curves to indicate a hotter surface just before the thermocouple became exposed, so the surfaces may not have been significantly hotter than indicated by the thermocouples. In this case, the high Cd content of the samples from Experiments 1 and 2 would imply that the decomposition rate is controlled by the heat transfer rate. This conclusion is reached by observing that in each experiment the amount of cadmium recovered is very roughly proportional to the product of the flux level (which is proportional to the measured reactant temperature) and the length of time at that flux level.

It was our original intention to continue each experiment until all the CdO loaded into the reactor had decomposed. This proved to be impractical for several reasons. First, two of the experiments were halted by clouds and by equipment malfunctions. Second, once the thermocouple junctions were exposed, temperature measurements were meaningless, so there was little point in continuing the experiment. And third, because the flux levels at the edge of the reactant bed were so much lower than at the center, the experiments would have to have been continued for several hours, long after the thermocouples were exposed, just to decompose the last traces of reactant. Therefore, in none of the experiments was a high degree of conversion of the initial load the goal. Rather, we were interested in high relative conversion (that is, a high ratio of metallic cadmium product to reacted cadmium oxide, some of whose decomposition products recombined). However, because it was not possible to do a mass balance, we could calculate neither the absolute nor relative conversions, but only the minimum absolute conversions. These are reported in

Table 5. These calculations are based on the amount of Cd actually recovered and analyzed and the initial charge of CdO. The actual conversions are higher because unknown quantities of cadmium trapped in the quartz wool are not taken into account, and not all the material was recovered from the quench heat exchanger; as much as 10% may have remained on the heat exchanger.

Table 5. ESTIMATED MINIMUM CONVERSION OF CdO TO Cd

Experiment No.	Cd Recovered		Initial CdO Load		Minimum Conversion, %
	g	m mol	g	m mol	
2	3.32	29.5	21.71	169.1	17.5
3	2.77	24.6	20.37	158.6	15.5
4	2.29	20.4	19.71	153.5	13.3

Analysis of TCD Output — Experiment 4

Only in Experiment 4 were sufficient data obtained even to begin an estimate of the reaction rate. Because these data (the TCD output) are of questionable accuracy, because the temperatures were far from being either constant or uniform, and because we have data from only one experiment, it must be emphasized that the reaction rates presented here are the crudest of estimates — ballpark figures at best. They are intended only to give us some idea of what rates to plan for in future work and should not be used in designing or sizing a reactor for CdO decomposition.

The data were analyzed as follows: First, the TCD readings were corrected for baseline drift by assuming that the baseline changed linearly during the course of the experiment. Values of emf were converted to oxygen mole fraction by means of the calibration curve, Equation 1. From the known argon flow rate, the oxygen production rate was calculated. Integration of the curve of oxygen production rate versus time gave the total amount of oxygen produced during the experiment as 0.066 mole. This corresponds to an 86% conversion. This seems unrealistically high when compared with the measured minimum conversion of 13.3% and when one considers that about a fourth of the reactant was dumped out of its channel and not reacted. The high estimate is probably caused mainly by an inaccurate treatment of baseline drift.

The reaction rate is reported in units of fraction converted per unit time. It is calculated from the oxygen production rate in mole minutes⁻¹ by

dividing by the number of moles of CdO in the reactant initially and multiplying by 2 to account for stoichiometry. The reaction rate is a function of time, or more correctly, a function of conversion. The maximum rate occurred just after the pulse was started, at 24 minutes after the experiment began (Table 6). A typical solid decomposition reaction begins with a relatively short acceleratory period, where the reaction rate is increasing, followed by a deceleratory period often of appreciable length, where the rate slowly decreases. This behavior was displayed by CdO in this experiment.

Table 6. CdO DECOMPOSITION REACTION RATES IN EXPERIMENT 4

<u>t, min</u>	<u>Calculated Fraction Converted</u>	<u>Reaction Rate, min⁻¹</u>
22	0.119	1.2×10^{-2}
23	0.139	2.9×10^{-2}
24	0.170	3.3×10^{-2}
25	0.203	3.2×10^{-2}
30	0.341	2.5×10^{-2}
40	0.556	1.8×10^{-2}
50	0.701	1.2×10^{-2}
60	0.797	6.3×10^{-3}
70	0.846	3.5×10^{-3}
80	0.860	0

Engineering Analysis of Cycle L-2

The preliminary flow sheet analysis of this cycle incorporating the following basic assumptions was previously performed⁴:

- Hydrogen is produced at 3.04 MPa pressure to avoid the penalties associated with compression to pipeline pressures.
- Oxygen by-product is vented to the environment; no credit is taken for possible beneficial applications.
- Cooling water is available at 27°C.
- The minimum ΔT across the heat exchangers is 25°C; larger ΔT 's are used where appropriate.
- Pumps, compressors, and turbines operate at efficiencies of 80%.
- Cadmium hydroxide decomposition is complete.

- Equilibrium conversions are obtained from the cadmium oxide decomposition/sublimation reactions.

In 1979, we developed a computer program to calculate the mass and energy balances and to perform the internal-heat-recovery-stream matching for the process. This program enables us to treat several areas parametrically, because some portions of the process — the hydrogen-producing step, for example — have not yet been fully characterized. In addition, the operating conditions in other areas, such as the decomposition of cadmium oxide, are somewhat flexible; therefore, we can determine the conditions that result in the highest process efficiencies. We did not, however, perform a formal optimization of this process.

