SOLAR THERMAL HYDROGEN PRODUCTION PROCESS

ANNUAL TECHNICAL PROGRESS REPORT

January - December, 1979

prepared for
THE UNITED STATES DEPARTMENT OF ENERGY

WESTINGHOUSE ELECTRIC CORPORATION

Advanced Energy Systems Division

P.O. Box 10864

Pittsburgh, Pennsylvania 15236

G.H. Parker, Project Manager

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.

CONTENTS

	<u>Page</u>
LIST OF FIGURES	iv
LIST OF TABLES	viii
APPENDICES	ix
1.0 INTRODUCTION AND SUMMARY	1-1
2.0 SOLAR HYDROGEN PLANT OPERATIONAL STUDIES	2-1
2.1 Summary of Results	2-1
2.2 Reference Plant Description	2-4
2.3 Operational Modes	2-10
2.4 Operational Performance Analysis	2-14
2.5 Economic Assessment	2-30
2.6 References	2-35
3.0 SOLAR RECEIVER/REDUCTION REACTOR CONCEPT STUDY	3-1
3.1 General Approach	3-2
3.2 Description of Selected Configuration	3-2
3.3 Supporting Trade Studies and Alternative Configurations	3-8
4.0 REDUCTION REACTOR MATERIALS EVALUATIONS	4-1
4.1 Background	4-1
4.2 Summary of Results	4-1
4.3 Experimental Procedures	4-6
4.4 Detailed Discussion of Results	4-11
4.5 Future Work	4-45
4.6 References	4-46
5.0 REDUCTION REACTION CATALYST EVALUATION	5-1
5.1 Background	5-1
5.2 Summary of Test Results	5-4
5.3 Experimental Procedure	5-7

CONTENTS (continued)

	<u>Page</u>
5.3.1 SO ₃ Reduction Catalyst Test Evaluation (Anhydrous and Wet Environments)	5-7
5.3.2 Acid Decomposition Test Facility	5-9
5.3.3 Laboratory Model Test Evaluation	5-11
5.4 Detailed Discussion of Test Results	5-11
5.4.1 SO ₃ Reduction Catalyst Screening Test Results	5-11
5.4.1.1 Catalyst CE-1 Test Results	5-12
5.4.1.2 Catalyst Alfa-2 Test Results	5-16
5.4.1.3 Catalyst Alfa-3 Test Results	5-19
5.4.1.4 Catalyst Alfa-4 Test Results	5-21
5.4.1.5 Catalyst Alfa-5 Test Results	5-29
5.4.2 SO ₃ Reduction Catalyst Endurance Test Results	5-29
5.4.2.1 MB-3 Endurance Test Results	5-29
5.4.2.2 Alfa-4 Endurance Test Results	5-30
5.5 Future Work	5-33
5.6 References	5-34
6.0 ACID VAPORIZER MATERIALS EVALUATION	6-1
6.1 Objective and Background	6-1
6.2 Summary of Results	6-2
6.3 Experimental Procedure	6-5
6.4 Discussion of Results	6-9
6.4.1 Tests at 361°C	6-9
6.4.2 Tests at 452°C	6-28
6.5 Future Work	6-32
6.6 References	6-33

LIST OF FIGURES

	<u>Page</u>
2-1 Solar/Hydrogen/Chemical Plant Arrangement	2-5
2-2 Plant Block Schematic	2-6
2-3 Process Flow Sheet for Solar Hydrogen Plant Daytime Operation	2-7
2-4 Solar Flux Versus Time-of-Day for Three Days of the Year	2-17
2-5 Heliostat Field Layout with Representative Heliostat Locations	2-19
2-6 Calculated Solar Field Cosines	2-21
2-7 Thermal Power Absorbed in Steam Receiver Versus Time-of-Day and Time-of-Year	2-24
2-8 Thermal Power Absorbed in Hot Air Receiver Versus Time-of-Day and Time-of-Year	2-25
2-9 Power Absorbed in Receiver Versus Time	2-28
2-10 Ammonia Production Cost Versus Design Parameters	2-33
3-1 Schematic of Acid Vaporization/Reduction Equipment	3-1
3-2 Receiver to DR-1 Air Heat Transport System	3-3
3-3 Decomposition Reactor	3-7
3-4 Solids Heat Transport Concept	3-14
4-1 SO ₃ Reduction Reactor Materials Test Facility - Inlet Conditions	4-7
4-2 Schematic of Experimental Apparatus for Evaluating Materials Under Reduction Reactor Inlet Conditions	4-8
4-3 SO ₃ Reduction Reactor Materials Test Facility - Outlet Conditions	4-9
4-4 Schematic of Experimental Apparatus for Evaluating Materials Under Reduction Reactor Outlet Conditions	4-10
4-5 Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR 482HI3	4-13
4-6 Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR 482HI4	4-14
4-7 Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR 482HI5	4-15

LIST OF FIGURES (continued)

	<u>Page</u>
4-8 Visual Appearance of Samples in Run RR 482HI3	4-16
4-9 Visual Appearance of Samples in Run RR 482HI4	4-17
4-10 Visual Appearance of Samples in Run RR 482HI5	4-18
4-11 Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR 871HI1	4-20
4-12 Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR 871HI2	4-21
4-13 Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR 871HI3	4-22
4-14 Visual Appearance of Samples in Run RR 871HI1	4-23
4-15 Visual Appearance of Samples in Run RR 871HI2	4-24
4-16 Visual Appearance of Samples in Run RR 871HI3	4-25
4-17 Reduction Reactor Screening Test Results in Steam Environment - Outlet Conditions - Run RR 650H01	4-28
4-18 Reduction Reactor Screening Test Results in Steam Environment - Outlet Conditions - Run RR 650H02	4-29
4-19 Reduction Reactor Screening Test Results in Steam Environment - Outlet Conditions - Run RR 650H03	4-30
4-20 Visual Appearance of Samples in Run RR 650H01	4-31
4-21 Visual Appearance of Samples in Run RR 650H02	4-32
4-22 Visual Appearance of Samples in Run RR 650H03	4-33
4-23 Reduction Reactor Screening Test Results in Steam Environment Outlet Conditions - Run RR 871H01	4-36
4-24 Visual Appearance of Samples in Run RR 871H01	4-37
4-25 Surface Characteristics of Hastelloy C-276	4-39
4-26 Surface Characteristics of Carpenter Type 20 Cb-3	4-40
4-27 Surface Characteristics of SS 18-18-2	4-41
4-28 Surface Characteristics of Inconel 625	4-42
4-29 Surface Characteristics of SS 310	4-43
4-30 Surface Characteristics of Incoloy 825	4-44
5-1 Comparison of Anhydrous Test Results - Catalyst CE-1	5-14
5-2 Comparison of Wet Test Results - Catalyst CE-1	5-15
5-3 Comparison of Anhydrous Test Results - Catalyst ALFA-2	5-17

LIST OF FIGURES (continued)

	<u>Page</u>
5-4 Comparison of Wet Test Results - Catalyst ALFA-2	5-18
5-5 Comparison of Anhydrous Test Results - Catalyst ALFA-3	5-20
5-6 Photograph of Catalyst ALFA-3 Prior To and After Testing	5-22
5-7 Anhydrous Test Results - Catalyst ALFA-4	5-24
5-8 Wet Test Results - Catalyst ALFA-4 SV = 1000 and 5000 hr ⁻¹	5-25
5-9 Comparison of Lab Model Tests Versus Screening Tests for Catalyst ALFA-4	5-27
5-10 H ₂ SO ₄ Decomposition Test Results for Catalyst ALFA-4	5-28
5-11 Enduranc ^t Test Results - Catalyst MB-3	5-31
5-12 Endurance Test Results for Catalyst ALFA-4	5-32
6-1 Apparatus for Testing of Acid Vaporizer Materials	6-6
6-2 Acid Vaporizer Materials Sample Holder, Showing Manner in which Three Samples of Each Materials are Supported	6-8
6-3 Duriron Test Vessel	6-8
6-4 Schematic of Quartz Sample Holders for Acid Vaporizer Test at 452°C	6-10
6-5 Visual Appearances of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C	6-11
6-6 Visual Appearances of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C	6-18
6-7 Visual Appearances of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C	6-19
6-8 Visual Appearances of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C	6-20
6-9 Visual Appearance of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C	6-21
6-10 Visual Appearance of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C	6-22
6-11 Visual Appearances of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C	6-23
6-12 Visual Appearance of Samples Before Exposure to 98 w/o Sulfuric Acid at 361°C	6-25
6-13 Visual Appearance of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C	6-26

LIST OF FIGURES (continued)

	<u>Page</u>
6-14 Visual Appearances of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C	6-27
6-15 Visual Appearance of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C	6-29
6-16 Visual Appearances of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C	6-30
6-17 Visual Appearance of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C	6-31

LIST OF TABLES

	<u>Page</u>
2-1 System Descriptions	2-9
2-2 Subsystem Operating Modes	2-11
2-3 Heliostat Field Efficiency	2-22
2-4 Receiver Collection Efficiency	2-22
2-5 Steam Receiver	2-29
2-6 Capital Cost Summary (Millions of 1978 Dollars)	2-31
2-7 Solar/Hydrogen/Ammonia Production Costs	2-32
3-1 Reduction Reactor Characteristics	3-6
3-2 Arrangement Considerations for the Solar Hydrogen Design Options	3-12
3-3 Safety Assessment of Solar Thermal Hydrogen Production Processes	3-15
3-4 Safety Assessment of Solar Thermal Hydrogen Production Processes	3-16
3-5 Comparison of Thermochemical Receiver Design Options	3-19
4-1 Summary of Reduction Reactor Materials Test Program	4-2
4-2 Reduction Reactor Material Samples Tested	4-3
5-1 Catalysts and Test Parameters Evaluated in 1979	5-3
5-2 Maximum Conversion Rates Obtained in Screening Test Facility	5-5
5-3 Equilibrium Conversion at Various Temperatures and H_2SO_4 Feed Concentrations	5-13
6-1 Acid Vaporizer Materials Test Program	6-3
6-2 Acid Vaporizer Materials Tests at 361°C	6-4
6-3 Acid Vaporizer Screening Test Results	6-13

APPENDICES

	<u>Page</u>
Appendix A - Operation of Acid Decomposition Test Facility	A-1
Appendix B - Determination of Space Velocity for the H_2SO_4 Decomposition Test Facility	B-1
Appendix C - Operation of the Laboratory Model	C-1
Appendix D - Catalyst Test Data	D-1
Appendix E - Reduction Reactor Materials Test Data	E-1

1.0 INTRODUCTION AND SUMMARY

Westinghouse is currently under contract to DOE for technology development of the Sulfur Cycle, a hybrid thermochemical-electrochemical process for the production of hydrogen and oxygen from water. The development work has been co-funded by the Conservation (STOR) and Solar Divisions of DOE.

The process, in its most general form, consists of two chemical reactions - one for producing oxygen and the other for producing hydrogen. The production of oxygen occurs via the thermal reduction of sulfur trioxide obtained from sulfuric acid.

Catalysts are available for accelerating the rate of sulfur trioxide reduction to sulfur dioxide and oxygen. The process is completed by using the sulfur dioxide from the thermal reduction step to depolarize the anode of an electrolyzer. The overall reaction occurring electrochemically is;

The net result of Reactions 1 and 2 is the decomposition of water into hydrogen and oxygen and the sulfur oxides are involved as recycling intermediates. Although electrical power is required in the electrolyzer, much smaller quantities than those necessary in conventional water electrolysis are needed.

The energy needs of the process are thermal energy, for the acid vaporization and sulfur trioxide reduction steps, and electrical energy for the electrolysis and auxiliary power (e.g., pumps, circulators, etc.). The temperature levels desired for the thermal inputs are compatible with the capability of solar collectors. The electrical power can be provided by a solar-electric plant, by

fuel cells fed with a portion of the hydrogen and oxygen produced in the process, or by power from a remote generating plant.

The present contract form DOE/Solar was initiated in January 1978. Originally for twelve months, the contract was extended in 1979 for an additional twelve months. Emphasis during 1979 has been on three experimental tasks, process/application studies and subsystem design.

During 1979, operational studies have been conducted and have resulted in definitions of operating modes for solar/hydrogen plants and in assessments of the day/night and annual variations in performance that will influence the operating modes and the sizing of plant subsystems.

Conceptual design studies have been conducted for process components that interface with the solar receiver. From related trade-off studies, a preferred configuration emerged that involves an intermediate working fluid (e.g., hot gas) between the solar receiver and the sulfuric acid decomposition reactor. The design of the reactor has been based on a shell and tube type heat exchanger configuration with catalyst placement on the shell side.

A number of candidate materials for structural use in the acid decomposition reactor also have been evaluated experimentally. Materials have been exposed to a sulfur trioxide/steam environment and to a sulfur dioxide/oxygen/steam environment at temperatures up to 870°C. From the tests, a set of silicon based materials has demonstrated good corrosion resistance. Other tests have indicated that metals such as alonized Incoloy 800 and alonized Inconel 625 also should be acceptable materials for this application.

Screening tests and endurance tests with potential catalysts (to accelerate the rate of sulfur trioxide cracking) have been conducted with encouraging results. A platinum catalyst on alumina substrate has been endurance tested for 1000 hours at 870°C with no degradation in performance. Recent tests with a form of iron oxide on alumina substrate have indicated that, in all probability, less expensive, non-noble metal based catalysts will be acceptable for use in the process.

Approximately three dozen candidate materials for use in constructing the acid vaporizer have been tested for corrosion resistance to the expected environment. From these tests, conducted at temperatures up to 450°C and 20 atmospheres, in 98 w/o sulfuric acid, several materials have shown excellent corrosion resistance. Silicon carbide, polycrystal silicon and silicon nitride have shown the best corrosion resistance during 1000 hour tests. Several metallic based materials e.g., Duriron and Durichlor 51, also have shown good corrosion resistance.

Sections 2-6 of this annual report provide detailed discussions of the results obtained during 1979 from the five technical tasks.

2.0 SOLAR HYDROGEN PLANT OPERATIONAL STUDIES (W. A. Summers)

During the preceding calendar year, 1978, process studies were performed that identified several design approaches for a solar driven hydrogen production plant employing the Sulfur Cycle. In addition, specific chemical and fuel processes that need hydrogen as a feedstock were identified for integration with the solar hydrogen plant. Based on several simplifying assumptions with regard to solar energy availability and plant operational considerations, process flowsheets were prepared and economic assessments were made.

The objective of the present task, conducted during 1979, has been to perform a more thorough examination of the operational aspects of an integrated solar/hydrogen/chemical plant. Specific areas examined included definition of subsystem operating requirements, identification of plant operating modes, estimates of solar availability and plant performance, and an assessment of the impact of operational considerations on solar/hydrogen/chemical plant design and economics.

2.1 SUMMARY OF RESULTS

A reference plant design has been defined having five major groups of subsystems, encompassing solar thermal electric production, energy storage, hydrogen generation, solar thermochemical decomposition, and ammonia synthesis. The functions and operating requirements of major components within each of the five groups have been specified, and this information has been used to aid in defining a tentative set of plant operating modes. Six modes have been indicated based on the premise that the plant should produce ammonia 24 hours/day. A sequence has been defined by which the plant would move through appropriate daily operating modes as the sun rises, reaches maximum intensity, then declines and sets. The modes needed for day and night plant operation involve several combinations of heat storage and chemical energy storage to assure a steady production rate of hydrogen feedstock to the ammonia plant.

A potentially attractive alternative to the reference plant has been identified in which hydrogen storage would be added as a buffer between the electrolytic subsystem and the ammonia plant. This configuration, however, is not seen as a means to replace the other forms of energy storage, but instead as a way for the plant to gain additional operational flexibility, particularly for those periods when several consecutive cloudy days occur.

Because the earlier 1978 scoping studies had indicated that the economics of a solar/hydrogen/ammonia plant tend to be dominated by the solar collection and energy storage subsystems, the current operational studies included an assessment of plant performance and economics. This assessment was based on calculating hourly and seasonal variations in system performance by estimating the variations in direct normal solar flux, field cosine losses, heliostat field efficiency, and receiver collection efficiency. Yearly plant performance and overall plant economics were determined for solar subsystem sizes based on achieving rated plant performance on three different "design days" - the winter solstice, vernal equinox, and summer solstice. A second-level optimization was performed by varying the maximum solar receiver design capacity in conjunction with each design day.

It was found that the optimum basis for plant sizing was a choice of a summer solstice "design day" and a solar receiver design capacity of 520 watts per m² of collector surface. This receiver capacity is equivalent to the available solar energy at 2:00 PM on the winter solstice, requiring incident solar energy to be "dumped" whenever the solar flux exceeds the 2:00 PM winter solstice value. This "dumping" of available energy is more than offset, however, by the reduced cost of the solar receiver and the increased annual receiver capacity factor.

The optimum plant design results in an annual production rate of 37,380 tons of anhydrous ammonia. This represents a 64 percent plant capacity factor based on the 160 TPSD design capacity. The estimated ammonia "gate price" is \$762 per ton, which was calculated for comparison purposes and may or may not represent actual production costs. (See Section 2.5, Economic Assessment). This cost is approximately the same as the costs estimated during the 1978 scoping studies.