In this work we have parametrically studied the effects of the temperature of the high-temperature step — decomposition of cadmium oxide — and the heat recovery from products of cadmium oxide decomposition. Two cases have been considered — complete heat recovery and complete heat loss (quenching). In practice, it may be necessary to quench the products to prevent reoxidation of the cadmium. On the other hand, a complete quench may have such a devastating effect on the efficiency of the process that partial heat recovery will be necessary.

Figure 23 shows the effect of cadmium oxide decomposition temperature, T_{R-3} , on the flow sheet efficiency when Reaction 1 is operated at 0.2 V. Work (electricity) is produced from heat at half the Carnot efficiency. The heat for work generation can come from the primary heat source (at a temperature 25°C higher than the cadmium oxide decomposition temperature), from cooling steps within the process that could not be matched with a step requiring heat (but only if the cooling stream starts above 327°C), or from both. If heat from the products of the cadmium oxide decomposition can be completely recovered (that is, if the heat can be used either by steps required heat, or in work generation), the process efficiency will be very high, ranging from 53.7% to 61.1% as the temperature of the cadmium oxide decomposition step ranges from 1027° to 1627°C. Under these conditions, more work is generated from internally recovered heat than the amount that is required by the process; no primary heat is needed for work generation.

It may be necessary to quench the cadmium oxide decomposition products to prevent the recombination of gaseous cadmium and oxygen. In this case,

A81051034

Figure 23. EFFECT OF CADMIUM OXIDE DECOMPOSITION TEMPERATURE
ON PROCESS EFFICIENCY (Reaction 1 Cell Potential 0.2 V)

neither any of the sensible heat released in cooling cadmium and oxygen nor any of the latent heats of vaporization and fusion of cadmium can be recovered for internal use, or for work generation. The lower curve in Figure 23 shows the effect of quenching on the process efficiency. Over the range of cadmium oxide decomposition temperatures from 1027° to 1627°C, the cycle efficiency is reduced to a range of 37.8% to 42.1%.

Even with quenching, the efficiency of this process is quite respectable when compared with that of other thermochemical hydrogen-producing cycles. Nevertheless, great potential is lost when the decomposition products are quenched. Though some degree of quenching probably is unavoidable, the effort to design the process so at least some of this high-quality heat is recoverable will be amply rewarded with substantially higher efficiencies. Just how this portion of the process should be designed should become apparent as more experimental data become available.

Operated under the conditions of Experiment 4 — CdO decomposition temperatures of 1400°C with quenching of the products — the efficiency of the process would be 41%. If high temperature heat could be recovered from the decomposition products, the efficiency could be raised to 59%.

DISCUSSION AND CONCLUSION

Reactor Design

Overall, the reactor designed for the cadmium oxide dissociation experiment functioned successfully. Problems encountered were associated with materials, transient effects of clouds, effects of argon flow on reaction, temperature measurement, and nonuniformity of the concentrated solar flux.

Problems with materials centered on gaskets, windows, and ceramics. The gasket used to seal the window was an asbestos material with a styrene-butadiene binder. The binder degraded when exposed to high temperatures emitting acrid fumes. Window sealing was not a problem as the gasket retained structural integrity, and each run used a new gasket. However, it was necessary to prevent the fumes from interfering with experimental results by protecting the gasket from exposure to high temperatures. This was done by replacing the original 4.75-inch (12-cm) diameter water-cooled aperture with a 3-inch (7.6-cm) aperture and by inserting a Fiberfrax ceramic felt liner around the inside perimeter of the window mounting flange. The gaskets still emitted fumes even with this protection, but at a lower rate than when unprotected. More important, there was no evidence that any fumes were evolved inside the reactor. In future work, careful attention must be paid to the material compositions.

Windows suffered from problems of devitrification and clouding. In the first experiment, when argon flow became too low as the quartz wool plug became clogged, the window rapidly became clouded by material condensing on the inside surface. This buildup must have caused a significant rise in the temperature of the glass, because subsequent observation showed clouding (devitrification) inside the window material. In other experiments, material condensed around the outside of the diameter of the water-cooled aperture, but where the solar radiation penetrated, the window was generally clear. These results indicate although inert gas injection around the window does help, it is not completely effective in keeping the window clear. Solar radiation penetrating the window will vaporize reactant material in its path, but material may condense on parts of the window that are not being irradiated. Future reactor designs must pay careful attention to keeping the window clear and cool.

Although the zirconia channels did not crack or show any reaction with reactants or reaction products, the alumina and mullite ceramics suffered greatly from thermal shock. To an extent, this is caused by the fairly rapid rise in reactor temperature required by constraints on time to run the experiments. The components of the reactor were deliberately designed to maintain the exposure of the reactant even with ceramic failure and succeeded to this extent. Future work demands consideration of the thermal environment of the reactor, attention to materials compatibility, and perhaps the use of custom components such as specially shaped reactant channel supports.

Another problem occurred when a cloud obscured the sun during an experiment. With no solar input to a reactor having little thermal inertia and high heat loss rates, cooling rates up to 600°C per minute were observed. Future reactor designs should have either considerable thermal inertia to damp-out such transients, or an extremely low thermal inertia that would allow reactant feed rate to be coupled to the level of solar flux. This kind of control would only be possible in a continuous reactor.

The use of thermocouples as a means to evaluate reaction temperature was imperfect. The surface of the reactant could be much hotter than measured because poor conduction through a loosely packed bed of reactant, or the tip of the thermocouple may become exposed leading to a spurious reading. Pyrometry is also imperfect as an alternative. Reactant emissivity is poorly characterized, and the size of the spot is not necessarily representative of average reactant temperature. Of course, the nonuniform nature of the flux leads to a nonuniform reactant temperature.