However, due to changes in the plant process flowsheet, the present cost was obtained with considerably higher energy input per ton of product, which otherwise would have raised the estimated costs by more than 40 percent. It is clear, therefore, that solar plant operational and performance characteristics need to be taken into account when determining solar/hydrogen plant performance and economics. This approach will ensure that appropriate assumptions are used in sizing the solar subsystems, which tend to dominate plant economics. While simplified assumptions such as those used in the 1978 studies (e.g. a specified annual capacity factor and nine hours per day of constant insolation) are adequate to get cursory estimates, these kinds of simplified assumptions tend to obscure subtle but important considerations that need to be taken into account before final designs are specified. This is particularly important for solar plants such as a solar/hydrogen plant that are designed to collect sufficient solar energy to operate the process plant on a continuous twenty-four hour per day basis.

2.2 REFERENCE PLANT DESCRIPTION

The reference plant is based on previous solar hydrogen plant process studies and consists of an integrated solar/hydrogen/ammonia complex. A sketch of a typical plant arrangement is shown in Figure 2-1. Sulfuric acid from the electrolyzer is vaporized and decomposed with thermal energy provided by an air-cooled, high-temperature solar receiver. Electric power is generated in a solar thermal electric plant that utilizes a steam cycle and a separate solar receiver. Additional electric power is generated in a low pressure steam cycle and an oxygen expander, which operate with waste heat from the SO_3 decomposition system. Energy storage systems are employed to permit continuous (24 hours per day) operation of the ammonia plant. A block schematic of the plant is shown in Figure 2-2, and a process flow sheet is shown in Figure 2-3.

The plant is composed of a number of major and secondary subsystems, as indicated on the block schematic, Figure 2-2, and listed below.

- Group A - Solar Thermal Electric Plant
 - A-1 - Steam Receiver Subsystem
 - A-2 - Steam Cycle Equipment
 - A-3 - Thermal Storage Subsystem
- Group B - Sulfur Cycle Electrochemical Subsystem
 - B-1 - Electrolyzer and Auxiliaries
- Group C - Storage Subsystems
 - C-1 - Sulfuric Acid Storage
 - C-2 - Sulfur Dioxide Storage
 - C-3 - Water Storage
- Group D - Sulfur Cycle Thermochemical Subsystem
 - D-1 - Hot Air Solar Receiver
 - D-2 - Acid Vaporization and Decomposition Subsystem
 - D-3 - Low Pressure Steam Cycle Equipment
 - D-4 - Oxygen Gas-Turbine Cycle
 - D-5 - SO_2/O_2 Separation System
- Group E - Ammonia Production Plant
 - E-1 - Synthesis Plant and Accessories

Figure 2-1. Solar/Hydrogen/Chemical Plant Arrangement

Figure 2-2. Plant Block Schematic

Figure 2-3. Process Flow Sheet for Solar Hydrogen Plant Daytime Operation

The major components, functions, and operating requirements of each of the major subsystems are shown in Table 2-1.

The plant can produce ammonia on a continuous 24 hour basis because energy storage systems are provided to account for the daily cycling of the solar collectors. These same storage systems can accommodate short-term variations in solar intensity. Extended reductions in total insolation, however, may require reductions in the ammonia production rate. Loss of solar insolation for more than one day would necessitate total plant shutdown. The components subjected to the most severe thermal cycling are the steam and hot air receivers, the hot air circulation system, the acid vaporization and decomposition system, and the LP steam oxygen turbines.

TABLE 2-1
SYSTEM DESCRIPTIONS

No.	Subsystem	Major Components	Functions	Operating Requirements
A-1	Steam Receiver System			
A-1.1	Heliostat Field	Heliostats, Control System	Redirect solar radiation onto external rec.	Acquire and track sun. Normal stowage at end of day. Emergency stowage (high winds or loss of coolant). Partial defocusing to control flux.
A-1.2	Receiver Tower	Concrete tower, receiver/boiler, assoc. piping (i.e., risers, dem.)	Absorb solar rad. and generate HP steam	Maintain steam conditions (960°F, 1500 psig) with varying flowrates and flux levels. Diurnal thermal cycling.
A-2	H.P. Steam Turb./Gen.	Turbine, Gen., FW HX, Condensor, Dry Cooling Tower System	Produce AC Power from HP and TS Steam	Operate with HP steam. Operate with TS steam. Operate with HP and TS steam. Load-follow plant demand.
A-3	Thermal Energy Storage	Oil/Rock storage unit, TS Heaters, Steam Generator	Storage thermal energy from HP steam and generate TS steam on demand	Charge with HP steam. Discharge by generating TS steam. Maintain standby condition.
B-1	Electrolyzer	Electrolyzer, Power Supply, Associated process Equipment	Produce H ₂ and H ₂ SO ₄ from SO ₂ and DC power	Continuous operation. Turndown as required by solar energy availability.
C-1	H ₂ SO ₄ Storage	Storage Tanks, HX, Accessories	Provide H ₂ SO ₄ storage during night	Store H ₂ SO ₄ from electrolyzer at night; feed H ₂ SO ₄ to decomp. system (as required) during day.
C-2	SO ₂ Storage	Storage Tanks, condensers, Accessories	Condense and storage SO ₂ during day	Accept SO ₂ as available during day and condense. Feed SO ₂ to electrolyzer at night.
D-1	Hot Air Receiver			
D-1.1	Heliostat Field	Heliostats, Control System	Redirect solar radiation inside the cavity	Acquire and track sun. Normal stowage at end of day. Emergency stowage (high winds or loss of coolant). Partial defocusing to control flux levels on receiver.
D-1.2	Receiver Tower	Concrete tower, cavity, SiC receiver	Heat up air to 1800°F	Maintain outlet air temperature with varying flowrates and flux levels. Diurnal thermal cycling.
D-1.3	Hot Air Circulation System	Compressed air ducting, Circulators	Circulate hot air between rec. and decomp. system	Maintain desired decomp. system operating conditions by varying flowrate. Diurnal thermal cycling.
D-2	Acid Vap. and Decomp. System	Preheaters, Vaporizers, Steam Separator, Decomp. Reactor, Accessories	Decompose H ₂ SO ₄ into SO ₂ and O ₂	Vary flowrate to match hot air heat input. Accommodate short outages of solar heat. Diurnal cycling.
D-3	Low Pressure Steam Turbine Cycle	Steam Generator, Steam Turbine, Generator, Condenser, FW Heater	Generate power from separated acid steam	Follow steam supply from separator. Diurnal cycling.
D-4	Oxygen Turbine Cycle	O ₂ Heater, O ₂ Turbine, Generator	Generate power from separated oxygen	Follow oxygen supply from separation system. Diurnal cycling.
D-5	SO ₂ /O ₂ Separation System	Knock-out drums, condensers, absorption towers, PV&F	Separate SO ₂ and O ₂	Operate during day only. Follow demand. Diurnal cycling.
E-1	Ammonia Plant	Synthesis System, Air separation plant, storage and shipping facilities	Synthesize ammonia from from air and H ₂	Continuous operation except for long-term solar outages.

2.3 OPERATIONAL MODES

The solar hydrogen plant is required to operate in a number of different operating modes to accommodate the variations in solar thermal input and the daily plant cycling. There are six basic operating modes, defined as follows:

MODE	MAJOR CHARACTERISTICS
1	<ul style="list-style-type: none">● Steam receiver supplying HP turbine and TES● Hot air receiver operating normally● Sulfur dioxide storage charging
2	<ul style="list-style-type: none">● Storage subsystems all in standby because insolation insufficient to charge● Hot air receiver operating normally
3	<ul style="list-style-type: none">● Steam receiver and TES supplying HP turbine● Hot air receiver operating normally● Sulfur dioxide storage discharging● Supplemental electric power (grid) required
4	<ul style="list-style-type: none">● Steam receiver in standby● Hot air receiver in standby● TES supplying HP turbine● Sulfuric acid storage charging● Supplemental electric power (grid) required
5	<ul style="list-style-type: none">● Steam receiver charging TES● Hot air receiver charging SO₂ storage● Electrolyzer in standby
6	<ul style="list-style-type: none">● All subsystems shutdown

The individual operating modes of the various subsystems during the six plant operating modes are shown in Table 2-2.

TABLE 2-2

SUBSYSTEM OPERATING MODES

Subsystem	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5	Mode 6	
A-1 Steam Rec.	O	O	O	S	O	S	O = Operating S = Standby C = Charging D = Discharging
A-2 H.P. Turb./Gen.	O	O	O	O	S	S	
A-3 Thermal Stor.	C	S	D	D	C	S	
B-1 Electrolyzer	O	O	O	O	S	S	
C-1 H ₂ SO ₄ Stor.	D	S	C	C	D	S	
C-2 SO ₂ Stor.	C	S	D	D	C	S	
D-1 Hot Air Rec.	O	O	O	S	O	S	
D-2 Acid Decomp.	O	O	O	S	O	S	
D-3 L.P. Turb./Gen.	O	O	O	S	O	S	
D-4 O ₂ Turbine	O	O	O	S	O	S	
D-5 SO ₂ /O ₂ Sep.	O	O	O	S	O	S	
E-1 Ammonia Plt.	O	O	O	O	S	S	
Aux. Elec. Power	No	Yes/No	Yes	Yes	No	No	

Typical daily operation, assuming a clear day and design solar insolation levels, is as follows. The day begins in Mode 4. As the sun rises above the horizon, heliostats are commanded to acquire the sun and begin tracking. During this time the receivers are gradually brought up to temperature. When the intensity of solar radiation increases to 50 percent of the design value, the receivers are brought on line and the plant moves into Mode 3. Energy collected by the solar receivers is used to displace the energy being drawn from the storage systems. A continued increase in collected solar radiation permits the plant to move into Mode 2, where no energy from storage is required. Assuming a day of design insolation, the solar intensity will continue to increase and the plant will enter Mode 1. Sufficient energy will be supplied to the storage systems to charge them for continuous operation during the night. Following the solar peak at noon, insolation levels begin to decline and the plant moves successively back through Modes 2, 3 and 4.

Whenever the solar flux on the receiver exceeds the receiver design capacity, selected heliostats are defocused to maintain a constant peak flux. For the optimum plant design (See Section 2.5), the design peak flux can be maintained for about 8.5 hours on the summer solstice (i.e., 4.25 hours before solar noon to 4.25 hours after), 7 hours during an equinox day, and 4 hours on the winter solstice. These periods correspond to operation in Mode 1.

Modes 2 and 3 are transient modes and correspond to the periods when the solar flux is increasing or decreasing rapidly. With proper methods of control and adequate thermal inertia of the system, steady operation in either of these modes should be maintained. Otherwise, the HP turbine and SO_3 decomposition systems would have to be operated either entirely from energy storage or entirely from solar energy.

It should be noted that the reference plant does not provide for storage between subsystems B-1 and E-1. Therefore, the hydrogen generation rates follows the ammonia plant demand. This is a reasonable situation considering the fairly constant, full-load operation that is expected from the ammonia synthesis plant.

With this arrangement, a decreased output in ammonia demand would waste available solar energy. Therefore an alternative to the reference plant would use a hydrogen storage subsystem between the electrolyzer (B-1) and ammonia (E-1) subsystems.

If a hydrogen storage system were employed, normal plant operation will be maintained until the storage system was filled, even at reduced ammonia plant capacity. If the ammonia plant was shutdown for an extended period, the plant would first fill the hydrogen storage system in the normal manner, then enter Mode 5, where all the collected solar energy would be used to fully charge the energy storage systems. Once this is accomplished, the plant would shutdown, (Mode 6) until the ammonia subsystem is ready to resume production.

2.4 OPERATIONAL PERFORMANCE ANALYSIS

Estimates of plant operational performance have been performed in order to quantify the operation of the solar hydrogen plant, particularly variations as functions of time-of-day and time-of-year. In addition to identifying operating requirements, the determination of time-variant plant performance can lead to the identification of trade-offs for optimizing system sizing and annual performance. For example, comparisons can be made between a plant designed for winter solstice conditions (large collector field) and summer solstice or equinox conditions (smaller collector field).

Similar performance trade-offs have been conducted by others for solar thermal electric power plants, i.e., utilizing such techniques as the MIRVAL computer code. However, those studies generally have computed point performance for one time of day (solar noon) at various times of the year. In addition, those studies have assumed, in almost all cases, a constant solar flux during the hours that the plant operated. This does not lead to great errors in computing daily or yearly performance, but has a major effect on hourly performance for any given day. The objectives of the present study are to adapt the earlier work where appropriate and to extend it to include hourly performance over the entire operating day. In this manner, the hourly power input and daily start-up and shutdown times for the reference plant can be estimated. This is especially important for this reference plant since energy storage systems must be designed to provide 24-hour operation.

To determine the overall performance of the solar collection system (heliostat field, receiver, and heat transfer system), the various individual subsystem losses must be identified and evaluated. In general, these losses can be subdivided into three main groups:

- Incident radiation losses
- Heliostat field losses
- Receiver collection losses

The incident radiation losses are those resulting from reduced incident solar flux and field cosine angle losses (mirror foreshortening). The incident solar flux varies as a function of day, time of year, and atmospheric conditions (mainly cloud cover and dust loading). The cosine angle losses depend on the angle of incidence of the solar radiation.

The heliostat field losses result from shadowing by the receiver tower, shadowing by adjacent heliostats, blocking of reflected rays by heliostats, mirror surface reflectivity, and atmospheric attenuation between the heliostats and the receiver.

The receiver collection losses include spillage due to reflected rays missing the target (aiming losses), receiver reflectivity, receiver radiation and convection, and heat transfer piping thermal losses.

The net thermal energy absorbed by the solar receiver system can then be computed as follows:

$$\text{Net Thermal Energy Absorbed} = [\text{Solar Flux}] \times [\text{Avg. Field Cosine}] \\ \times [\text{Heliostat Field Efficiency}] \times [\text{Receiver Collection Efficiency}]$$

Determination of Direct Normal Solar Flux

The direct normal solar flux varies with the altitude of the site and the zenith angle of the sun. By taking data from observations made by Laue (1970) in the Mojave Desert, Meinel and Meinel⁽¹⁾ have developed the following empirical equation:

$$I(z, h) = I_0 (1 - ah)e^{-c(\sec z)^S} + ahI_0,$$

where: $I(z, h)$ = direction normal solar flux, $\frac{\text{watts}}{\text{m}^2}$

z = zenith distance, degrees

h = site elevation, km

I_0 = exoatmospheric solar flux, $\frac{\text{watts}}{\text{m}^2}$

$$\begin{aligned} a &= 0.14 \text{ per kilometer altitude} \\ c &= 0.357 \\ s &= 0.678 \end{aligned}$$

By establishing a site location, such as Albuquerque, New Mexico as used in this study, the elevation is known and the zenith distance can be calculated for various times of the day and times of the year.

It should be pointed out that although the exoatmospheric solar flux (I_0) is normally taken as the value of the solar constant (1353 watts per square meter), it actually varies seasonally due to the orbital eccentricity of the earth. In the northern hemisphere, this seasonal variation amounts to -3.27% at the aphelion and +3.42% at the perihelion. Since the perihelion (the time of nearest approach to the sun and highest solar flux) nearly coincides with the winter solstice (the time of poorest plant performance), the difference between winter and summer plant output is partially offset.

The results of the above described solar flux calculations for a representative site near Albuquerque, New Mexico are shown graphically in Figure 2-4. It can be seen that the peak values at solar noon for the summer solstice and the equinox are both approximately equal to 1030 watts per square meter. The noon solar flux on the winter solstice is 960 watts per square meter, or 7% less. The solar flux variation between the approximate time of daily plant startup and solar noon is in excess of 25%.

The data points (∇) shown in Figure 2-4 are measurements at Albuquerque on day 183 (July 2, 1976) as reported by Sandia Laboratories.⁽²⁾ By comparison to the curve for the summer solstice, the data tends to verify the empirical equation employed.

Average Field Cosine

Since the normal to each heliostat mirror surface must bisect the angle between the incident radiation and the receiver target, the reflective surface area is foreshortened by the cosine of the angle of incidence. Therefore, the

Figure 2-4. Solar Flux Versus Time-of-Day for Three Days of the Year

amount of redirected solar energy is directly proportional to the average field cosine.

The field cosine varies with location in the heliostat field, elevation angle of the sun, and azimuthal angle of the sun. Before an average field cosine can be calculated, the receiver target height and each individual heliostat location must be fixed. For each time-of-day and time-of-year, the average field cosine is then calculated as the mean of the cosines for each individual heliostat. For a 200 MW_t receiver, the number of heliostats is approximately 8200.

Rather than prepare a detailed field layout designating the coordinates of each heliostat, it was decided to choose five representative heliostat locations and base the average field cosine on the calculated mean for these five heliostats. The representative locations were chosen based on previous Westinghouse heliostat field modeling for a 50 MW_e (approximately 200 MW_t) solar hybrid repowered plant. The heliostats were assumed to be deployed in a north biased modified circular field as shown in Figure 2-5.

The five representative heliostat locations are shown as points A through E. The validity of choosing these particular five locations was established by comparing average field cosines for the five heliostats to previously calculated average field cosines, using the MIRVA code, for all 8160 heliostats in the 50 MW_e field. The MIRVAL calculations could not be used exclusively since calculations were available only for one time of day (solar noon).

The field cosine for each of the five heliostat locations was then calculated for hourly increments on the winter solstice, spring equinox, and summer solstice. The height of the receiver centerline was taken as 185.5 meters above the centerline of the heliostats. The calculations were performed by use of an algorithm previously developed by Westinghouse. The computer code employed allows input of the site latitude, heliostat and receiver location, and day of the year, and computes the elevation and azimuthal angles of the sun, elevation and azimuthal angles of the heliostat, angle of incidence, and effective cosine.

Figure 2-5. Heliostat Field Layout with Representative Heliostat Locations

The results of these calculations are presented in Figure 2-6. As with the incident solar flux, the maximum average field cosine is seen to occur during the summer solstice. The maximum average field cosine at the equinox is less than 1% below that at a summer solstice, while it is about 5% less at the winter solstice. The variation from daily start-up to solar noon is approximately 20%.

Heliostat Field Efficiency

The heliostat field efficiency is calculated by determining percentage losses for shadowing by the receiver tower, shadowing by adjacent heliostats, blocking of reflected rays by other heliostats, mirror surface reflectivity, and atmospheric attenuation between the heliostats and the receiver. Since the variations in these parameters is a weak function of time-of-day and time-of-year, the heliostat field efficiency was assumed to be constant for all operating times.

Values for the various efficiency factors were obtained from a number of references (3, 4, 5, 6), along with results of calculations performed with the MIRVAL computer code. Estimated values for the solar hydrogen plant are shown in Table 2-3.

Receiver Collection Efficiency

The receiver collection losses include spillage due to reflected rays missing the target (aiming losses), receiver reflectivity, receiver radiation and convection, and heat transfer piping thermal losses. The solar hydrogen plant utilizes two separate solar receivers of differing designs, requiring different efficiency factors. The steam receiver is of the external type and operates at approximately 1000°F. The hot air receiver is a cavity receiver that operates at 1700°F.

The various collection efficiencies were estimated from information taken from a number of different references (3, 4, 5, 6). These values are shown in Table 2-4. The spillage, reflectivity, and piping thermal losses are assumed

Figure 2-6. Calculated Solar Field Cosines

TABLE 2-3
HELIOSTAT FIELD EFFICIENCY

<u>Loss Factor</u>	<u>Efficiency (% of Power Transmitted)</u>
Receiver Tower Shadowing	99.8%
Blocking and Shadowing	98.5
Mirror Reflectivity	90.0
Atmospheric Attenuation	<u>95.0</u>
Net Heliostat Field Efficiency =	84.0%

TABLE 2-4
RECEIVER COLLECTION EFFICIENCY

<u>Loss Factor</u>	<u>Efficiency (% of Incident Power Collected)</u>					
	<u>Steam Receiver</u>			<u>Hot Air Receiver</u>		
Rays Missing Target (Spillage)	99.8%			90%		
Receiver Reflectivity	95.0			96.2		
Piping Thermal Losses	99.6			99.0		
Receiver Radiation and Convection:	Winter	Equinox	Summer	Winter	Equinox	Summer
	88.7	89.8	90.9	85.5	86.2	86.8
Net Receiver Collection Efficiency	Winter	Equinox	Summer	Winter	Equinox	Summer
	83.8	84.8	85.8	73.3	73.9	74.4

constant throughout the year. The radiation and convection losses, which are a function of ambient air temperature, are estimated for winter, equinox, and summer average conditions.

Net Thermal Energy Absorbed

The net thermal energy absorbed by the solar receiver system can be computed from the aforementioned efficiency factors by the following equation:

$$\text{Net Thermal Energy} = [\text{Solar Flux}] \times [\text{Avg. Field Cosine Angle}] \times [\text{Heliostat Field Efficiency}] \times [\text{Receiver Collection Efficiency}]$$

The results for a steam external solar receiver and a hot air cavity receiver are shown in Figures 2-7 and 2-8. These curves give the power absorbed in the receiver (per square meter of heliostat reflective surface) as a function of hours from solar noon. The total power absorbed by the working fluid in the receiver at any time of day can be determined by multiplying the value found from the appropriate curve (Figure 2-7 or 2-8) by the total reflective surface area of a given heliostat field.

Field Sizing and Yearly Performance

The design rated capacity of the solar/hydrogen/ammonia plant is 160 TPSD of anhydrous ammonia (see the process flowsheet, Figure 2-2). This capacity requires solar thermal energy inputs of 1251 MW_t-hrs. per day to the steam receiver and 1800 MW_t-hrs. per day to the hot air receiver. If the solar energy input was constant for nine hours per day, the power to the receivers would be 139 MW_t and 200 MW_t, respectively, as shown in the flowsheets.

However, the solar energy to the receivers varies significantly as a function of time of day. In addition, there are differences in both intensity and duration of solar energy as a function of time of year. These variations have been discussed above and are summarized in Figures 2-7 and 2-8. Integration

Figure 2-7. Thermal Power Absorbed in Steam Receiver
Versus
Time-of-Day and Time-of-Year

Figure 2-8. Thermal Power Absorbed in Hot Air Receiver
Versus
Time-of-Day and Time-of-Year

of these power versus time curves gives daily energy collection per m^2 of collector surface. By calculating daily performance in this manner for several days of the year, a daily energy collection versus day of the year curve can be constructed. Subsequent integration of this curve gives yearly energy collection.

In order to optimize the cost and performance of the total plant, plant costs and yearly production rates must be calculated for various choices of system design. The approach taken here was to size all the solar subsystems (i.e. heliostat fields, receiver towers, and storage systems) for a particular "design day." On the design day, sufficient energy must be collected during the solar operating hours to supply the hydrogen and ammonia plants for twenty-four hours at rated capacity. After the system was sized for the design day, the performance of the plant at other times of the year was calculated. Integration of the daily performance versus time curve then gives yearly energy collection (100 percent sunshine) as discussed earlier. Actual yearly energy collection was calculated from the theoretical performance by assuming a 77 percent annual availability of solar energy.

Three choices were made for "design day." These were winter solstice, vernal equinox, and summer solstice because these three days bracket the performance for all other days of the year. In addition, these same three days were used to calculate yearly performance once a particular system size had been established. The daily performance was calculated on the winter solstice (minimum performance), summer solstice (maximum performance) and each equinox day, and these points were used to construct the yearly performance curve by assuming a sinusoidal relationship.

Before proceeding with the daily energy calculations, one additional variable had to be considered, the design capacity of the solar receiver. By considering various receiver capacities (watts absorbed per square meter of collector surface) the integration path along the curves of Figures 2-7 and 2-8 are affected. For example, if the receiver capacity is less than the available

solar power at noon, the performance would follow a path similar to that shown in Figure 2-9. The power absorbed in the receiver rises with the increasing solar flux until it reaches the receiver capacity. The performance then declines until the solar plant is shut down. Startup and shutdown capacities have been taken as 50 percent of the design receiver capacity.

The advantage of limiting the receiver capacity to less than the maximum available solar energy is better utilization of the receiver. This can best be realized when the design day is taken as the summer solstice. Sizing the receiver to accommodate the solar flux at noon on the summer solstice would result in a receiver capacity of 646 watts per m^2 of collector surface (calculated for the steam receiver, Figure 2-7). This capacity would only be obtainable on a clear day at solar noon on the summer solstice. At all other times of the year the available solar energy would be less than the receiver capacity. On the other hand, if the receiver capacity

were limited to 400 watts per m^2 , this capacity would be realized for over 13 hours on a clear summer solstice day and 7 hours on the winter solstice. All other days of the year would fall between these two extremes. The trade-off is between a smaller receiver tower and energy storage system and a larger heliostat field (required to obtain rated capacity on the design day with a smaller tower).

The results of the calculations of system sizing and yearly energy collection are shown in Table 2-5. The receiver capacities have been chosen to correspond to a particular time of day on a particular day of the year (e.g. 646 watts per m^2 corresponds to solar noon, summer solstice). The choice of receiver capacity is somewhat arbitrary, and the use of values corresponding to particular times was done to give a more easily relatable meaning to the numbers.

Figure 2-9. Power Absorbed in Receiver Versus Time

TABLE 2-5

STEAM RECEIVER

DESIGN DAY	RECEIVER DESIGN POINT Watts/m ²	Time/Day	HELIOSTAT (m ²)	RECEIVER (MW)	STORAGE (MW-HRS)	YEARLY ENERGY (MW-HRS)
Winter Solstice	564	Noon/ Winter Sol.	305,900	172.5	812.1	351,600
Equinox	564	Noon/ Winter Sol.	223,800	126.2	679.7	321,600
	633	Noon/ Equinox	217,600	137.7	696.4	317,600
Summer Solstice	400	3:30 PM/ Winter Sol.	246,300	98.5	570.2	300,400
	518	2 PM/ Winter Sol.	201,800	104.5	581.7	295,000
	564	Noon/ Winter Sol.	192,500	108.6	590.1	292,300
	633	Noon/ Equinox	185,300	117.3	605.7	287,000
	646	Noon/ Summer Sol.	185,600	119.9	610.9	286,400

HOT AIR RECEIVER

Winter Solstice	493	Noon/ Winter Sol.	507,500	250.2	1168.5	505,800
Equinox	493	Noon/ Winter Sol.	371,000	183.1	978.0	462,700
	552	Noon/ Equinox	361,000	199.3	1002.0	456,900
Summer Solstice	350	3:30 PM/ Winter Sol.	408,600	141.7	820.5	432,100
	453	2 PM/ Winter Sol.	334,600	151.6	837.0	424,100
	493	Noon/ Winter Sol.	319,400	157.5	849.0	420,600
	552	Noon/ Equinox	307,500	169.7	871.5	413,000
	560	Noon/ Summer Sol.	308,000	172.5	879.0	412,100

2.5 ECONOMIC ASSESSMENT

The system designs shown in Table 2-5 were compared on a cost-effectiveness basis by estimating capital and operating costs for each design. This was accomplished by prorating from cost estimates made as part of the 1978 Process Studies on solar/ hydrogen/ammonia plants. Capital costs were estimated for each solar subsystem and these were summed along with balance of plant costs (i.e. hydrogen production plant, ammonia synthesis unit, auxiliaries, etc.) to give total plant capital costs. The capital costs were adjusted to give total plant investments by adding contingencies, indirect costs, and interest during construction. Amortized capital costs and operating costs were divided by the annual production rate to give ammonia "gate prices." The results are shown in Table 2-6. A breakdown of the production costs is given in Table 2-7.

It should be noted that the cost estimates shown were calculated for comparative purposes, and their absolute values should not be given unnecessary emphasis. The estimates of solar system capital costs, while representing the best information available at the time of the estimate, are subject to rather large uncertainties. In general, it is felt that the costs used in this study were on the conservative-side, and further development and testing of solar thermal systems may warrant a lowering of these estimates.

A plot of ammonia costs versus design receiver capacity for each of the three design days is given in Figure 2-10. The "summer solstice" design day results in the lowest production costs for all receiver capacities. The minimum cost is realized for a summer solstice design day and a maximum receiver design capacity of approximately 520 watts per m^2 collector surface. The receiver capacity is equivalent to the available solar energy at 2:00 PM on the winter solstice.

The optimized production cost of \$762 per ton is comparable to the 1978 estimates which showed costs of \$600 to \$800 per ton, depending on the percentage of purchased electrical power. However, the process energy balance for the present design has been revised considerably since the earlier estimates, resulting in the energy requirements per SCF of hydrogen being increased nearly 40 percent. The additional energy requirements are mainly a result of an updated estimate

TABLE 2-6

CAPITAL COST SUMMARY (MILLIONS OF 1978 DOLLARS)

DESIGN DAY Receiver Design (Reference Time)	Winter Solstice		Winter Solstice		Summer Solstice			
	Noon-W.S.	Noon-W.S.	Noon-Eq.	3:30PM-W.S.	2:00 PM-W.S.	Noon-W.S.	Noon-Eq.	Noon-S.S.
Steam Field	21.02	15.38	14.95	16.92	13.86	13.22	12.73	12.75
Steam Tower	9.75	7.14	7.79	5.57	5.91	6.14	6.63	6.78
Thermal Storage	6.86	5.74	5.88	4.82	4.92	4.99	5.12	5.16
Hot Air Field	35.42	25.92	25.20	28.53	23.36	22.29	21.46	21.50
Hot Air Receiver	46.74	34.20	37.23	26.47	28.32	29.41	31.70	32.22
Chemical Storage	12.62	10.56	10.82	8.86	9.04	9.17	9.41	9.49
BOP	34.05	34.05	34.05	34.05	34.05	34.05	34.05	34.05
Capital Cost	166.46	132.99	135.92	125.22	119.46	119.28	121.1	121.95
Total Plant Investment (Incl. Contingencies, Indirects, IDC)	242.16	193.47	197.73	182.16	173.78	173.52	176.17	177.41
Annual Production (TPY)	44,970	41,130	40,620	38,420	37,730	37,380	36,710	36,630
Ammonia "Gate Price" (\$/Ton)	886	778	804	784	762	768	793	800

TABLE 2-7

SOLAR/HYDROGEN/AMMONIA PRODUCTION COSTS

Utility Financing
 1978 Cost Basis
 77% Available Sunshine
 Location: Albuquerque, N.M.

Design Day: Summer Solstice

Receiver Design Point: 2 PM Winter Solstice

<u>Cost Item</u>	<u>Cost Per Ton of Product</u>
Depreciating Capital (15%)	\$691
Operating and Maintenance	
- Solar/H ₂ Plant	35
- Ammonia Plant	24
Oxygen Credit (\$25/ton O ₂)	-41
Purchased Power (3¢/KW-hr)	53
Ammonia "Gate Price"	\$762/ton

Figure 2-10. Ammonia Production Cost Versus Design Parameters

of electrolyzer performance and a reduction in sulfuric acid concentration from 80 percent to 60 percent. Therefore, the optimization of system sizing and performance resulted in roughly the same production costs for nearly 40 percent more energy consumption compared to the simplified estimates prepared in 1978.

2.6 REFERENCES

1. Meinel, A. B., and Meinel, M. P., Applied Solar Energy, Addison-Wesley Publishing Company, Reading, Massachusetts, 1977.
2. Sandia Laboratories, Helios: A Computer Program for Modeling the Solar Thermal Test Facility, SAND76-0346, Albuquerque, New Mexico, March, 1977.
3. Public Service Company of New Mexico, "Technical and Economic Assessment of Solar Hybrid Repowering, Final Report," SAN/1608-4-1, September, 1978.
4. McDonnell Douglas Astronautics Company, "Central Receiver Solar Thermal Power System, Phase 1, CDRL Item 2 Pilot Plant, Preliminary Design Report, Vol. III, Collector Subsystem," SAN-1108-76-8, MDC-66776, October, 1977.
5. Boeing Engineering and Construction, "Closed Cycle, High-Temperature Central Receiver Concept for Solar Electric Power," EPRI ER-629, January, 1978.
6. Black and Veatch Consulting Engineers, "Open Cycle Gas Turbine Solar Electric System, Conceptual Design of High Temperature Receiver and Turbine Interfaces, "Section 9, Proceedings of Semiannual EPRI Solar Program Review Meeting and Workshop, EPRI ER-371-SR, October, 1976.

3.0 SOLAR RECEIVER/REDUCTION REACTOR CONCEPT STUDY

(W. A. Summers, L. Van Bibber, B. R. Krasicki)

The thermochemical portion of the Sulfur Cycle consists of a sulfuric acid vaporization and SO_3 reduction system, followed by separation of the resultant sulfur dioxide and oxygen. The sulfuric acid vaporization/reduction system is shown schematically in Figure 3-1. Two process components, the solar vaporizer and the reduction reactor, require thermal input, while the remaining heat exchangers are recuperators. The objectives of this task are to perform a concept study on the solar receiver/reduction reactor, including preliminary tradeoff evaluations, and to prepare a conceptual design of a full scale solar driven reduction reactor.

Figure 3-1. Schematic of Acid Vaporization/Reduction Equipment

3.1 GENERAL APPROACH

Several options exist for the design of the reduction reactor. The first consideration in supplying solar thermal energy to the process is whether or not a secondary heat transfer is required. Direct solar heat input, either through a window or a tube wall, requires the least amount of equipment and is the most energy efficient. However, indirect heating, employing air, helium, or another heat transfer fluid, avoids many safety and materials problems and simplifies the operation of the process and the replacement of the reduction catalyst. Other trade-offs include the use of a central receiver versus distributed collectors and adiabatic versus isothermal reduction.

The general approach to the concept studies was to establish basic ground rules, propose several alternate designs, conduct trade studies, choose the most attractive configuration, and prepare a conceptual design for a full scale reactor (designated DR-1).

3.2 DESCRIPTION OF SELECTED CONFIGURATION

Based on the results of trade studies (discussed in Section 3.3), an indirectly heated DR-1 utilizing air as the heat transfer fluid was selected as the base case. The general arrangement of the air heat transport system is shown in Figure 3-2.