As noted above, argon flow generally kept the window clear and swept reactant products toward the quench heat exchangers, as desired. However, the upward-curving reactant support channels apparently swept the gas flow upward, and material did not impinge squarely on the front row of the quench heat exchanger tubes as planned, reducing heat transfer rates. The use of a blower to cool the top of the reactor helped offset this effect, condensing substantial material on the ceiling as well as on the quench heat exchanger. But the flow of argon caused rapid convective heat transfer from the reactant, lowering reactor efficiency. The use of an inert gas creates a problem in condensing reaction products because the presence of a noncondensable gas significantly reduces heat transfer to the condensable

materials and also tends to form a mist or smoke of particles that are carried with the gas. Thus, the use of an inert gas to keep the reaction products below equilibrium concentration creates problems in the recovery of reaction products and has an impact on reactor efficiency. On a practical basis, recovery and recycle of a carrier or sweep gas must be considered if it is used.

The ability to characterize mass and energy balances around a reactor is essential for process evaluation. Although the thermal conductivity cell used to detect oxygen evolution suggested the presence of oxygen, the concentration was usually not sufficiently above the baseline to give unequivocal answers on reaction rate. A more sensitive instrument must be used. Although not required in this study, reactor energy balance must be developed to characterize process efficiency as this cycle progresses in development.

The reactor developed for this study performed satisfactorily in establishing the feasibility of cadmium oxide decomposition under the realistic conditions of the solar-furnace environment. The solar-furnace environment is very appropriate for the evaluation of design concepts. However, the solar furnace probably cannot give precise rate data. The flux is too nonuniform, so temperatures of reactant and corresponding reaction rates are also nonuniform.

Feasibility of cadmium oxide decomposition has been established. Problems in reactor design have been identified and the process of finding solutions started. Further development work to precisely measure reaction rates needs to be undertaken and the development of continuous experimental reactors for solids begun.

Field Testing of Solar Experiments

There are certain difficulties in performing solar field tests of chemical experiments that are not normally encountered in the usual laboratory environment, and it is felt that some experiences we had in setting up and operating this project can be of value to future experimenters who are not familiar with a solar installation.

The Operational Group at the White Sands Solar Facility, headed by Mr. Richard Hays, were very cooperative and their advice and assistance were invaluable in helping us plan and perform our experiments. These comments on

the operation of a solar field test are, therefore, not meant in any way to reflect on the quality of the White Sands Solar Facility or its operation.

In planning a solar field test, it is most important to remember that the items normally available in a chemical laboratory are not present at the solar facility. All material and equipment that might be required in operating the experiment must be taken to the site (a considerable amount of equipment, even for a relatively simple experiment). While it is necessary to consider the alternatives to be taken in the event of an unforeseen experimental outcome or an equipment failure, it is virtually impossible to provide for total coverage of these contingencies.

The time factor is also of prime importance in planning a solar field test. Because time on the solar facility is both limited and costly, there is very little room for revision of the experimental setup or operation. In other words, the field test must follow the planned schedule very closely. When using a relatively untried apparatus or experimental procedure, it would probably be best to schedule the field test in two time segments, with an intervening time period. During this intervening time, problems that are discovered in the initial trials could be corrected and the final field tests should yield better data.

Our recommendations for conducting a solar field test are as follows:

- Plan to take all necessary chemicals, materials and support equipment to the solar facility.
- Have a contingency plan for unexpected experimental outcomes and possible equipment failures.
- Request sufficient time on the solar facility to allow for the possibility of rain or cloud cover.
- If possible, schedule the solar tests in two time segments to allow for revisions of apparatus and/or experimental operation.

Decomposition of Cadmium Oxide

One of the most important results of this project was the recovery of samples from the quench heat exchanger that contained a surprisingly large amount of metallic cadmium. The fact that the sample taken from the quench heat exchanger was metallic in appearance and contained between 67% and 84% metallic cadmium would tend to indicate recombination of cadmium vapor and

oxygen can be effectively prevented by the quenching operation. It would also tend to confirm recent studies that show cadmium oxide does not sublime appreciably.

Determination of the decomposition rate of cadmium oxide was severely limited by fluctuating and nonuniform reactant temperatures and baseline drift in the oxygen sensor. However, the estimated rate based on a single run seemed to follow a typical solid decomposition rate pattern with an initial acceleratory period, followed by a longer deceleratory period.

Cycle Efficiency

From a preliminary flowsheet analysis of the cadmium-cadmium oxide cycle, it was determined that at a cadmium oxide decomposition temperature of 1400°C and a requirement of 0.2 V in the electrolyzer the efficiency was 41%, assuming total quenching of the cadmium oxide decomposition products. This efficiency could increase to a maximum of 59% if total recovery of the latent heats of vaporization and fusion of the decomposition products is possible.

FUTURE WORK

To bring the cadmium hybrid cycle to the stage where a complete demonstration unit for the process could be built, the most critical questions that remain to be answered concern the recovery of the cadmium from the cadmium oxide decomposition and the form of the cadmium electrode for the electrolysis step. Both problems are interconnected and future programs should consider both questions.

While the results of this work have proved the feasibility of solar decomposition of cadmium oxide, a more refined and detailed investigation of this step is required. The next generation of solar reactor to be used in the cadmium oxide decomposition should have the following capabilities:

- Improved temperature measurement of reactants and products
- More uniform reactant temperature
- Operation with or without inert carrier gas
- More efficient use of solar flux and better instrumentation to determine energy balance.