The starting point for the DR-1 design was a concept, utilizing helium heat transfer, that Westinghouse had designed during an earlier study for the National Aeronautics and Space Administration. In order to adapt the NASA concept to the present design effort, the following criteria were adopted:

Figure 3-2. Receiver to DR-1 Air Heat Transport System

- The general concept will be a tube and shell configuration with packed catalyst to promote the reduction of sulfur trioxide.
- The catalyst will be located on the shell-side of the heat exchanger, with air flow through the tubes.
- No separate preheater section will be employed. The initial portion of the DR-1 will be loaded with a bed of spheres or rings not containing catalyst, but solely for increasing the heat transfer rate.
- Spherical catalyst beads, consisting of platinized alumina spheres, will be used.
- The tube diameter to catalyst diameter ratio is to be in the range of 5 to 10.
- Acid vapor side pressure drop is to be less than 50 psi.
- Space velocity will be maintained less than 5000 hr⁻¹.
- The total flow of acid vapor will be divided among three reactors each sized for ~50 MW(t). This sizing is consistent with a large solar receiver and power tower sized at ~200 MW(t).

The sizing of the reactor was found by an iterative procedure. One inch O.D. tubes were chosen to contain the air flow. The tube spacing was varied to obtain a set of acid-side (shell-side) flow velocities. The catalyst size was adjusted to maintain a tube diameter (based on a wetted-perimeter) to catalyst diameter ratio in the range of 5 to 10. The length of the reactor was determined by the required heat transfer surface area. The resultant acid-side pressure drop was compared against the maximum allowed (50 psi) and further iterations were conducted until heat transfer, pressure drop, and reaction kinetics (space velocity) requirements were all satisfied.

Characteristics of the DR-1 conceptual design are summarized in Table 3-1 and a sketch of the unit is shown in Figure 3-3.

The design consists of approximately 3400 metal tubes of 1" O.D. arranged on a 1-1/2" triangular pitch. The spaces between the tubes are packed with alumina spheres. The upper half of the reactor zone contains plain 3/8" alumina spheres, while the lower half contains 3/16" alumina spheres with supported platinum catalyst. The hot air from the solar receiver, entering at 1800°F, flows upward through the tubes. The acid vapor, entering at 845°F, flows downward around the tubes and past the alumina spheres. The outlet acid temperature is 1600°F.

This design results in a moderate process fluid pressure drop of 28 psi and a relatively low space velocity of 520 hours⁻¹. The hot air, maintained at a pressure 50 psi greater than the acid vapor, experiences a 21 psi pressure drop.

The header design employed in the earlier NASA design was re-evaluated and found to be satisfactory. The increased volumetric flowrate of air, compared to the previously assumed helium, required sizing modifications, but no major structural changes are anticipated. The shell is required to contain 328 psia acid vapor, as opposed to the earlier requirement of 55 psia. A heavier wall thickness is needed, but again no major design changes are required.

Appropriate materials of construction were identified. The reference tube material was chosen as alonized Incoloy 800. This material has proven successful in previous materials tests at ISPRA and General Atomics, and is planned for testing as part of this contract. Alonized Inconel 625, which has already been tested under this contract, also was identified as a candidate material. The headers for the DR-1 were chosen as alonized Incoloy 800. The shell is constructed of Incoloy 800 and lined with acid-proof brick. A suitable coating may be required, but was not identified at this time.

TABLE 3-1

REDUCTION REACTOR CHARACTERISTICS

Type of Design	Shell and Tube
Flow Direction	Countercurrent
Heat Duty, MW	47
Inside Diameter, ft.	8
Length (w/o headers), ft.	35
Tube Outside Diameter, in.	1
Number of Tubes	3403
Tube Pitch (triangular spacing), in.	1.5
Heat Transfer Surface, ft. ²	31,200
Shell Side Characteristics	
Fluid	SO ₃ , H ₂ O, SO ₂ , O ₂
Mass Flowrate, lb/hr	190,800
Volumetric Flowrate, ACFM	3740
Linear Velocity, fps	2.3
Inlet Temperature, °F	845
Outlet Temperature, °F	1600
Inlet Pressure, psia	328
Outlet Pressure, psia	300
Catalyst Volume, ft. ³	298
Catalyst Particle Diameter, in.	3/16
Tube Diameter/Catalyst Diameter Ratio	8
Space Velocity, hr ⁻¹	520
Tube Side Characteristics	
Fluid	Air
Mass Flowrate, lb/hr	787,000
Volumetric Flowrate, ACFM	29,800
Linear Velocity, fps	50
Inlet Temperature, °F	1800
Outlet Temperature, °F	1045
Inlet Pressure, psia	371
Outlet Pressure, psia	350

Figure 3-3. Decomposition Reactor

3.3 SUPPORTING TRADE STUDIES AND ALTERNATIVE CONFIGURATIONS

Central Receiver Versus Distributed Collectors

Solar thermal energy to power the thermochemical reduction may be collected in either of two ways - a central receiver surrounded by a field of heliostats or a number of smaller distributed collectors operating in parallel. To obtain the temperatures required, the distributed collectors would probably be of the parabolic dish type. A qualitative comparison between central receivers (power towers) and distributed collectors was conducted. It was concluded, for the following reasons, that a central receiver appears more practical and cost effective for a solar plant requiring ~200 MW(t).

- The maximum reaction temperature of 1600°F requires very high concentration ratios
- The large power requirements of the plant would result in a large number of distributed collectors connected in parallel. At a rated capacity of 100 KW_t per collector, approximately 2500 collectors would be required for the thermal decomposition portion of the plant.
- The distributed collective approach would require a complex network of high temperature/high pressure piping. A significant part of this piping would have to be acid resistant and capable of handling hot acid in excess of 800°F over a long distance.
- Catalyst handling and replacement and overall maintenance would be substantially greater for the distributed system due to an increase in the number of reduction reactors required.
- Pumping power requirements would be greater with the distributed collector system due to larger line losses resulting in a decrease in overall plant efficiency.
- Initial capital cost of major equipment, insulation, instrumentation and auxiliaries would be greater for the distributed system due to the larger number of components required. This is particularly true of the large number of regenerative heat exchangers required.

Some of these judgments would remain valid for small (1-10 MWt) plants as well. However, the rationale for a central receiver approach would not be nearly as strong for a small plant. Most likely, a quantitative comparison (beyond the scope of this study) would be needed to select a preferred configuration for a small plant.

Adiabatic Versus Isothermal Reduction

The thermal reduction of SO_3 to SO_2 and O_2 is an endothermic process. In order to maintain a constant reaction temperature (isothermal reduction), heat must be added to the system. It should be noted, however, that the proposed concept is not completely isothermal. Since catalyst is present during the heating of the gas from approximately 1400°F to the maximum temperature of 1600°F , reduction occurs throughout the entire temperature range. The significant feature of this design, however, is the fact that heat must be supplied to the reactor. This requires the reduction reactor to be designed as both a heat exchanger and a chemical reactor.

An alternative to isothermal reduction is adiabatic reduction. In this case the gas is preheated above the reaction temperature in a separate heat exchanger with no catalyst present. The hot gas is then passed through an insulated, non-heated reduction reactor where the heat of reaction is supplied by the cooling of the gas stream. The gas may initially be heated to 2400°F and reduced in one step, or may be heated to a lower maximum temperature and reduced in several steps. The advantage of adiabatic reduction is the separation of the heat exchange and chemical reaction functions. In this manner, each device may be optimized separately. This may also permit simpler catalyst placement and removal. The disadvantage of adiabatic reduction is the higher temperatures required and the more complicated circuitry.

A preliminary evaluation of the two reduction methods indicates that isothermal, or heated, reduction is preferred. Materials constraints for operation at high temperatures limit the maximum temperature. Multiple heating and reduction steps would result in serious control problems and overly complicate the circuitry. In addition, catalyst degradation and catalyst redepository at high temperatures need to be verified. On the other hand, catalyst replacement techniques for an isothermal reduction reactor are not simple.

It was decided to use an isothermal reduction reactor consisting of an air-heated countercurrent heat exchanger. If a direct solar heated reduction reactor were chosen during future work, reconsideration should be given to separating the heat exchanger and chemical reactor by the use of adiabatic reduction.

Alternate System Configurations

Assuming a central receiver tower concept with an isothermal reduction process, several system design alternatives were evaluated and compared to determine a preferred concept. Factors that were considered in varying degree in this trade-off study included safety, materials, design practicality, energy utilization and cost.

Specific items that were analyzed included equipment sizing, component weight and location, heat transfer requirements, power requirements, thermal storage considerations, and seismic and wind loadings.

A solar central receiver concept was assumed with either a direct or indirectly-heated decomposition reactor. The system includes a central tower with a receiver at the top surrounded by a heliostat field. The facility would have capability for either thermal or chemical storage and would be used for a chemical or fuel process application.

For a directly heated reduction reactor, the reactor would be an integral part of the central receiver. Solar radiation would be absorbed directly in the reactor either through a window or through tube walls. Acid would flow through a catalyst bed in the receiver tubes, reach 1600°F and isothermally decompose in the receiver/reduction reactor at the very top of the tower. Hot steam, SO₂ and O₂ would then be regeneratively cooled and sent to various condensation, separation and extraction systems. The SO₂ recovered would be recycled back to the SO₂ electrolyzer where hydrogen is produced.

For an indirectly heated reduction reactor, a secondary loop of a heat transfer fluid would interface with the receiver. Thermal energy would be absorbed at the solar receiver by the heat transfer fluid and transported to the reduction reactor where it would be exchanged with the acid stream to thermally decompose the SO₃ into SO₂ and O₂ at 1600°F. The fluid would then be recycled back to the receiver. The heat transfer medium could be air, helium, sand, or some other fluid or solid.

Variations in equipment location and heat transfer media were considered. Eight options were selected as potentially attractive configurations based on previous experience and engineering judgment. These eight system alternatives for "trade-off" evaluations are shown in Table 3-2.

Option 1 consists of hot sulfuric acid moving up and down the tower with the decomposition reactor (DR-1) at the very top of the tower. It should be noted that the DR-1 can be either directly or indirectly coupled to the central receiver. Most of the Sulfur Cycle plant equipment for Option 1 also is located at the top of the tower (≈ 1800 tons) with only the electrolyzer and selected auxiliary equipment located near the base of the tower. The acid lines are at approximately 310°F with this arrangement, permitting Teflon-lined piping to be used.

Options 2 through 5 consist of other arrangements with the DR-1 located at the top of the central tower. As in Option 1, the receiver can either be directly or indirectly coupled to the decomposition reactor. Differences among these options pertain to the location of major components. Progressing from Option 1 to 5 more of the heat exchanger equipment is located at the base of the tower. Options 1 - 5 provide a trade-off in the tower weight and associated structural requirements to meet seismic and wind loads versus acid transport temperatures and the associated piping material considerations.

Option 6 is an indirectly heated system in which air is used as a heat transfer media between the solar receiver and the acid reduction reactor. For this option the thermochemical system is coupled to the tower only by the air transport system. This option results in a reduced tower weight and minimizes the problems of transporting sulfuric acid. These advantages are partially offset, however, by the large piping system required for air transport. Option 7 is similar to Option 6 except that helium is the transport fluid. This option offers a trade-off with Option 6 between reduced piping and pumping power requirements for Option 7 versus increased safety problems and cost.

The last system arrangement was Option 8 which considered a fluidized bed and/or a solid sand concept as the heat transport media. In this concept the reduction reactor is located at the base of the tower. Low temperature sand is transported

TABLE 3-2

ARRANGEMENT CONSIDERATIONS FOR THE SOLAR HYDROGEN DESIGN OPTIONS

NOTE: Options 1 through 5 are Applicable for Both Direct and Indirect Use. Options 6, 7, and 8 are for Indirect Use Only.

to the receiver by a conveyor, heated by a solar radiation, and returned to the reduction reactor. The general arrangement is shown in Figure 3-4. This option offers the special advantage of high temperature energy storage, thus avoiding the problems of diurnal cycling of the thermochemical system.

These options were evaluated and compared based on the criteria defined above. From a safety point-of-view, the direct system has more problems and concerns than an indirect system. A major concern is a rupture of the combined solar receiver/reduction reactor. For Options 1 - 5, where the acid flows directly through the central receiver tubes, any major rupture of these tubes would allow hot 1600°F sulfuric acid to spray out over the tower and heliostat field, presenting a major safety hazard to personnel.

Tables 3-3 and 3-4 summarize the qualitative safety assessment and rating of the various options. Various accident conditions were considered for both direct and indirect heat transfer systems. Air, helium, sand, and a fluidized bed were considered for the indirect heat transfer media. The overall assessment considered probability and consequences of each of the accidents. A rating of very low (VL) to very high (VH) was used. Overall, the safety assessment ranked the air indirect system (Option 6) with the highest safety rating. The sand and/or fluidized bed (Option 8) was ranked second on safety. The direct systems (Option 1 - 5) had the lowest safety ratings.

Considering materials and design practicality, a direct system would require the solar receiver to be leak free (no hot acid can escape to environment). This requirement may be difficult with a high temperature refractory tubing receiver, e.g., silicon carbide. Present design concepts for these tubes include spring fittings which are susceptible to leakage. Also, a direct system would have very little thermal storage capability in the event of an accident. Any rupture or small leak could immediately shut down the solar facility. This lack of thermal inertia also complicates control of the system during transients caused by interruption in solar availability (i.e., the passage of clouds).

As previously discussed, Options 1 - 5 varied primarily in terms of the amount of heat exchanger equipment located at the top of the tower. These variations

Figure 3-4. Solids Heat Transport Concept

TABLE 3-3

SAFETY ASSESSMENT OF SOLAR THERMAL HYDROGEN
PRODUCTION PROCESSES

ACCIDENT	DIRECT	AIR	HE	SAND	FLD. BED
REC. RUPTURE	L/M	VL/VL	VL/VL	VL/L	VL/L
CAVITY RUPTURE	VL/VH	VL/VL	VL/VL	VL/H	VL/H
HEAT TRANSFER PIPE SYSTEM RUPTURE	--	VL/L (VL/M) [≠]	VL/L (VL/M)	VL/L (VL/M)	VL/L (VL/M)
HEAT TRANSFER PIPE SYSTEM LEAK	--	L/VL (H/VL)	M/L (H/M)	VL/L (H/L)	L/L (H/L)
ACID PIPE RUPTURE	L/L H/M	L/L (--)	L/L (--)	L/L (--)	L/L (--)
STORAGE SYSTEM RUPTURE	--	--	--	VL/L	VL/L
D.R. VESSEL RUPTURE	--	L/M	L/M	L/M	L/M
H.P. PIPE WHIP	VL/M	VL/H	VL/H	VL/M	VL/M

* ALL ACID HX AT BOTTOM OF TOWER EXCEPT DR-1 FOR DIRECT SYSTEM

NOTE: VL - VERY LOW

L - LOW

M - MEDIUM

H - HIGH

VH - VERY HIGH

PROBABILITY/CONSEQUENCES

TABLE 3-4

SAFETY ASSESSMENT OF SOLAR THERMAL HYDROGEN
PRODUCTION PROCESSES

ACCIDENT	DIRECT	AIR	HE	SAND	FLD. BED
REC. RUPTURE	L/M	--	--	--	--
CAVITY RUPTURE	--	--	--	--	--
HEAT TRANSFER PIPE SYSTEM RUPTURE	--	--	--	--	--
HEAT TRANSFER PIPE SYSTEM LEAK	--	--	M/L (H/M)*	-- (H/L)	-- (H/L)
ACID PIPE RUPTURE	-- (H/M)	--	--	--	--
STORAGE SYSTEM RUPTURE	--	--	--	--	--
D.R. VESSEL RUPTURE	--	L/M	L/M	L/M	L/M
H.P. PIPE WHIP	--	--	--	--	--
SAFETY RATING	9 (4)	10 (10)	8 (5)	10 (7)	10 (7)

* ALL ACID HX AT BOTTOM OF TOWER EXCEPT DR-1 FOR DIRECT SYSTEM

NOTE: ALL VL FOR PROBABILITY AND/OR CONSEQUENCES ELIMINATED. ALSO L PROBABILITY WITH L CONSEQUENCES ASSUMED UNLIKELY.

were considered primarily to assess the amount of weight located in the tower and its effect on structural requirements. It was determined that the decomposition reactor weight was the most significant item, and, therefore, the actual variation in total weight was relatively small for the five options. An adverse affect of locating more equipment near the base of the tower is a resultant increase in the temperature level in the piping that transports the acid down the tower. For example, in Option 1, with the most of the equipment located at the top, the acid temperature level would be approximately 310°F. For this arrangement Teflon-lined piping could be used. For Options 2 - 5 the acid temperature level would be 420°F, 1340°F, 1600°F, and 1600°F, respectively. At these levels the piping material selection would represent a significant problem. Because of these problems, versus the relatively small penalty in tower structural requirements, it was concluded that Option 1 was the most preferred of the first five options.

Options 6 and 7 were compared from a safety and cost standpoint. As shown in Table 3-4, Option 6 is preferred in terms of safety primarily due to concerns pertaining to helium leakage in personnel access areas. From a cost standpoint it was determined that the helium makeup system required for Option 7 would be a more significant cost item than the larger piping requirements for Option 6, thus Option 6 would be less expensive. Option 6 was therefore preferred over Option 7.

Options 1 and 6 are similar in that air could be used in the primary heat transfer loop. Option 1 has the air transport loop at the top of the tower interfacing with the receiver. Acid at 310°F is then transported up and down the tower to the hydrogen electrolyzer at the base. In Option 6, air is transported in the tower and interfaces with the hot sulfuric acid streams at the base of the tower. Therefore, from safety, materials and engineering design practicality, Option 6 was judged to be more desirable than Option 1 and was selected for the conceptual design effort.

Option 8, is similar to the selected design in that an inert heat transfer media is used to transport thermal energy up and down the tower. The real advantages of Option 8 over Option 1 are the large thermal storage capability with compar-

able power requirements to circulate the heat transfer media. Option 8 was judged to be a potentially attractive concept that could be considered as second generation technology.

A qualitative comparison of the four primary design options is summarized in Table 3-5. As discussed above, the indirect system utilizing an air heat transport fluid (Option 6) was the selected configuration.

TABLE 3-5

COMPARISON OF THERMOCHEMICAL RECEIVER DESIGN OPTIONS

	<u>DIRECT</u>	<u>INDIRECT W/AIR</u>	<u>INDIRECT W/HELIUM</u>	<u>INDIRECT W/SAND</u>
ENERGY EFFICIENCY	GOOD	FAIR	FAIR	FAIR
SAFETY RATING	FAIR	GOOD	FAIR	GOOD
MATERIALS COMPATIBILITY	POOR	GOOD	GOOD	FAIR
OPERABILITY	POOR	GOOD	GOOD	UNKNOWN
RELATIVE COST	FAIR/GOOD	GOOD	FAIR	UNKNOWN
STATUS OF TECHNOLOGY	POOR	GOOD	GOOD	POOR

4.0 REDUCTION REACTOR MATERIALS EVALUATIONS

(R. L. Ammon, H. A. Irwin).

4.1 BACKGROUND

The objective of this task is to screen potential materials for compatibility with reduction reactor conditions in the temperature range of 482°C to 871°C. Table 4-1 summarizes the planned test program which includes screening tests, Part 1, and endurance tests, Part 2. During 1978, screening test sets 1.1 and two runs of test set 1.2 were completed and were reported previously.⁽⁴⁻¹⁾ During 1979 the remaining three runs of test set 1.2 were completed, as were two runs in test set 1.3 and two runs in test set 1.4. Test are continuing for one run in test set 1.3, one run in test set 1.4, and one run in test set 1.5. The remaining runs in test sets 1.3, 1.4, and 1.5 are scheduled for 1980 as are the endurance test sets 2.1 and 2.2.

4.2 SUMMARY OF RESULTS

Table 4-2 itemizes all the materials samples that have been tested through the end of 1979. Since the test program began, six materials have been exposed to an environment of anhydrous SO_3 and argon at 482°C. Thirty-two materials have been exposed for up to 1000 hours to an environment of SO_3 , steam and argon at 482°C. Ten materials have been exposed to the same environment for up to 1000 hours at 871°C. Twenty-one materials have been exposed for up to 1000 hours to an environment of SO_3 , SO_2 , O_2 and steam at 650°C and four materials have been exposed to the same environment for 417 hours at 871°C.

From tests to date, it appears that silicon, silicon carbide, and silicon nitride have the best corrosion resistance irrespective to the test environment. The metallic substrates which have exhibited the best corrosion resistance to date are Inconel 625, Hastelloy G, and Incoloy 800.

TABLE 4-1
SUMMARY OF REDUCTION REACTOR MATERIALS TEST PROGRAM

	Test Set Identification	Test Environment*		Duration - Hours	
		Temperatures, °C	Vapor Constituents	Increments	Total
PART 1 SCREENING TESTS	1.1	482	SO ₃ , Ar	100	500
	1.2	482	SO ₃ , Ar, Steam	100	1,000
	1.3	871			
	1.4	650	SO ₃ , SO ₂ , O ₂ , Steam	100	1,000
	1.5	871			
PART 2 ENDURANCE TESTS	2.1	871	SO ₃ , Ar, Steam	500	5,000
	2.2	871	SO ₃ , SO ₂ , O ₂ , Steam	500	5,000

*All tests at atmospheric pressure.

TABLE 4-2
REDUCTION REACTOR MATERIAL SAMPLES TESTED

TEST SET IDENT.	TEST ENVIRONMENT	RUN IDENT.	MATERIALS TESTED
1.1	Furnace Temp., °C - 482 SO ₃ Flow Rate, scc/min - 12 SO ₂ Flow Rate, scc/min - 0 O ₂ Flow Rate, scc/min - 0 Ar Flow Rate, scc/min - 128 Steam Flow Rate, scc/min - 0	RR 482AI1	Hastelloy C-276 Cartech Type 20Cb3 Incoloy 825 Inconel 625 SS 310 SS 18-18-2
1.2	Furnace Temp., °C - 482 SO ₃ Flow Rate, scc/min - 25 SO ₂ Flow Rate, scc/min - 0 O ₂ Flow Rate, scc/min - 0 Ar Flow Rate, scc/min - 78 Steam Flow Rate, scc/min - 58	RR 482HI1	Hastelloy C-276 Cartech Type 20Cb3 Incoloy 825 Inconel 625 SS 310 SS 18-18-2
		RR 482HI2	Macor Polycrystal Silicon Hot Pressed Silicon Nitride Alonized Inconel 625 Hot Pressed Silicon Carbide Inconel 657
		RR 482HI3	Hastelloy G CS 1018 Alonized CS 1018 SS 316 Alonized SS 316 Preanodized Tantalum
		RR 482HI4	Sialon 80 Sialon 81 Sialon 88 Alumina Hastelloy B2 Zirconium 702 Titanium Diboride
		RR 482HI5	Duro Acid-Proof Brick Duriron Vitreous Carbon Durichlor 51 Aluminum Silicate M-120 Inconel 617 Tungsten - powder sintered, swaged

TABLE 4-2 (CONTINUED)
REDUCTION REACTOR MATERIAL SAMPLES TESTED

TEST SET IDENT.	TEST ENVIRONMENT	RUN IDENT.	MATERIALS TESTED
1.3	Furnace Temperature, °C - 871 SO ₃ Flow Rate, scc/min - 25 SO ₂ Flow Rate, scc/min - 0 O ₂ Flow Rate, scc/min - 0 Ar Flow Rate, scc/min - 78 Steam Flow Rate, scc/min - 58	RR 871HI1	Polycrystal Silicon Hot Pressed Silicon Nitride Hot Pressed Silicon Carbide Inconel 657 Inconel 625 Alonized Inconel 625
		RR 871HI2	Durichlor 51 Alumina Hastelloy G Duro Acid-Proof Brick Duriron Aluminum Silicate M-120
		RR 871HI3	Inconel 671 Alonized Inconel 671 Incoloy 800 Alonized Incoloy 800
1.4	Furnace Temperature, °C - 650 SO ₃ Flow Rate, scc/min - 25 SO ₂ Flow Rate, scc/min - 47 O ₂ Flow Rate, scc/min - 23 Ar Flow Rate, scc/min - 0 Steam Flow Rate, scc/min - 169	RR 650H01	Polycrystal Silicon Hot Pressed Silicon Nitride Hot Pressed Silicon Carbide Inconel 657 Inconel 625 Alonized Inconel 625
		RR 650H02	Aluminum Silicate M-120 Durichlor 51 Hastelloy G Vitreous Carbon Duriron Hastelloy B2 Alumina Zirconium 702 Stainless Steel 310
		RR 650H03	Sialon 80 Sialon 81 Sialon 88 Hastelloy C-276 Cartech Type 20Cb3 Tungsten - powder, sintered, swaged

TABLE 4-2 (CONTINUED)
REDUCTION REACTOR MATERIAL SAMPLES TESTED

TEST SET IDENT.	TEST ENVIRONMENT	RUN IDENT.	MATERIALS TESTED
1.5	Furnace Temperature, °C - 871 SO ₃ Flow Rate, scc/min - 25 SO ₂ Flow Rate, scc/min - 47 O ₂ Flow Rate, scc/min - 23 Ar Flow Rate, scc/min - 0 Steam Flow Rate, scc/min - 169	RR 871H01	Inconel 671 Alonized Inconel 671 Incoloy 800 Alonized Incoloy 800

The surfaces of six materials which were tested in both test sets 1.1 and 1.2 - Hastelloy C-276, Cartech Type 20Cb3, SS 18-18-2, Inconel 625, SS 310 and Incoloy 825 - were characterized both in the as-received condition and the as-tested condition using scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDAX) data. For each material in both test sets, the surface concentrations of sulfur and silicon relative to its as-received condition has increased. This indicates an uptake of sulfur, perhaps as a metallic sulfide or sulfate, and also an uptake of silicon onto the sample surface which may have come from the walls of the quartz reaction tube.

4.3 EXPERIMENTAL PROCEDURES

The materials test beds utilize quartz structural materials for operations at or near atmospheric pressures. A quartz sample holder capable of holding six specimens 19 mm x 19 mm x 1.6 mm fits inside a 40 mm quartz combustion tube and is heated to the exposure temperature. The process steam for the inlet conditions is a once-through type supplied by an arrangement similar to the supply system for the Catalyst Screening Test Program, permitting either anhydrous SO_3 or SO_3 with superheated steam to be introduced past the material samples in proportion to the expected reduction reactor inlet process steam composition. The SO_3 Reduction Reactor Test Facility for inlet conditions is shown in Figure 4-1. A schematic diagram of the experimental inlet conditions test apparatus is presented in Figure 4-2.

A second materials test bed, simulating reduction reactor outlet conditions is similar to the reduction reactor inlet conditions test apparatus except for the addition of SO_2 and O_2 gas lines to simulate the outlet gas streams whose constituents include SO_3 , SO_2 , O_2 , and steam. Although the inlet conditions test utilize Ar as a carrier gas, no carrier gas is used in the outlet conditions tests. The SO_3 Reduction Reactor Test Facility for outlet conditions is shown in Figure 4-3. A schematic of the outlet conditions test apparatus is given in Figure 4-4.

Figure 4-1. SO₃ Reduction Reactor Materials Test Facility - Inlet Conditions.

6:5362-1A

Figure 4-2. Schematic of Experimental Apparatus for Evaluating Materials Under Reduction Reactor Inlet Conditions

**SO₂ REDUCTION REACTOR
TEST FACILITY
OUTLET CONDITIONS**

Figure 4-3. SO₂ Reduction Reactor Materials Test Facility - Outlet Conditions

Figure 4-4. Schematic of Experimental Apparatus for Evaluating Materials Under Reduction Reactor Outlet Conditions

At nominal 100 hour intervals, the tests were intentionally interrupted and the samples were removed for visual inspection, photographing, weighing and thickness measurements.

4.4 DETAILED DISCUSSION OF RESULTS

Table 4-2 gives the experimental parameters and materials tested in each run during 1978 and 1979. Detailed tabulated data for all tests performed in 1979 are presented in Appendix E.

The runs are identified as follows:

RR - means it is a test simulating dynamic reduction reactor conditions

482 } the number immediately after the RR indicates the
650 } test temperature in degrees centigrade
871 }

H - means the test is being conducted in the presence of steam

A - means the test is being conducted using anhydrous SO_3 with Argon as the carrier gas

I - simulated reduction reactor inlet gas stream composition

O - simulated reduction reactor outlet gas stream composition

1, 2, etc. - the number immediately after I or O indicates the run number in a particular test series

Test Set 1.2

All materials in this test series are tested at 482°C under simulated reduction reactor inlet environment using argon as a carrier gas. The gas flow rates are 25 scc/min SO_3 , 58 scc/min steam and 78 scc/min Ar. The SO_3 -steam ratio simulates the expected reduction reactor inlet environment.

The data pertaining to the two runs completed in CY 1978 have been previously reported. (4-2) Cumulative corrosion data expressed as weight change per unit

area for all the runs in test set 1.2 are plotted as a function of time in Figures 4-5 through 4-7. Macrophotographs of the pretest samples and the samples after 1000 hours are given in Figures 4-8 through 4-10.

Run RR 482HI3

Screening of Run RR 482HI3 materials which was initiated during the latter part of 1978 was completed in 1979. The samples consisted of Hastelloy G, carbon steel (CS) 1018, Alonized CS 1018, stainless steel 316, Alonized SS 316, and electrochemically preanodized tantalum. Alonizing is a commercial process for aluminizing the surface of a metal.

Two of the samples in Run RR 483HI3, CS 1018 and tantalum, showed sudden decreases in Δ weight/area due to spalling of the corrosion products during handling. After 155 hours exposure the Δ weight/area for the other four samples was positive and nearly constant. Of those four samples, the Hastelloy G appeared to have the highest degree of resistance to the above corrosive conditions based on weight change data alone.

Run RR 482HI4

In this run the materials included three Sialon compositions, Zirconium 702 (Zr 702), Hastelloy B2, titanium diboride (TiB_2), and high purity alumina, both of the last two from Duramic Products, Inc. The Sialon compositions are ceramic phases in the Si-Al-O-N systems and consist of one, two and three-dimensional arrangements of (Si, Al) (O, N)₄ tetrahedra. These new oxynitrides include structure types based upon α and β silicon nitride, silicon oxynitride, aluminum nitride and silicon nitride eucryptite, spinel, melilite and apatite. These materials are being explored for potential use in gas turbines and other high temperature engineering applications. (4-3)

The TiB_2 sample was completely disintegrated after the first interruption at 100 hours and was replaced with Zr 702. All of the samples in Run RR 482HI4 showed positive Δ weight/area with Zr 702 and Hastelloy B2 showing the greatest increases. After initial positive weight changes, the alumina and three Sialon samples showed very little change throughout the remainder of the test.

Figure 4-5. Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR 482HI3

Figure 4-6. Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR 482HI4

Figure 4-7. Reduction Reactor Screening Test Results in Steam Environment -
 Inlet Conditions - Run RR 482HI5

Figure 4-8. Visual Appearance of Samples in Run RR 482HI3.

SIALON
81

AL₂O₃

SIALON
88

B2

SIALON
81

AL₂O₃

SIALON
88

B2

TiB₂

Zr 702

SIALON
80

Zr 702

SIALON
80

0 Hours

TEST CONDITIONS:

FURNACE TEMPERATURE - 482°C
SO₃ FLOW - 25 scc/min
STEAM FLOW - 58 scc/min
ARGON FLOW - 78 scc/min

1000 Hours

LEGEND:

Sialon 80 - Sialon 80
Sialon 81 - Sialon 81
Sialon 88 - Sialon 88
B2 - Hastelloy B2
Zr702 - Zirconium 702
Al₂O₃ - Alumina
TiB₂ - Titanium Diboride

Figure 4-9. Visual Appearance of Samples in Run RR482HI4

0 Hours

1000 Hours

(336 Hours for Vitreous Carbon)
(568 Hours for Inconel 617)

LEGEND:

DURO BRICK	- Duro Acid-Proof Brick
DURIRON	- Duriron
INC 617	- Inconel 617
DURICHLOR	- Durichlor 51
TUNGSTEN	- Tungsten
ALUMINUM SILICATE	- Aluminum Silicate
VITREOUS CARBON	- Vitreous Carbon

TEST CONDITIONS:

FURNACE TEMPERATURE	- 482°C
SO ₃ FLOW RATE	- 25 scc/min
STEAM FLOW RATE	- 58 scc/min
ARGON FLOW RATE	- 78 scc/min

Figure 4-10. Visual Appearance of Samples in Run RR 482HI5.

Run RR 482HI5

The initial six samples in Run RR 482HI5 were Duro acid-proof brick, Duriron, vitreous carbon from Atomergenic, Inc., Durichlor 51, tungsten which was formed from powder and then sintered and swaged (PSS), and aluminum silicate M-120 from Duramic Products, Inc.

All samples except vitreous carbon in Run RR 482HI5 showed positive weight changes and appear to have adherent protective corrosion layers. Pitting of the vitreous carbon sample was observed at the first interruption at 75 hours. After 335 hours, the vitreous carbon sample was almost completely consumed and could not be further tested. It was replaced by Inconel 617, which was put into test after the interruption at 432 hours for a total exposure time of 468 hours. Based on weight change data alone, the Durichlor 51 appears to have the best corrosion resistance to date of the materials tested in Run RR 482HI5.

Test Set 1.3

All materials in this test series are tested at 871°C under simulated reduction reactor inlet environment conditions using argon as a carrier gas. The gas flow rates are 25 scc/min SO_3 , 58 scc/min steam and 78 scc/min Ar.

Cumulative corrosion data expressed as weight change per unit area for all the runs in test set 1.3 are plotted as a function of time in Figures 4-11 through 4-13. Macrophotographs of the pretest samples and the samples after 1000 hours for Runs RR 871HI1 and RR 871HI2 and after 108 hours for Run RR 871HI3 are given in Figures 4-14 through 4-16.

Run RR 871HI1

The materials chosen for Run RR 871HI1 were those which had exhibited the best corrosion resistance based on weight change data in Runs RR 482HI1, RR 482HI2, RR 482HI3, and RR 482HI4. They were polycrystal silicon, Inconel 625, Alonized Inconel 625, hot pressed silicon nitride from Ceradyne, Inc., Inconel 657, and hot pressed silicon carbide from Ceradyne, Inc.