In addition, the cadmium vapor from the product stream must be recoverable at the highest possible temperature, and any future solar reactor should be capable of varying the rate of cooling of the product stream. While the next step in the investigation of this process may not address all of these points, it would seem that a continuous type of reactor would provide for more flexible operation.

One major factor in future programs is the need for more operating time on the solar facility. It is imperative that investigators attempting to develop and use solar reactors for quantitative results have sufficient time on the solar facility to check the operation of their unit and make necessary revisions. The ideal situation would be to have a solar installation that is readily available. If this is not possible, the time at the solar installation should be scheduled in two or three increments to allow for equipment improvement between experiments.

REFERENCES

1. Pangborn, J. B. (assigned to American Gas Association), "Thermo-Electrochemical Process for Producing Hydrogen and Oxygen From Water," U.S. Patent No. 3,907,980 (1975) September 23.
2. Pangborn, J.B. and Sharer, J.C., "Thermochemical Hydrogen Production, Annual Report 1973, IGT Project IU-4-14, prepared for the American Gas Association. Chicago: Institute of Gas Technology, December 1973, 68-69.
3. Foh, S.E., Schreiber, J.D., Pangborn, J.B. and Whaley, T.P., "Thermochemical Hydrogen Production, Annual Report for 1979," IGT Project 30517, prepared for the Gas Research Institute. Chicago: Institute of Gas Technology, May 1980, 20-40.
4. Carty, R.H., Remick, R.J., Schreiber, J.D. and Mazumder, M.M., "Thermochemical Hydrogen Production, First Quarter 1980 Report," IGT Project 30517, prepared for the Gas Research Institute. Chicago: Institute of Gas Technology, March 1980, 9-14.
5. Pangborn, J.B. and Sharer, J.C., "Thermochemical Hydrogen Production, Annual Report 1974," IGT Project IU-4-14, prepared for the American Gas Association. Chicago: Institute of Gas Technology, December 1974, 33-35, 16-19.
6. Remy, H., Treatise of Inorganic Chemistry. New York: Elsevier Publishing Co., (1956), 450.
7. Jacobsen, C., Encyclopedia of Chemical Reaction, Vol. II, New York: Reinhold, (1948), 23.
8. Weast, R.C., Handbook of Chemistry and Physics, 50th Ed. B-95. Cleveland, Ohio: The Chemical Rubber Co., (1969).
9. Feiser, J., Metall u. Erg., 26, 269 (1929).
10. Hincke, W.B., "The Vapor Pressure of Cadmium Oxide," J. Am. Chem. Soc., 55, 1751-1753 (1933).
11. Brewer, L. and Mastick, D.F., "The Stability of Gaseous Diatomic Oxides," J. Chem. Phys., 19, 834-843 (1951).
12. Gilbert, I.G.F. and Kitchener, J.A., "The Dissociation Pressure of Cadmium Oxide," J. Chem. Soc., 3919-3921 (1956).
13. Glemser, O. and Stocker, U., "Das Dissoziationsgleichgewicht $\text{CdO(S)} = \text{Cd(g)} + 0.5 \text{ O}_2\text{(g)}$," Ber. Bunsenges. Physik. Chem., 67, 505-509 (1963).
14. Behrens, R.G. and Mason, C.F.V., "A Mass Spectrometric Investigation of the Vaporization Thermodynamics and Vapor Composition of Cadmium Oxide," J. Less-Common Metals, 77(2), 169-184, 1981.

15. Kelley, K.K., Contributions to the data on theoretical metallurgy, III. "The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances," U.S. Bur. Mines Bull., No. 383, U.S. Government Printing Office, Washington, D.C., 28 (1935).
16. Remy, H., Treatise on Inorganic Chemistry, Vol. II., 449, Amsterdam, The Netherlands: Elsevier Publishing Co., 1956.
17. Van Nostrand's Scientific Encyclopedia, 4th Ed., 257, Princeton: D. Van Nostrand Co., 1968.
18. Touloukian, Y.S., and DeWitt, D.P., Thermal Radiative Properties — Nonmetallic Solids, Vol. 8, 216, New York: IFI/Plenum, 1972.
19. Glawe, G.E., and Szaniszlo, A.J., "Long-Term Drift of Some Noble- and Refractory-Metal Thermocouples at 1600 K in Air, Argon, and Vacuum," in H.H. Plumb, Temperature, Its Measurements and Control in Science and Industry, Vol. 4, Part 3, 1645, Instrument Society of America: Pittsburgh, Pennsylvania, 1972.
20. Masterson, K., "Survey of Solar Thermal Test Facility," SERI/TR-34-083, August, 1979, C-16.
21. Hays, R., private communication, 1980.