Figure 4-11. Reduction Reactor Screening Test Results in Steam Environment -
 Inlet Conditions - Run RR 871HI1

Figure 4-12. Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR 871HI2

Figure 4-13. Reduction Reactor Screening Test Results in Steam Environment-Inlet Conditions - Run RR 871HI3

RUN RR871HI1

RUN RR871HI1

Si

Si₃N₄

Inc 625

Inc 657

Inc 625A

SiC

Si

Si₃N₄

Inc 625

Inc 657

Inc 625A

SiC

0 Hours

1000 Hours

TEST CONDITIONS:

FURNACE TEMPERATURE - 871°C
SO₃ FLOW - 25 scc/min
STEAM FLOW - 58 scc/min
ARGON FLOW - 78 scc/min

LEGEND:

Si	- Silicon
SiC	- Silicon Carbide
Si ₃ N ₄	- Silicon Nitride
625	- Inconel 625
625A	- Alonized Inconel 625
657	- Inconel 657

4-23

Figure 4-14. Visual Appearance of Samples in Run RR 871HI1

TEST CONDITIONS:

FURNACE TEMPERATURE - 871⁰C
SO₃ FLOW RATE - 25 scc/min
STEAM FLOW RATE - 58 scc/min
ARGON FLOW RATE - 78 scc/min

Figure 4-15. Visual Appearance of Samples in Run RR 871HI2

Figure 4-16. Visual Appearance of Samples in Run RR 871HI3

It is seen in Figure 4-11 that after an initial weight loss during the first 58-hour exposure period in Run RR 871HI1 for Alonized Inconel 625, it showed very little weight change throughout the remainder of the test. The decreasing weight changes per unit area for the Inconel 625 and Inconel 657 in Run RR 871HI1 after initial increases are due to spalling of the corrosion product. The silicon carbide and silicon nitride samples had small positive weight changes (except for the silicon carbide sample at 329 hours which could be due to weighting error).

Run RR 871HI2

The materials tested in Run RR 871HI2 were Durichlor 51, Hastelloy G, Duro acid-proof brick, Duriron, 99.9% alumina and aluminum silicate, both of the latter two from Duramic Products, Inc.

Except for aluminum silicate, which after an initial weight decrease showed negative nearly constant weight changes, all samples in Run RR 871HI2 showed positive weight changes. For the alumina and Hastelloy G samples, the weight changes were virtually constant after the initial weight increases. Except for the small black spots on the alumina samples, probably caused by the corrosion of a neighboring sample touching it, the visual appearances of the alumina, aluminum silicate, and Duro acid-proof brick samples appeared unchanged from their pre-test appearance. The other three samples formed black corrosion products. While Hastelloy G had an adherent corrosion product, spalling of the Duriron and Durichlor 51 corrosion layer was evident after 298 and 511 hours, respectively.

Run RR 871HI3

The materials tested in Run RR 871HI3 were Incoloy 800 and Inconel 671 which is used as a cladding for Incoloy 800, as well as aluminized samples of both Incoloy 800 and Inconel 671.

At the end of CY 1979 the samples in Run RR 871HI3 have been exposed to the conditions of test set 1.3 for a total of 108 hours. Positive weight changes were observed for all samples in Run RR 871HI3.

Test Series 1.4

A second materials test bed which permitted the testing of materials samples under outlet conditions was put on line during the first half of 1979. All materials in test series 1.4 are tested at 650°C under simulated reduction reactor outlet environment conditions. No carrier gas is used in tests under outlet conditions. The gas flow rates are 25 scc/min SO₃, 47 scc/min SO₂, 23 scc/min O₂, and 169 scc/min steam.

Cumulative corrosion on data expressed as weight change per unit area for all the runs in test set 1.4 are plotted as a function of time in Figures 4-17 through 4-19. Macrophotographs of the pretest samples and the samples after 1000 hours for Runs RR 650H01 and RR 650H02 and after 336 hours for Run RR 650H03 are given in Figures 4-20 through 4-22.

Run RR 650H01

The same materials that were tested in Run RR 871H11 under inlet conditions were tested in Run RR 650H01 under outlet conditions. They were polycrystal silicon, hot pressed silicon nitride from Ceradyne, Inc., Inconel 625, Alonized Inconel 625, hot pressed silicon carbide from Ceradyne, Inc., and Inconel 657.

All samples in Run RR 650H01 showed positive Δ weight/area with Inconel 657 showing the greatest increase. Although the Inconel 657, Inconel 625, and Alonized Inconel 625 appeared to have adherent protective corrosion layers, a small amount of spalling did occur during handling. White dots of residue were observed on the silicon nitride sample in Run RR 650H01 at the interruption at 496 hours which probably accounts for the relatively large weight increase observed. The residue was not present at the interruption at 612 hours, however.

While removing samples from the quartz tube during the interruption at 612 hours of Run RR 650H01, the silicon carbide sample was dropped and broken into two pieces. It was put together with two small gold bands and put back into test. As seen in Figure 4-17, the gold had virtually no catalytic effect on the silicon carbide sample.

Figure 4-17. Reduction Reactor Screening Test Results in Steam Environment - Outlet Conditions - Run RR 650H01

Figure 4-18. Reduction Reactor Screening Test Results in Steam Environment - Outlet Conditions - Run RR 650H02

Figure 4-19. Reduction Reactor Screening Test Results in Steam Environment - Outlet Conditions - Run RR 650H03

RUN 650-H0-1

0 Hours

TEST CONDITIONS:

FURNACE TEMPERATURE - 650°C
 SO₃ FLOW - 25 scc/min
 SO₂ FLOW - 47 scc/min
 O₂ FLOW - 23 scc/min
 STEAM FLOW - 169 scc/min

RUN 650-H0-1

1000 Hours

LEGEND:

Si	- Silicon
SiC	- Silicon Carbide
Si ₃ N ₄	- Silicon Nitride
625	- Inconel 625
625A	- Alonized Inconel 625
657	- Inconel 657

Figure 4-20. Visual Appearance of Samples in Run RR 650H01

0 Hours

LEGEND:

AL SILICATE - Aluminum Silicate
 DUR. 51 - Durichlor 51
 HAST. G - Hastelloy G
 HAST. B2 - Hastelloy B2
 DURIRON - Duriron
 AL₂O₃ - Alumina
 VIT. CARBON - Vitreous Carbon
 ZR 702 - Zirconium 702
 SS 316 - Stainless Steel 310

1000 Hours

(93 Hours for Vitreous Carbon)
 (94 Hours for Zirconium 702)
 (388 Hours for Hastelloy B2)
 (425 Hours for Stainless Steel 310)

TEST CONDITIONS:

FURNACE TEMPERATURE - 650°C
 SO₃ FLOW RATE - 25 scc/min
 SO₂ FLOW RATE - 47 scc/min
 O₂ FLOW RATE - 23 scc/min
 STEAM FLOW RATE - 169 scc/min

Figure 4-21. Visual Appearance of Samples in Run RR 650H02.

RR 650H03

TUNGSTEN

SIALON 80

SIALON 88

SIALON 81

CARTECH TYPE 20 Cb3

HASTELLOY C-276

0 Hours

RR 650H03

TUNGSTEN

SIALON 80

SIALON 88

SIALON 81

CARTECH TYPE 20 Cb3

HASTELLOY C-276

336 Hours

TEST CONDITIONS:

FURNACE TEMPERATURE - 650 °C
SO₃ FLOW RATE - 25 scc/min
SO₂ FLOW RATE - 47 scc/min
O₂ FLOW RATE - 23 scc/min
STEAM FLOW RATE - 169 scc/min

Figure 4-22. Visual Appearance of Samples in Run RR 650H03

Run RR 650H02

In this run the six materials initially tested were aluminum silicate M-120 from Duramic Products, Inc., Durichlor 51, Hastelloy G, vitreous carbon from Atomergenics, Inc., Duriron, and 99.9% alumina from Duramic Products, Inc.

The vitreous carbon was almost completely consumed by the first interruption at 93 hours. It was replaced by Hastelloy B2, which showed the greatest weight gain of the samples tested in Run RR 650H02, having a heavy, beaded, black corrosion layer at the interruption at 481 hours. It was then replaced by Zirconium 702 which, by the interruption at 575 hours, had lost 32% of its pre-test weight and had a heavy, white, powdery corrosion layer. It was replaced by stainless steel (SS) 310 which showed considerable spalling by 223 hours exposure. The SS 310 sample was tested until the completion of Run RR 650H02 when the following samples in Run RR 650H02 - aluminum silicate, Durichlor 51, Hastelloy G, Duriron, and alumina - had completed 1000 hours exposure. Thus, vitreous carbon was tested for a total of 93 hours, Hastelloy B was tested for a total of 388 hours, Zirconium 702 was tested for a total of 94 hours and SS 310 was tested for a total of 425 hours. Based on weight change data alone, alumina appears to have the best corrosion resistance of the materials tested in Run RR 650H02.

Run RR 650H03

In this run the materials included three Sialon compositions, Hastelloy C-276, Cartech Type 20Cb-3, and tungsten formed from powder and then sintered and swaged (PSS).

At the end of CY 1979, the samples in Run RR 650H03 have been exposed to the conditions of test set 1.4 for a total of 336 hours. For two samples in Run RR 650H03, Sialons 80 and 81, negative weight changes were observed. Except for the PSS tungsten sample which, by the interruption at 336 hours, had developed a flaky, green corrosion layer, the rest of the samples in Run RR 650H03 appeared to have adherent protective corrosion products.

Test Series 1.5

All materials in this test series are tested at 871°C in a simulated reduction reactor outlet environment of 25 scc/min SO₃, 47 scc/min SO₂, 23 scc/min O₂ and 169 scc/min steam. No carrier gas is used in the tests under outlet conditions. The gas flow rates are 25 scc/min SO₃, 47 scc/min SO₂, 23 scc/min O₂ and 169 scc/min steam.

Run RR 871H01

The materials tested in Run RR 871H01 were Incoloy 800, Alonized Incoloy 800, Inconel 671 and Alonized Inconel 671.

At the end of CY 1979 the samples in Run RR 871H01 have been exposed to the conditions of test set 1.5 for a total of 417 hours. Cumulative corrosion data for Run RR 871H01, expressed as weight change per unit area, are plotted as a function of time in Figure 4-23. Macrophotographs of the pretest samples and the samples after 417 hours are given in Figure 4-24.

Positive weight changes were observed for all materials except the Alonized Inconel 800 sample, which had a negative weight change after the first interruption at 120 hours, but small positive weight changes thereafter to 417 hours. Based on weight change data, the Alonized Incoloy 800 appears to have the best corrosion resistance to the conditions of test set 1.5 of the materials tested in Run RR 871H01.

SEM and EDAX Results

The surfaces of six materials which were tested in both test sets 1.1 and 1.2 during CY 1978 were characterized both in the as-received condition and the as-tested condition using scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDAX) data. The six materials in both runs were:

- Hastelloy C-276
- Cartech Type 20Cb3
- Stainless Steel 18-18-2
- Inconel 625
- Stainless Steel 310
- Incoloy 825

Figure 4-23. Reduction Reactor Screening Test Results in Steam Environment-
 Outlet Conditions - Run RR 871H01

Figure 4-24. Visual Appearance of Samples in Run RR 871H01.

The experimental conditions for Runs RR 482AI1 and RR 482HI1 in test sets 1.1 and 1.2, respectively, were as follows:

	<u>Test Set 1.1</u>	<u>Test Set 1.2</u>
	Run RR 482AI1 (Anhydrous)	Run RR 482HI1 (Wet)
FURNACE TEMPERATURE, °C	482	482
SO ₃ TEMPERATURE, °C	53	53
SO ₃ FLOW RATE, scc/min	12	25
STEAM FLOW RATE, scc/min	0	58
ARGON FLOW RATE, scc/min	128	78
TOTAL TEST TIME, hours	525	1007

Figures 4-25 through 4-30 show the SEM and EDAX results for the surfaces of Hastelloy C-276, Cartech Type 20Cb3, SS 18-18-2, Inconel 625, SS 310, and Incoloy 825, respectively.

In order to have a meaningful comparison of EDAX results for the anhydrous and steam exposures, the counts of the peak representing the most abundant element - nickel (Ni) or iron (Fe) in the above cases - were held nearly constant within individual materials. It is seen that for each material relative to its as-received conditions (which is shaded), the surface concentration of chromium (Cr) in the exposed samples is the same or greater and the surface sulfur (S) and silicon (Si) concentrations have increased. An uptake of sulfur is indicated perhaps as a metallic sulfide or sulfate. A comparison of the samples in Run RR 482AI1 and RR 482HI1 shows a higher surface concentration of S in Run RR 482HI1 samples but a higher surface concentration of Si in Run RR 482AI1 samples. The higher S concentration is expected for Run RR 482HI1 samples since they were exposed to higher SO₃ flow rates for a longer period of time than samples in Run RR 482AI1. Since Run RR 482AI1 was the initial run, it is possible that at the 482°C reaction temperature, Si may have migrated onto the samples from the quartz reaction tube and other quartz apparatus used in the system.

- a. SEI of surface, as received. b. SEI of surface after exposure to anhydrous environment for 525 hrs. c. SEI of surface after exposure to hydrous environment for 1007 hrs.

- d. EDA comparison of surface of as received condition (shaded) to surface exposed to anhydrous environment for 525 hrs.

- e. EDA comparison of surface of as received condition (shaded) to surface exposed to hydrous environment for 1007 hrs.

EXPOSURE CONDITIONS	Run RR492A11 (Anhydrous)	Run RR482H11 (Hydrous)
Furnace Temperature, °C	482	482
SO ₃ Temperature, °C	53	53
SO ₃ Flow Rate, SCC/min	12	25
Steam Flow Rate, SCC/min	-	58
Argon Flow Rate, SCC/min	128	78
Total Test Time, hours	525	1007

Figure 4-25. Surface Characteristics of Hastelloy C-276.

a. SEI of surface, as received.

b. SEI of surface after exposure to anhydrous environment for 525 hrs.

c. SEI of surface after exposure to hydrous environment for 1007 hrs.

d. EDA comparison of surface of as received condition (shaded) to surface exposed to anhydrous environment for 525 hrs.

e. EDA comparison of surface of as received condition (shaded) to surface exposed to hydrous environment for 1007 hrs.

EXPOSURE CONDITIONS	Run RR492A11 (Anhydrous)	Run RR482H11 (Hydrous)
Furnace Temperature, °C	482	482
SO ₃ Temperature, °C	53	53
SO ₃ Flow Rate, SCC/min	12	25
Steam Flow Rate, SCC/min	-	58
Argon Flow Rate, SCC/min	128	78
Total Test Time, hours	525	1007

Figure 4-26. Surface Characteristics of Carpenter Type 20 Cb-3

a. SEI of surface, as received.

b. SEI of surface after exposure to anhydrous environment for 525 hrs.

c. SEI of surface after exposure to hydrous environment for 1007 hrs.

d. EDA comparison of surface of as received condition (shaded) to surface exposed to anhydrous environment for 525 hrs.

e. EDA comparison of surface of as received condition (shaded) to surface exposed to hydrous environment for 1007 hrs.

EXPOSURE CONDITIONS	Run RR482A11 (Anhydrous)	Run RR482H11 (Hydrous)
Furnace Temperature, °C	482	482
SO ₃ Temperature, °C	53	53
SO ₃ Flow Rate, SCC/min	12	25
Steam Flow Rate, SCC/min	-	58
Argon Flow Rate, SCC/min	128	78
Total Test Time, hours	525	1007

Figure 4-27. Surface Characteristics of SS 18-18-2.

- a. SEI of surface, as received. b. SEI of surface after exposure to anhydrous environment for 525 hrs. c. SEI of surface after exposure to hydrous environment for 1007 hrs.

- d. EDA comparison of surface of as received condition (shaded) to surface exposed to anhydrous environment for 525 hrs.

- e. EDA comparison of surface of as received condition (shaded) to surface exposed to hydrous environment for 1007 hrs.

EXPOSURE CONDITIONS	Run RR492A11 (Anhydrous)	Run RR482H11 (Hydrous)
Furnace Temperature, °C	482	482
SO ₃ Temperature, °C	53	53
SO ₃ Flow Rate, SCC/min	12	25
Steam Flow Rate, SCC/min	-	58
Argon Flow Rate, SCC/min	128	78
Total Test Time, hours	525	1007

Figure 4-28. Surface Characteristics of Inconel 625.

a. SEI of surface, as received.

b. SEI of surface after exposure to anhydrous environment for 525 hrs.

c. SEI of surface after exposure to hydrous environment for 1007 hrs.

d. EDA comparison of surface of as received condition (shaded) to surface exposed to anhydrous environment for 525 hrs.

e. EDA comparison of surface of as received condition (shaded) to surface exposed to hydrous environment for 1007 hrs.

EXPOSURE CONDITIONS	Run RR492AI1 (Anhydrous)	Run RR482HI1 (Hydrous)
Furnace Temperature, °C	482	482
SO ₃ Temperature, °C	53	53
SO ₃ Flow Rate, SCC/min	12	25
Steam Flow Rate, SCC/min	-	58
Argon Flow Rate, SCC/min	128	78
Total Test Time, hours	525	1007

Figure 4-29. Surface Characteristics of SS310.

- a. SEI of surface, as received. b. SEI of surface after exposure to anhydrous environment for 525 hrs. c. SEI of surface after exposure to hydrous environment for 1007 hrs.

- d. EDA comparison of surface of as received condition (shaded) to surface exposed to anhydrous environment for 525 hrs.

- e. EDA comparison of surface of as received condition (shaded) to surface exposed to hydrous environment for 1007 hrs.

EXPOSURE CONDITIONS	Run RR492A11 (Anhydrous)	Run RR482H11 (Hydrous)
Furnace Temperature, °C	482	482
SO ₃ Temperature, °C	53	53
SO ₃ Flow Rate, SCC/min	12	25
Steam Flow Rate, SCC/min	-	58
Argon Flow Rate, SCC/min	128	78
Total Test Time, hours	525	1007

Figure 4-30. Surface Characteristics of Incoloy 825.

4.5 FUTURE WORK

All screening in test sets 1.1 and 1.2 has been completed. The last run of test set 1.4 will be completed early in CY 1980. Testing will continue in test sets 1.3 and 1.5 at 871°C on those materials exhibiting the best corrosion resistance at the lower temperatures.

SEM and EDAX data for alloying elements such as Ni, Cr, Fe as well as for Si and S will be obtained from the surfaces of both as-received and as-tested samples. The exposed samples will then be mounted and polished and SEM and EDAX data of the sample cross sections will be obtained.

Because materials with high silicon content appear to have better corrosion resistance than other more conventional alloys, effort will be directed toward procuring, testing, and characterizing metallic samples which have been coated with silicon and/or silicon compounds. Only those samples which display a superior degree of corrosion resistance will be used as substrate material for the siliconizing process. Also, advantage will be taken of the opportunity to utilize the Laboratory Model test loop for materials testing. Samples will be located in the acid vaporizer and reduction reactor at positions where temperatures and environmental conditions are known. Compatibility results from these tests will be compared with results obtained in the independent acid vaporizer test program.

During 1980 endurance testing of materials which survive the screening tests will begin. Endurance tests will utilize the same facilities in which the screening tests were conducted. A flash evaporator will be incorporated into these facilities so that an 80 w/o sulfuric feed can be used in place of the individual anhydrous SO_3 and steam feeds to simulate 80 w/o sulfuric acid and thus eliminate the need for a carrier gas. Tests will be initiated at 871°C for a total test time of 5000 hours as outlined in Table 4-1 for both inlet and outlet conditions. Samples will be examined at incremental time intervals to assess the degree of interaction. During 1980, endurance testing of candidate reduction reactor materials should be completed.

4.6 REFERENCES

1. Westinghouse Electric Corp., "Solar Thermal Hydrogen Generation Process - Annual Technical Progress Report," DOE Contract No. ET-78-C-02-4705, Report C00-4705-19, January-December 1978.
2. Ibid
3. K. H. Jack, "Review Sialons and Related Nitrogen Ceramics," Journal of Materials Sciences 11, 1135-1158, 1976.

5.0 REDUCTION REACTION CATALYST EVALUATION

(J. F. Pierre)

5.1 BACKGROUND

In the Westinghouse Sulfur Cycle for hydrogen production, the critical high temperature step involves the reduction of sulfur trioxide, obtained through the thermal decomposition of sulfuric acid, to sulfur dioxide and oxygen. In its simplest form, the hydrogen production process can be described by two basic equations:

and

Reaction (1) takes place in a thermal reduction reactor and reaction (2) occurs in a sulfuric acid electrolyzer.

As is evidenced in Reaction (1-b), the reduction of sulfur trioxide is an integral part of the hydrogen production process. In order to effect heat economy and to decrease the recycle mass rates, it is important to achieve the maximum possible conversion to SO_2 per pass through the reduction reactor. If only a small reduction is achieved per pass, the recycle rate of undecomposed SO_3 is large. A large recycle rate requires additional equipment, power consumption, etc., thereby increasing capital and operating costs. A low conversion also reduces the thermal efficiency of the process. In order for the sulfur trioxide decomposition step to be efficient, equilibrium conversions must be approached at temperatures and space velocities compatible with the process requirements.

Although the reduction of sulfur trioxide to sulfur dioxide can be accomplished thermally, it proceeds at an extremely slow rate. Therefore, it is of interest to identify a catalyst that can accelerate the conversion rate to the minimum performance level.

The SO₃ Reduction Catalyst Screening Program is not intended to design or develop a catalyst but to examine commercially prepared and available catalysts that have been tentatively identified as attractive by Westinghouse and others. (1,2)

A suitable catalyst must fulfill two major criteria:

- 1) Achieve near equilibrium conversion at high space velocities; with space velocity defined here as:

$$\text{Space Velocity (SV)} = \frac{\text{total gas flow}}{\text{catalyst volume}} \quad 5-1$$

which has the units of reciprocal hours (hr⁻¹), and

- 2) Maintain equilibrium conversions over an extended period of time.

Candidate catalysts are procured from various vendors and preliminary testing is initiated. The experimental test systems provide the ability to quickly examine each respective catalyst under a variety of test parameters including space velocity, temperature and environment.

Catalysts that display satisfactory conversion rates in any of the screening tests are then evaluated under process conditions over an extended period of time (generally 1000 hours). These endurance tests, designed to measure catalyst efficiency as a function of time, are conducted in the SO₃ Reduction Catalyst Endurance Test Facility.

During the past report period, five different types of catalysts were examined over a spectrum of test parameters in the catalysts screening test facility. The catalysts are identified and listed along with test conditions in Table 5-1.

TABLE 5-1
CATALYSTS AND TEST PARAMETERS EVALUATED IN 1979

CATALYST	COMPOSITION & GEOMETRY	ANHYDROUS	WET	VAPORIZED ACID
CE-1	Fe ₂ O ₃ Powder, >10 mesh, <20 mesh	1000 hr ⁻¹ 5000 hr ⁻¹	1000 hr ⁻¹ 5000 hr ⁻¹	Not Performed
ALFA-2	0.5% (by wt.) Pd on alumina, 3.2 mm (right circular cylinders)	1000 hr ⁻¹ 5000 hr ⁻¹	1000 hr ⁻¹ 5000 hr ⁻¹	Not Performed
ALFA-3	Cr ₂ O ₃ 15% by wt. on alumina, 6 mm pellets (right circular cylinders)	1000 hr ⁻¹ 5000 hr ⁻¹	1000 hr ⁻¹ 5000 hr ⁻¹	Not Performed
ALFA-4	20% Fe ₂ O ₃ on alumina (by wt.), 3.2 mm (right circular cylinders)	1000 hr ⁻¹ 5000 hr ⁻¹ 10,000 hr ⁻¹ 20,000 hr ⁻¹ 25,000 hr ⁻¹	1000 hr ⁻¹ 5000 hr ⁻¹ 10,000 hr ⁻¹ 20,000 hr ⁻¹ 25,000 hr ⁻¹	Not Performed
ALFA-5	MgO, 98% by wt. 3.2 mm pellets	1000 hr ⁻¹ 5000 hr ⁻¹	1000 hr ⁻¹ 5000 hr ⁻¹	Not Performed
MB-3	1% Pt on alumina (by wt.), 3.2 mm (right circular cylinders)	Not Performed	10,000 hr ⁻¹	Not Performed

NOTE: Catalysts were screened over a temperature of 650° to 900°C, in 50°C increments.
Catalyst MB-3 was only examined at 871°C for a 1000 hour endurance test.

Catalysts Supplied by:

CE - Combustion Engineering, King of Prussia, PA
ALFA - Alfa Division, Ventron Corp., Danvers, MA
MB - Mathey - Bishop, Malvern, PA

In the catalyst screening tests, the anhydrous condition involves a reactant process stream consisting of an argon carrier containing 8 percent SO_3 by volume. The wet test conditions consist of argon carrier containing 11 percent SO_3 and 26 percent steam by volume. The unit test condition simulates 80 percent (by weight) sulfuric acid in the vapor state, excluding the inert argon carrier. In addition to the screening tests, two catalysts, MB-3 and Alfa-4 were each exposed to wet screening test conditions for 1000 hours to evaluate the catalytic activity as a function of time. The endurance test facility was subsequently modified to permit vaporized sulfuric acid to be substituted for the simulated wet reactant process stream. This was accomplished by the installation of a flash evaporator and a precision metering pump. Alfa 4 was reevaluated under the modified test conditions.

5.2 SUMMARY OF TEST RESULTS

Table 5-2 summarizes the maximum conversion rates along with its test parameters for each catalyst.

Catalyst CE-1 displayed maximum conversions of 57.5 percent in the anhydrous environment and 42.7 percent in the wet environment. Both of these were obtained at a space velocity of 1000 hr^{-1} and a temperature of 900°C .

Catalyst Alfa-2 achieved its maximum conversion notes at a space velocity of 5000 hr^{-1} and 900°C . The rates observed were 64.2 percent for the anhydrous tests and 68.0 percent for the wet tests. These rates were comparable, but did not exceed earlier results with MB-3, a platinum based catalyst. Therefore, Alfa-2, while judged to be acceptable, was not tested further because of the existing broad data base with MB-3.

The evaluation of Alfa-3 produced the highest conversion rates, 75.7 percent in the anhydrous environment. The wet test produced a maximum conversion rate of 52.6 percent. Both of these results were obtained at a space velocity of 5000 hr^{-1} and 900°C . However, this catalyst physically deteriorated by migration within the reaction tube during the screening. For this reason, no further tests were conducted with Alfa-3.

TABLE 5-2

MAXIMUM CONVERSION RATES OBTAINED IN SCREENING TEST FACILITY

CATALYST	SPACE VELOCITY	% CONVERSION	
		ANHYDROUS	WET
CE-1	1000 hr ⁻¹	57.5	42.7
ALFA-2	5000	64.2	68.0
ALFA-3	5000	75.7	52.6
ALFA-4	1000	57.2	48.3
ALFA-5	5000	32.1	-
	1000	-	6.6

All maximum conversions occurred at a temperature of 900°C

Catalyst Alfa-5 proved to be the poorest of the candidates, displaying maximum notes of 32.1 percent in the wet phase. The anhydrous rate was achieved at a space velocity of 5000 hr^{-1} , while the wet rate was observed at 1000 hr^{-1} . Both tests were performed at 900°C .

Catalyst Alfa-4 was more efficient in the anhydrous environment, possessing a 57.2 percent conversion rate. The optimum wet conversion was 48.3 percent. Both of these rates were achieved at a space velocity of 1000 hr^{-1} and 900°C .

In addition to the screening tests, two catalysts, Alfa-4 and MB-3, were evaluated as a function of time in the endurance test facility. Catalyst MB-3 was selected for the endurance based on previous results^(3,4,5). The endurance tests were conducted under conditions equal to those of the wet screening tests. Catalytic activity was measured over a period of 1000 hours. Catalyst Alfa-4 maintained a conversion rate of 53 percent, while catalyst MB-3 sustained a rate of 72 percent. Both catalysts maintained these conversion rates throughout the 1000 hour test.

The acid decomposition test facility evolved from the redesign of the endurance test facility. By incorporating a flash evaporator and acid metering pump, this new test facility provides the ability to evaluate catalysts under conditions similar to those of the actual process. This includes the use of a sulfuric acid feed rather than the simulated feed employed in the screening and endurance tests. The use of the sulfuric acid feed eliminates the need for the argon carrier gas.

Because of its reputed good performance reported in the literature^(1,2), catalyst Alfa-4 was also evaluated in the acid decomposition test facility. The results obtained from the tests were encouraging with conversion rates approaching equilibrium values at 800 to 900°C . At 900°C the measured conversion rate was ~88 percent, while the equilibrium value was ~90.5 percent. Space velocity appeared to have no significant effect on the catalyst's performance, at 8800 hr^{-1} the conversion rate was ~90 percent, while at $20,000 \text{ hr}^{-1}$ it was ~87 percent.

It is apparent that there is a difference in the conversion rates between the wet screening tests and the acid decomposition tests. This is most likely due to the elimination of the carrier gas in the decomposition tests.

In addition to the previously described tests, catalysts Alfa-4 was also examined in the laboratory model. Conversion rates of 74.8 and 84.0 percent were obtained at temperatures of 815 and 890°C. These observed rates compare favorably to the equilibrium values of 80.0 and 89.5 percent. The laboratory model tests used at 80 w/o H_2SO_4 feed that translated to a space velocity of $\sim 750 \text{ Hr}^{-1}$.

5.3 EXPERIMENTAL PROCEDURE

The procedure for evaluating candidate catalysts differs for each of the four systems involved. The following three sections will describe, for each respective system, the procedure used for calculating the conversion rates of the candidate catalysts.

5.3.1 SO_3 REDUCTION CATALYST TEST EVALUATION (ANHYDROUS AND WET ENVIRONMENTS)

The operation of the SO_3 Reduction Catalyst Screening Test Facility is described in a previous report⁽³⁾. The test facility includes a DuPont Model 400 Photometric SO_2 analyzer and provides the capability to evaluate a range of space velocities using a constant catalyst bed volume. This is accomplished by changing the total gas flow to effect a change in space velocity. Once a space velocity range is determined, the total gas flow is calculated so that the respective gas flows (Ar, steam and SO_3) are not at the extreme upper or lower limits of their respective flow meters, but in mid-range, thereby reducing the amount of potential error in the flows.

Space velocities of 1000 and 5000 hr^{-1} , and $10,000$ to $25,000 \text{ hr}^{-1}$ are examined using separate catalyst bed volumes. Although the system is flexible, it does not have the physical capacity to perform over a 25 fold increase in the total gas flow. In all cases the ratio of gases is kept constant for anhydrous and

wet tests. Under anhydrous conditions the gas stream consists of 92 volume percent argon and 8 percent sulfur trioxide. The wet test environment is composed of 63 volume percent argon, 26 percent steam, and 11 percent sulfur trioxide. The steam-sulfur trioxide ratio simulates an 80 percent (by weight) sulfuric acid feed stream.

For a specified space velocity range and total gas flow, the required catalyst bed volume is calculated using Equation 5-1. Then for a selected catalyst with known density, the mass required is calculated so that the proper quantity can be loaded into a reaction tube. This tube is then installed into the test apparatus.

After installation, the catalyst is kept under a constant argon stream while the system is heated to the desired temperature. After reaching thermal equilibrium, the SO_3 (and steam in wet tests) is admitted to the system. The SO_3 feed flow rate is constantly monitored along with the SO_2 product stream. The SO_2 analyzer provides the percent of SO_2 in the product stream. By measuring the product stream's volumetric flow rate with a bubble flow meter, the amount of SO_2 produced can be calculated.

The conversion rate is then calculated using Equation 5-2.

$$\% \text{ Conversion} = \frac{\text{SO}_2 \text{ Flow}}{\text{SO}_3 \text{ Flow}} \times 100 \quad 5-2$$

During a test, the SO_3 feed flow, SO_2 percent, product stream flow, temperature, etc., are monitored and recorded. Tests are conducted over a temperature range of 650° to 900°C, in 50° increments. The operation of the endurance test facility is analagous to the wet environment mode of the screening test facility.

5.3.2 ACID DECOMPOSITION TEST FACILITY

While the SO_2 Reduction Catalyst Screening Test Facility provided an adequate means to rapidly examine catalysts, the need for a more sophisticated test facility became apparent. An area of concern was the effect of the carrier gas on the screening tests. Therefore, a test facility that was capable of reproducing actual process conditions became desirable. A redesign of the Endurance Test Facility, that included the installation of a flash evaporator and an acid metering pump, resulted in such a facility. The new facility, identified as the Acid Decomposition Test Facility, employs a sulfuric acid feed rather than a simulated feed, thereby eliminating the need for a carrier gas.

The operating procedure and a schematic diagram for the Acid Decomposition Test Facility are presented in Appendix A. Catalysts evaluated in this system are transferred directly from the Screening Test Facility in their reaction tube. Therefore, the catalyst bed volume is determined in the same manner as described in the preceeding section of this report. However, since this system employs liquid sulfuric acid as the feed, the space velocity is calculated as demonstrated in Appendix B.

The liquid sulfuric acid feed, along with the cryogenic separator, provides the ability to calculate the conversion rate in any of four methods:

1) SO_2 Flow Conversion Calculation

Using this method, the conversion rate is calculated using the SO_2 analyzer. The SO_2 content of the product stream is determined using the SO_2 analyzer and bubble flow meter. The conversion rate is then calculated using Equation 5-3.

$$\% \text{ Conversion} = \frac{\text{Moles } \text{SO}_2 \text{ Produced}}{\text{Moles } \text{H}_2\text{SO}_4 \text{ Deliveres}} \times 100$$

5-3

2) Specific Gravity Conversion Calculation

The specific gravity and temperature of sulfuric acid feed are measured and recorded. Condensate samples from the water-cooled condenser are taken intermittently during a test and their specific gravity and temperatures measured and recorded. This data is then converted to degrees Baume' and the conversion rate calculated.