WJ/wpc

APPENDIX A. Functional Description of Cadmium Oxide Reactor Components

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

APPENDIX A. FUNCTIONAL DESCRIPTION OF CADMIUM OXIDE REACTOR COMPONENTS

<u>Component</u>	<u>Function</u>
Window Flange	Material: 304 stainless steel. Provides a mounting surface for quartz window. Contains four argon injection ports — two radial and two tangential. Argon injection keeps the window cool, flushes material away from the window, thus keeping it clean, and sweeps reaction products away from reactant bed, which helps prevent back reaction by keeping a low reaction product concentration above the reactant bed. Window flange contains a 3/8-inch x 3/8-inch water channel to help maintain a low temperature environment for window and window gaskets. Window flange is attached to mating flange on body of reactor with six, 1/4-28 cap screws, 5/8-inch in length, torqued to 20 in./lb.
Window	Material: General Electric Type 124 fused quartz. Source: Mark Optics, Inc., Santa Ana, California. Thickness: 0.5 inch Diameter: 6.5 inches
Window Gaskets	Material: Asbestos with styrene-butadiene binder. Two gaskets are used. An inner gasket between window and flange provides sealing of window to flange and an outer gasket distributes window retaining ring load evenly around window perimeter. Dimensions: OD = 6.5 inches; ID = 5.75 inches Uncrushed Thickness = 1/8 inch
Window-Retaining Ring	Material: 304 stainless steel. Retaining ring secures window to flange. Dimensions: OD = 8.0 inches; ID = 5.75 inches Thickness = 3/16 inches Retaining ring fastened to flange using six 3/4-inch, 10-32 cap screws torqued to 40 in./lb.
O-Ring	Material: Silicon rubber. Seals window flange to mating flange on reactor body. Dimensions: OD = 8.5 inches; ID = 8 inches O-ring sits on groove cut in window flange.
Pressure Gauge Tap	The window flange is equipped with a pressure gauge tap to determine pressure within the reactor.
Pressure Gauge	A pressure gauge is connected to the pressure gauge tap on the window flange. Copper tubing connects the gauge to the tap. Pressure gauge range is 0 to 35 psig (101 to 343 kPa). Reactor pressure is monitored to avoid excessive pressure buildup within the reactor, to evaluate reactor leakage, and to determine pressure drop through the reactor and associated gas lines.

Component	Function
Pressure Relief Valve/ Purge Valve	A pressure relief valve is inserted just ahead of the pressure gauge. It is set to open at 22 psig (253 kPa). The pressure relief valve prevents excessive pressure buildup in the reactor. It is combined with a purge valve to purge the line to the pressure gauge of air during reactor start-up.
Reactor Shell	Material: 304 stainless steel. The reactor shell contains the reactant, reactant supports, ceramic reactor liners, quench heat exchanger, and has penetrations to allow the use of thermocouples to monitor reactant temperature and exit gas temperature and to provide an exit port for gases exhausted from the reactor. The reactor is about 6-inches in diameter and about 7.5-inches long as measured from window retaining ring to gas exit port. It is stepped down in diameter toward the rear of the reactor to minimize void space that could trap oxygen evolved from CdO dissociation. A cooling channel is wrapped circumferentially around the reactor just behind the mating flange for the window mounting flange. This cooling channel has inside dimensions of 1-inch along the axis of the reactor and 0.25-inch radially. The cooling channel serves to cool the shell of the reactor forward of the reactant support channels.
Reactant Support Channels	The reactant support channels are part of a ceramic assembly that serves to line and insulate the front of the reactor (the part exposed to high radiant heat flux) and locate and support the reactants. This assembly consists of a cylindrical outer liner and concentric inner liner. In addition, behind the outer and inner liners there is a system comprising a front support ring, spacer ring, rear support ring, and ceramic pegs supporting and separating the channels. Four reactant support channels are used in the reactor. They provide a method of loading the reactor so a vertical bed of CdO may be directly exposed to the concentrated sunlight. Spaces between the channels allow products of reaction to be swept, by argon gas flow, toward the quench heat exchanger at the rear of the reactor where cadmium and cadmium oxide are condensed out and the oxygen-containing-argon exhausted through the gas exit port. The reactant support channels also serve to locate four thermocouples, one in each channel buried in the CdO, which sense reactant temperature. The reactant support channels are zirconia (ZrO_2) stabilized with 3 weight percent MgO. Known as composition 1706, the material is made by Zircoa Products, Ceramic Products Division, Corning Glass Works, Solon, Ohio 44139. The channels are made from slip cast tubes, 3/4-inch OD, 5/8-inch ID, 6-inches long, which are slit lengthwise and then cut to length.

<u>Component</u>	<u>Function</u>
Outer Liner	The outer liner is a cast tube of mullite with dimensions of 5.5-inches OD, 5.125-inches ID, and 2-7/8 inches long that fits in the shell of the reactor just behind the window-mounting flange. The outer liner protects the reactor shell from high temperatures. The mullite outer liner made by Coors Procelain Company of Golden, Colorado has four, 1/8-inch holes drilled in it to allow the thermocouples that sense reactant temperature to pass through from the reactor shell.
Inner Liner	Concentric with the outer liner is an alumina (Coors AD-998, nominally 99.8% pure Al_2O_3) inner liner. The inner liner, with its greater thermal shock resistance than the mullite outer liner, is exposed to the radiant heat flux and together with the outer liner protects the reactor shell from excessive temperatures. The liners also function to locate and help support the reactant support channels. The inner liner is a cast tube, 5-inches OD, 4-5/8 inches ID, and 1-9/16 inches long.
Front Support Ring	The front support ring is a disc of 94% alumina (Coors), 4.9-inches in diameter and 0.4-inch thick (originally), machined to 3/8-inch thick, with a 3-inch diameter hole in the center and eight 0.25-inch holes drilled through it for reactant channel support pegs. It is concentric with the outer liner and is positioned just behind the inner liner and just in front of the reactant support channels.
Rear Support Ring	The rear support ring is identical to the front support ring, but has no holes for pegs. It is positioned concentric with the outer liner, but behind the reactant support channels.
Spacer Ring	The spacer ring, made of Coors AD-998 alumina, is a cast tube 5-inches OD, 4-5/8 inches ID, and 9/16-inch long with four 1/8-inch holes drilled in it for thermocouples to pass through to reactant support channels. The spacer ring is concentric to the outer liner, between front and rear support rings, and serves to define the space in which the reactant support channels are positioned.
Reactant Channel Support Pegs	These Coors AD-99 (99% Al_2O_3) 0.25-inch diameter alumina rods, and 3/4-inch long, are inserted into holes drilled in the front support ring. These pegs serve to support, locate, and separate the reactant support channels.
Quench Heat Exchanger	Located behind the rear support ring is the water-cooled quench heat exchanger (QHX). It provides a cold surface to cool the products of reaction to a temperature low enough so that back reaction is minimized and cadmium and cadmium oxide are condensed. The QHX also cools the noncondensable gases. Made of 304 stainless steel tubing (0.5-inch OD),

ComponentFunction

	<p>the quench heat exchanger has a reverse return flow configuration and employs a double row of staggered tubes. Any condensables not "caught" by the QHX are removed from the gas stream by a quartz wool plug inserted during reactor assembly between the QHX and the exit gas port at the rear of the reactor.</p>
Reactant Temperature Measurement	<p>Each of the four reactant support channels is instrumented with a 0.008-inch (Omega Engineering Inc.) platinum versus platinum-13% rhodium (Type R) thermocouple. Each thermocouple is sheathed in a Coors AD-99 alumina sheath. Sheaths are extruded double bore tubes 1/16-inch OD with holes that are 1/64-inch ID. Sheaths are cut to length (about 2.7 inches). The thermocouples penetrate the wall of the reactor just to the rear of the cooling channel on the forward part of the reactor shell. CONAX fittings (transducer gland, lava sealant) with 1/8-inch NPT effectively seal the thermocouple. Thermocouples sit in the bottom of the reactant support channels and are covered by reactant.</p>
Effluent Gas Temperature	<p>The temperature of the gases are measured just after they pass the quench heat exchanger by a platinum versus platinum-13% rhodium (Type R) thermocouple. The thermocouple, sheath, and method of sealing are identical to the system used to measure the temperature of the reactant.</p>
Quench Heat Exchanger Inlet/Outlet Temperatures and Flow Rates	<p>The inlet and outlet temperatures and flow rate of cooling-water are measured to account for latent and sensible heat transfer from reaction products and argon to the QHX. Temperatures are measured with a Type K, grounded junction Chromel-Alumel thermocouple in a 304 stainless steel sheath. The flow rate of cooling water through the QHX is measured with a Dwyer Instrument Inc., 0.3 to 3.6 gpm rotameter.</p>
Reactor Surface Temperature Measurement	<p>The surface temperature of the shell of the reactor is measured with Type K thermocouples to estimate heat losses from the reactor shell. Shell temperatures are measured at the top of the reactor shell over the reactant support channels, at the side of the reactor just to the rear of the four thermocouple penetrations, and at the top of the reactor over the quench heat exchanger. Thermocouples are secured to the shell with stainless steel, worm-drive clamps.</p>
Effluent Heat Exchanger	<p>The temperature of the gases exiting the reactor is too high for the oxygen analyzer. This effluent is cooled to about 28°C by a countercurrent, water-cooled, heat exchanger with the water contained in a jacket around a 4-feet long, 1/4-inch OD stainless steel tube, through which the gas is passed. The effluent exchanger is</p>

ComponentFunction

constructed of Swagelock fittings and is fastened directly to the exit gas port at the rear of the reactor. The temperature of the gas exiting the effluent exchanger is measured using a Type K, Chromel-Alumel thermocouple with an exposed junction contained in a 304 stainless steel sheath.

Water-Cooled
Aperture

At the focal plane the total beam diameter is 6.5 inches. This exceeds the inner liner inside diameter of 4-5/8 inches. Because the diameter of the area of the reactor containing the reactant is only 3 inches, it is only necessary to allow the center 3 inches of the beam of concentrated radiation to enter the reactor and directly contact the reactant. Allowing additional energy to reach the insides of the reactor will provide greater energy to the reactant, but because the capability of the WSSF exceeds the energy requirements to conduct the reaction, it is desired to minimize exposure of the window asbestos gaskets and the inner liner to the flux and primarily irradiate the reactant. A water-cooled aperture with a 3-inch aperture was located at the focal plane to accomplish this. The window retaining ring is positioned just behind the water-cooled aperture.

Plumbing

Water and gas lines are made of clear, laboratory quality tubing. Connections are made using Swagelock fittings.

APPENDIX B. Experimental Plan

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

APPENDIX B. EXPERIMENTAL PLAN

The essential goal is to achieve ten experimental runs during the time at the solar furnace facility to evaluate cadmium oxide (CdO) decomposition rate at temperatures ranging from 1200° to 1500°C.

The specific temperatures at which the CdO dissociation experiments will be run are —

Run 1	1200°C
Run 2	1200°C
Run 3	1200°C
Run 4	1400°C
Run 5	1300°C
Run 6	1500°C
Run 7	1300°C
Run 8	1400°C
Run 9	1500°C
Run 10	Open

The purpose of the first three runs at 1200°C is to ensure the reproducibility of experimental results. The fourth run at 1400°C will establish the reaction rate at a higher temperature and permit some informed decision-making on whether higher temperature runs are worthwhile. If the reaction is very fast at 1400°C, it may mean the reaction rate is not important in reactor design and suggests heat transfer is the limiting factor. This will answer the experimental question and probably preclude further high temperature runs. However, if the reaction is slow, higher temperature runs will be of interest. To ensure a range of reaction rate data at several temperatures, and to avoid possible damage to the ceramic parts of the reactor, the higher temperature run at 1500°C is reserved until a run at 1300°C is carried out. Runs at 1300°, 1400°, and 1500°C (if necessary) will be repeated to check the reproducibility of the results. The tenth run has been purposely left open. It will be used to run an additional experiment or a modified experiment. Modifications may be made as experimental results from initial runs are reviewed and questions arise that require modification to the original experimental approach.

The whole experimental plan is subject to change based upon results from the runs at 1200°C, although the current plan is based on the best understanding we have of the problem, at this time.

Program Variations

Three scenarios for carrying out the experiments are proposed. These scenarios relate to the number of experimental runs that can be accomplished each day. Because the times required for reactor heat-up, cooldown, assembly and disassembly, and oxygen detector stabilization are not known, it is difficult to anticipate the precise number of runs accomplishable per day.

Plan no. 1 is the most conservative: It allows for only one run per day.

Plan no. 2 is more optimistic: It allows one run each on the first and second days, followed by two runs the third day, one the fourth, two the fifth day, etc. This allows sufficient time on the first two days to gain complete familiarity with the solar furnace and the experimental procedure. After the first two days, the alternation of one run and two runs per day assures sufficient time to setup the experiment for the two-run days.

Plan no. 3 is the most optimistic: It provides for two runs per day for five days. Table B-1 summarizes the three scenarios.

Table B-1. ALTERNATIVE EXPERIMENTAL PLANS

	<u>Day No.</u>												
	1	2	3	4	5	6	7	8	9	10	11	12	
	<u>Date</u>												
July	5	7	8	9	10	11	12	14	15	16	17	18	
	<u>Day of Week</u>												
	Sat	Mon	Tue	Wed	Thu	Fri	Sat	Mon	Tue	Wed	Thu	Fri	
	<u>Number of Experiments to be Carried Out</u>												
Plan No. 1	*	1	1	1	1	1	*	1	1	1	1	1	(10 runs total)
Plan No. 2	*	1	1	2	1	2	*	1	2				(10 runs total)
Plan No. 3	*	2	2	2	2	2							(10 runs total)

* It is anticipated that Saturdays will be used to setup the equipment in preparation for the runs on Monday. Thus, it is necessary to have access to laboratory and furnace facilities of Saturday, July 5 and 12. No experimental work will be carried out on these days.

The following steps are involved in carrying out each experimental run:

1. Reactor setup. Requires only the project team members.* This includes all component setup, including measurement equipment.
2. Leak test system. Requires only the project team members.*
3. Bringing the reactor to initial temperature. This involves the use of the solar furnace to heat the reactor to between 800° and 1100°C. No reaction will take place at these temperatures. Relatively slow heating is required to limit thermal stresses on the ceramic components of the reactor. Requires the furnace operator and one member of the project team.
4. Heating the reactor to the reaction temperature. It is desirable to heat the reactor to the reaction temperature as quickly as possible to minimize reactions at intermediate temperatures. It is anticipated that a substantial fraction of the output of the solar furnace will be required to overcome the thermal inertia of the reactants and reactor. The furnace operator and both members of the project team are required to carry out this step.
5. Take data. When the reactants reach the reaction temperature, the attenuator will be adjusted (and its position noted) to maintain the reactants within $\pm 25^{\circ}\text{C}$ (or as closely as possible) to this temperature. Reactant temperature will be monitored by thermocouples and perhaps by pyrometry. In any case, arrangements will be made to have a temperature signal available for the furnace operator to observe so attenuator settings may be adjusted as necessary. However, exact attenuator settings (or equivalently desired flux levels) to hold the reaction at the desired temperature are difficult to specify. Because the heat transfer processes in the reactor are difficult to model, some sensitivity studies on anticipated reactor performance were carried out to estimate flux requirements. The results of the sensitivity studies indicate that flux levels required to hold the reactor at the desired temperature are certainly less than $50 \text{ cal/cm}^2\text{-s}$ ($\sim 6.6 \times 10^5 \text{ Btu/hr-ft}^2$), corresponding to a very inefficient reactor; with flux levels of about 25 to $30 \text{ cal/cm}^2\text{-s}$ (3.3×10^5 to $4 \times 10^5 \text{ Btu/hr-ft}^2$) typically required. The furnace operator and both members of the project team are required to carry out this step.
6. Reactor cooldown. After completing the experimental run, the solar flux is shutoff and the contents of the reactor, which may be as hot as 1500°C , must be cooled to a temperature where the reactor can be removed for disassembly. Heat transfer from the reactor will occur by maintaining diluent flow through the reactor and cooling-water flow through the front flange, the reactor cooling jacket, and the quench heat exchanger. The same thermocouples used to monitor temperatures in the experiment will be

* There are two members of the project team: Bernard D. Yudow and James D. Schreiber.

used to monitor temperatures inside the reactor. It is planned that the reactor will be removed to the lab for final cooldown after an initial cooling period so another experiment can be setup as rapidly as possible. The reactor will be considered ready for removal when it is cool enough to be handled with insulated gloves and when the interior temperature of the reactor is substantially below the melting point of cadmium (321°C, 610°F) so no cadmium vapors are evolved to the atmosphere. Criteria for cooldown are: internal reactor temperature < 500°F, or reactor surface temperature < 250°F. Both members of the project team are required to carry out this step. It is anticipated that the cooling operation in the control room of the solar furnace will take from one to two hours. The completion of the cooling operation will occur in the lab.

7. Reactor removal. After the initial cooling of the reactor in the control room of the solar furnace, the water and diluent gas lines will be disconnected from the reactor, thermocouple connections to the reactor will be removed, plugs placed over reactor openings to prevent leakage of cooling water and cadmium vapors,* and the reactor removed to the laboratory. In a laboratory hood, diluent gas and cooling-water lines will be reconnected and further cooldown and disassembly will occur. Both members of the project team are required to carry out this step.
8. Cleanup. Before another experiment can be carried out, the reactor must be disassembled, and the critical parts of the reactor cleaned or replaced. Two reactors will be available to allow the possibility of carrying out two experiments in any one day. Because of the presence of Cd and CdO, the reactor will be disassembled and cleaned under a hood. Once the reactor is cleaned of Cd and CdO, reassembly can occur outside of the hood. (Handling of CdO in loading the reactor should not require use of a hood.) Proper safety procedures for handling Cd and CdO will be observed and will include the use of appropriate breathing apparatus to prevent inhalation of Cd or CdO. Both members of the project team are required to carry out this step.
9. Data reduction. After each experimental run, or at the end of each day of experiments, preliminary evaluation of experimental results must be carried out. At this time, all observations are reviewed and comments are added to notes taken during experimental runs. Data are checked for consistency and possible systematic errors. Some treatment of recorded data values is accomplished so the results of the experiment can be evaluated and future experiments modified as necessary. It is not anticipated that complete data reduction will be accomplished, but a mass balance will be determined and a preliminary oxygen evolution rate vs. time curve developed. Both members of the project team are required to carry out this step.

* This is very unlikely because the low temperature inside will ensure a very low cadmium vapor pressure.

In accordance with the three scenarios outlined, schedules have been developed estimating the timing of the various tasks and are presented in Figure 1 through 3. The initial experiments will determine the actual timing and thus the scenario chosen.

Figure B-1 shows the maximum time to carry out the operations associated with completing a single experimental run in one day. It assumes no preparation (such as reactor setup) is accomplished the previous day. Figure B-1 may be regarded as the most conservative projection of the time to carry out the tasks required to complete one experimental run. Under this schedule, the reactor cannot be removed from the furnace control room until about 6:30 p.m. As a result, access to the control room would be required after the time at which the facility is usually closed. However, the operations of cooling the reactor and the removal of the experimental apparatus will not require that any WSSF personnel be available, except as security or safety provisions require. Reactor cleanup and data reduction requires access to laboratory facilities after working hours.

Figure B-2 describes the schedule to conduct a single, complete experiment in one day. The schedule assumes some degree of setup the previous day. Setup activities would include the mounting of the reactor on the three-dimensional table, the connecting of gas lines, water lines, and instrumentation. Final setup of the reactor would take place during the morning of the experiment. This schedule assumes that setup, initial heating of the reactor, data taking, reactor cool down, removal and cleanup will take half the time assumed in Figure B-1. Because completion of the removal of the first reactor should be accomplished by 2:00 p.m., the setup of the second reactor to begin the next day's testing should be completed during working hours. Reactor cleanup and data reduction requires access to laboratory facilities after working hours.

Figure B-3 describes the schedule to conduct two complete experiments in one day. To carry out two experiments in one day requires access to the control room of the solar furnace after working hours to install and leak test the reactor used in the first experiment of the day. Cooling and disassembly of the second reactor also requires access to the control room of the solar furnace after working hours. Cleanup and data reduction tasks require access to laboratory facilities after working hours.

Figure B-1. SCHEDULE OF TASKS — MAXIMUM TIME TO
CARRY OUT A SINGLE EXPERIMENT IN ONE DAY

Figure B-2. SCHEDULE OF TASKS — MINIMUM TIME TO
CARRY OUT A SINGLE EXPERIMENT IN ONE DAY

1 Hr

1 Hr

1 Hr

REACTOR NO. ONE

0.5 Hr

0.5 Hr

0.45 Hr

1 Hr

1 Hr

Clean Reactor

Tasks
Carried 1 Hr
Out at - 2 Hr
Night

Data Reduction

8AM	9	10	11	12Noon	1	2	3	4	5PM
-----	---	----	----	--------	---	---	---	---	-----

Setup Reactor

1 1 Hr 2

Leak Test System

1 Hr

Bring to
Initial Temp

1 Hr

Run Up to
Reaction Temp

0.5 Hr

Take Data

0.5 Hr

Lunch

Cool Down

1 Hr

Take Down Reactor

REACTOR NO: TWO

1 Hr

Clean Reactor

} Tasks - 1 Hr
 } Carried
 } Out at - 2 Hrs
 } Night

Data Reduction

Figure B-3. SCHEDULE OF TASKS — TIME TO CARRY OUT TWO EXPERIMENTS IN ONE DAY

To carry out two experiments in one day requires the completion of installation and leak testing of reactor number one be accomplished in about one hour. Time spent in heating and cooling reactor number one must be used in preparing reactor number two so setup and leak testing of this reactor can be accomplished as rapidly as possible. As reactor number two is heated and cooled, cleaning operations on reactor number one will begin.

Figures B-1 and B-2 bracket the range of estimates of time to carry out the tasks required to conduct a single experiment in one day. Figure B-3 outlines the timing of the tasks required to conduct two experiments in one day. Figures B-1, B-2, and B-3 thus describe the scheduling of tasks required to accomplish the ten experiments to be conducted at the solar furnace facility under one of the three alternative experimental plans presented in Table B-1.

118(3000)/65030Tas3