3) Conversion Calculation Using Acid-Base Titration

This procedure simply involves titrating the feed acid and the condensate samples. The conversion rate is then calculated using Equation 5-4.

$$\text{Conversion} = \frac{[X_o] - [X_s]}{[X_o]} \times 100 \quad 5-4$$

Where

X_o = initial concentration, mol/liter

X_s = sample concentration, mol/liter

4) O₂ Flow Conversion Calculation

To measure the oxygen content of the product stream, the stream is diverted to the cryogenic separator. Here the SO₂ is condensed out, leaving an almost 100 percent O₂ stream. This stream is then piped to the SO₂ analyzer. Since the product consists only of SO₂ and O₂, the O₂ content of the stream is assumed to be:

$$\% O_2 = 100 - \% SO_2 \quad 5-5$$

The O_2 flow is then determined in the same manner as the SO_2 flow and the conversion rate is simply:

$$\% \text{ Conversion} = \frac{2(\text{Moles } O_2/\text{min Produced})}{(\text{Moles } H_2SO_4 \text{ Delivered})} \times 100$$

For any particular test, one or all of the methods were employed.

5.3.3 LABORATORY MODEL TEST EVALUATION

The operation of the laboratory model is outlined in Appendix C. Space velocity is calculated as per Appendix B. Conversion calculations are made using one or all of the procedures described in Section 5.3.2.

5.4 DETAILED DISCUSSION OF TEST RESULTS

In this section, the results of the tests conducted on each catalyst are discussed. Section 5.4.1 presents the results obtained in the SO_3 Reduction Catalyst Screening Test Facility and the H_2SO_4 Decomposition Test Facility. Section 5.4.2 discusses the results of the tests performed in the SO_2 Reduction Catalyst Endurance Test Facility. Detailed test data are contained in Appendix D.

5.4.1 SO_3 REDUCTION CATALYST SCREENING TEST RESULTS

Five candidate catalysts were examined in the screening test facility during 1979. The results of these tests will be presented in Sub-Sections 5.4.1.1 through 5.4.1.5. Also included where applicable, will be the test results obtained in the decomposition test facility.

To provide a reliable basis for comparison between the candidate catalysts, their respective conversion rate at any particular temperature, will be compared to the equilibrium conversion at that temperature. By normalizing the experimental results with the calculated equilibrium conversion, a conversion efficiency is determined for each test. A valid comparison between catalyst efficiencies is then possible.

Equilibrium conversions, based purely on thermodynamic properties, were calculated using NASA Computer Code TRAN72⁽⁶⁾. Equilibrium conversions are a function of temperature, pressure, acid concentration, and the presence of inerts. Table 5-3 presents the calculated equilibrium conversions of various feed acid concentrations throughout the temperature range of interest. All calculations were made at atmospheric pressure since the test facilities operate at ambient pressure.

5.4.1.1 CATALYST CE-1 TEST RESULTS

Catalyst CE-1, a 10 mesh iron oxide (Fe_2O_3) powder, was examined at space velocities of 1000 and 5000 hr^{-1} under both anhydrous and wet environments, throughout a temperature range of 650°C to 900°C. The tests were conducted first in the anhydrous environment then the wet. For each environment, the lower space velocity was examined, the gas flows increased accordingly, then the higher space velocities were tested. Both space velocities used the same catalyst bed.

A graphical comparison of the observed anhydrous conversions with the calculated equilibrium conversions is given in Figure 5-1. A similar comparison for the wet tests is presented in Figure 5-2. Catalyst CE-1 displayed maximum anhydrous conversion rates of 57.5 percent and 50.2 percent at space velocities of 1000 and 5000 hr^{-1} .

In the wet environment, the maximum rates were 42.7 percent and 38.2 percent. These conversions translate to efficiencies of ~61 percent and 53 percent in the anhydrous phase and 47 percent and 48 percent in the wet phase, respectively. The maximum efficiencies were achieved at 900°C.

In neither environment was the graph of observed conversions parallel to the graph of equilibrium conversions. If these curves were parallel, it would indicate that the reduction of SO_3 was reaction rate controlled. In this case, due to the deviation from the equilibrium curve, it appears that the reaction were mass transfer controlled, the higher space velocity would most likely produce higher conversions. This would be a result of a more turbulent,

TABLE 5-3

EQUILIBRIUM CONVERSION AT VARIOUS TEMPERATURES
AND H_2SO_4 FEED CONCENTRATIONS

TEMP. °C	WEIGHT PERCENT OF H_2SO_4 FEED			
	8	50	80	100% SO_3
650	63.0	58.5	48.5	37.0
700	71.5	67.3	60.0	49.6
750	79.5	75.6	69.0	60.5
800	86.5	88.5	78.0	70.8
850	91.5	89.7	85.0	80.8
900	94.5	93.5	90.5	84.9

Figure 5-1. Comparison of Anhydrous Test Results - Catalyst CE-1

Figure 5-2. Comparison of Wet Test Results - Catalyst CE-1

and therefore homogeneous, gas stream, thereby reducing the laminar boundary layer that envelopes the individual catalyst particles. However, the higher space velocity did not produce a greater conversion efficiency, indicating that the reaction is not controlled by the mass transfer rate of SO_3 to the active catalyst sites.

Further study revealed the possibility that a reaction between the catalyst and the feed stream was occurring. At the lower temperatures (650 to $\sim 775^\circ\text{C}$) there is a distinct possibility that the iron oxide catalyst is reacting with the SO_3 and producing an iron sulfate species. This reaction would have an adverse effect on catalyst efficiency at these temperatures. However, at the higher temperatures ($>800^\circ\text{C}$) the reaction does not occur due to the free energies of formation. At these temperatures, the iron oxide catalyzes the reduction of SO_3 rather than reacting with it. This is supported by the data above 800°C where the observed curve and the equilibrium curve are relatively parallel.

The wet test data shows a more pronounced effect of the reaction between the iron oxide and SO_3 than the anhydrous test data.

5.4.1.2 CATALYST ALFA-2 TEST RESULTS

Screening tests on catalyst Alfa-2 (0.5 percent Pd on 3.2 mm alumina substrate) were conducted at space velocities to 1000 and 5000 hr^{-1} , in both anhydrous and wet environments, over a temperature range of 650° to 900°C . A graphical comparison, relative to the appropriate equilibrium data, is given in Figure 5-3 for the anhydrous tests and Figure 5-4 for the wet tests. Maximum conversions, all obtained at 900°C , were 57.8 percent and 64.2 percent for 1000 and 5000 hr^{-1} anhydrous, and 64.0 percent and 68.0 percent for wet 1000 and 5000 hr^{-1} .

These conversions when normalized with their respective equilibrium values, result in efficiencies of 61 and 68 percent for the anhydrous space velocities of 1000 and 5000 hr^{-1} . The wet test efficiencies are 71 and 75 percent. In both environments, the maximum efficiency was obtained at the higher space velocity. Additionally, the presence of steam produced a beneficial effect

Figure 5-3. Comparison of Anhydrous Test Results - Catalyst Alfa-2

Figure 5-4. Comparison of Wet Test Results - Catalyst Alfa-2

on conversion efficiency. This phenomena, along with a slight divergence from the equilibrium at the highest temperatures, indicates that the reaction is temperature controlled at the lower temperatures but at the higher temperature it may be mass transfer limited.

The possibility that the catalyst bed was not receiving an adequate heat input was also explored. Since the reduction of sulfur trioxide is endothermic, it requires an input of thermal energy. Therefore if the catalyst bed is not being supplied with sufficient heat, a significant temperature drop in the catalyst bed would be observed during the reduction reaction. The internal temperature of the catalyst bed was monitored using a quartz sheathed Pt-Pt 10 percent Rh thermocouple. The thermocouple was located immediately downstream of the first row of the reduction reaction occurs. This temperature was monitored before, during and after the reduction reaction.

The recorded data revealed a slight temperature drop in all of the tests. The 5000 hr^{-1} tests experienced the largest drop, $\sim 4-6^\circ\text{C}$. This temperature drop indicates a higher degree of energy consumption, i.e., higher conversion rates. This is supported by the data for each individual test that reveal higher conversion rates at the higher space velocity. The temperature incurred by the catalyst bed is determined to be insignificant and it is confidently assumed that the energy demands of the system are being fulfilled. The less than equilibrium conversion rates have been attributed to the mass transfer of sulfur trioxide to the active sites.

5.4.1.3 CATALYST ALFA-3 TEST RESULTS

The evaluations of Catalyst Alfa-3, 15 percent Cr_2O_3 on 6 mm alumina pellets, were conducted under the same test parameters as the two previously described catalysts. The observed anhydrous conversion rates are graphically presented in Figure 5-5. The maximum conversion, 75.7 percent, occurred at 900°C at an anhydrous space velocity of 5000 hr^{-1} . This represents an efficiency of ~ 80 percent. However, the behavior of the catalyst was very peculiar during the tests. In this series of tests, the 5000 hr^{-1} anhydrous tests were

Figure 5-5. Comparison of Anhydrous Test Results - Catalyst Alfa-3

conducted first, followed by the 1000 hr^{-1} anhydrous tests. The anhydrous tests at 1000 hr^{-1} produced higher conversion rates at 650 and 700°C . At 750 and 800°C the 1000 hr^{-1} tests revealed conversions slightly below the 5000 hr^{-1} tests. Above 800°C the conversion rate actually decreased at a significant rate. At 900°C the conversion rate was 41.6 percent, a value below the observed rate at 750°C (42.1 percent). Tests were then conducted at 900°C in a wet environment at both 1000 hr^{-1} and 5000 hr^{-1} . The tests revealed nearly identical rates of 51.4 and 52.6 percent. Testing was terminated at this point so that the system could be inspected for malfunctions of the analyzer, leaks, etc. During this inspection it was discovered that a significant portion of the catalyst had been transported downstream of the catalyst bed, leaving only the exposed alumina substrate in its original location. Figure 5-6 shows the reaction tube prior to evaluation and after removal from the system. The transported catalyst is noticeable as the darkest region of the reaction tube, to the right of the catalyst bed. The catalyst did not appear to be displaced from any single area in the catalyst bed. It was evident throughout the entire catalyst bed due to a color change in the bed. Apparently the Cr_2O_3 vaporized in the hot zones of the furnace and deposited in colder region downstream from its original location. Due to this migration it appears that catalyst Alfa-3, at least in its present form, is not an acceptable candidate.

5.4.1.4 CATALYST ALFA-4 TEST RESULTS

Several sources^(1,2) have reported that iron oxide (Fe_2O_3) has achieved near equilibrium conversions at temperatures above 800°C . Therefore, a second type of iron oxide was evaluated throughout a broad spectrum of test parameters. This catalyst, identified as Alfa-4, is 20 percent Fe_2O_3 on a 3.2 mm alumina substrate. Tests were conducted at space velocities of 1000, 5000, 10,000, 20,000 and $25,000 \text{ hr}^{-1}$ in both anhydrous and wet environments, and throughout a temperature span 650°C to 900°C . Two catalyst beds were used in the testing, one for the 1000 hr^{-1} tests, another for the remainder of the space velocities.

Prior to Evaluation

INLET

OUTLET

After Evaluation

INLET

OUTLET

Cr_2O_3

NOTE: Darkest Region is Cr_2O_3 Deposition on Tube Wall

Figure 5-6. Photograph of Catalyst Alfa-3 Prior To and After Testing

Figure 5-7 and 5-8 present comparisons of the observed conversion rates with their respective equilibrium conversions. From these figures it is evident that the observed conversions are substantially below equilibrium conversions.

The anhydrous tests produce results that reveal decreasing conversions with increasing space velocity. This indicates that the reduction of sulfur trioxide is reaction rate limited. At the lower temperatures, 650°C to ~800°C, it appears that the sulfate reaction (described in Section 5.4.1.1) is again occurring. It is not evident at the low space velocity but is quite obvious at space velocities of 10,000 hr⁻¹ and higher.

Catalyst Alfa-4 achieved its maximum anhydrous conversion rate, 57.2 percent, at a space velocity of 1000 hr⁻¹ at 900°C. This represents an efficiency of ~61 percent.

In order to provide a more rapid examination, the wet tests were not conducted at all the temperatures, as the anhydrous test. This decision was made when the 900°C tests at the high space velocities revealed extremely poor performance.

The wet tests produced a maximum conversion rate at 900°C, of 48.4 percent at a space velocity of 1000 hr⁻¹. This translates to an efficiency of ~53 percent.

However, a literature search revealed that Fe₂O₃ is capable of producing conversion rates in the order of 69 to 79 percent at temperatures of 800°C to 850°C⁽¹⁾. These conversions represent efficiencies of 88 to 93 percent.

To fully assess the situation, catalyst Alfa-4 was then loaded into the Lab Model for evaluation. The Lab Model provides an ideal test facility in that it uses a sulfuric acid feed (of desired concentration). Additionally, it has the capability of calculating the conversion rate using any of the methods outlined in Section 5.3.2 of this report. The need for a carrier gas is also eliminated when the Lab Model is employed as a test facility.

Figure 5-7. Anhydrous Test Results - Catalyst ALFA-4

Figure 5-8. Wet Test Results - Catalyst ALFA-4
SV = 1000 and 5000 hr⁻¹

A series of tests using an 80 weight percent H_2SO_4 feed was conducted at several temperatures. The physical capacity of the Lab Model dictated a space velocity of $\sim 750 \text{ hr}^{-1}$. This was a result of an extremely large catalyst bed and a relatively low feed rate, 4.1 cc/min of liquid H_2SO_4 . These tests resulted in conversion rates much greater than those obtained in the screening test facility. Figure 5-9 compares the screening tests, Lab Model tests and the equilibrium conversions. The screening test data used represents the tests under a wet environment at a space velocity of 1000 hr^{-1} .

The Lab Model test results provide conversion rates near equilibrium, specifically 84.0 percent at 890°C . This represents an efficiency of ~ 94 percent. At 871°C the process requires 70 percent conversion (~ 81 percent efficiency), in Lab Model, at 871°C the catalyst displays conversion rate of ~ 81.5 percent (~ 94 percent efficient). (Note that the Lab Model conversion rate was extrapolated from available data).

To provide a more accurate assessment on the acceptability of catalyst Alfa-4 another test facility was constructed, the H_2SO_4 Decomposition Test Facility. This new facility has the ability to use liquid H_2SO_4 as the feed by incorporating a flash evaporator into its design. Extensive testing was then conducted over a temperature range of 650° to 900°C .

The space velocity ranged from 8800 hr^{-1} to $\sim 20,000 \text{ hr}^{-1}$. The variation was due to the non-reproducibility of the positive displacement acid feed pump. Conversions were calculated using one or all of the previously outlined methods (see Section 5.3.2).

Figure 5-10 presents a summarization of the tests compared to the equilibrium values. A conversion rate of 87.8 percent was observed at 900°C , resulting in an efficiency of 97.0 percent.

On the basis of these tests, which are supported by various other sources^(1,2) Alfa-4 appears to be an acceptable candidate for the hydrogen production process. It is tentatively the leading candidate as it possesses sufficient

Figure 5-9. Comparison of Lab Model Tests
Versus
Screening Tests for Catalyst Alfa-4

Figure 5-10. H_2SO_4 Decomposition Test Results for Catalyst Alfa-4

activity and is less expensive than the previously identified candidate, MB-3^(3,4,5).

5.4.1.5 CATALYST ALFA-5 TEST RESULTS

The final candidate catalyst, Alfa-5 (98 percent MgO on 3.2 mm alumina pellet) was determined to be unacceptable. Initial tests were conducted in both anhydrous and wet environments at space velocities of 1000 and 5000 hr⁻¹. The greatest efficiency, 35 percent, was obtained under an anhydrous environment, at 900°C, at a space velocity of 5000 hr⁻¹. The wet tests revealed an efficiency of 8 percent at 1000 hr⁻¹ and 7 percent at 5000 hr⁻¹, both at 900°C. Catalyst Alfa-5 was then examined in the decomposition test facility and produced approximately the same level of performance as in the screening test. Due to its relatively poor performance, testing of Alfa-5 was terminated at this point.

5.4.2 SO₃ REDUCTION CATALYST ENDURANCE TEST RESULTS

A catalyst must not only possess the ability to accelerate the reduction of SO₃ to a minimum acceptable rate, it must also be able to sustain this level of performance over an extended period of time.

To measure catalytic activity as a function of time, the SO₃ Reduction Catalyst Endurance Test Facility was constructed and operated during 1979.

Two catalysts, MB-3 and Alfa-4, were evaluated over a time period of 1000 hours. The following two sub-sections discuss the results obtained in the two endurance tests. Detail test data are presented in Appendix C.

5.4.2.1 MB-3 ENDURANCE TEST RESULTS

Catalyst MB-3, 1 percent Pt on a 3.2 mm alumina substrate, was selected for an endurance test because of its ability to achieve acceptable conversion rates at temperatures and space velocities compatible with process requirements⁽³⁾. The endurance test was conducted using a (simulated) 80 w/o H₂SO₄ feed, at a temperature of 871°C and space velocity of 10,000 hr⁻¹.

The conversion rate was measured at least twice a day, generally the first thing in the morning and immediately prior to leaving in the afternoon. The system operated unattended overnight and through weekends.

An initial conversion rate of ~65 percent gradually increased to greater than 70 percent in approximately 65 hours. From 65 hours on, the conversion rate for the endurance test averaged approximately 74 percent, with a spread of ± 3 percent. This spread is well within the limits of experimental error, considering the furnace cycling, rotameter fluctuations, etc. Figure 5-11 displays the conversion rate as a function of time. The equilibrium conversion for this specific test is ~87 percent, resulting in an efficiency of ~85 percent. As is evidenced in Figure 5-11, there is no observable decline in the conversion rate throughout the entire 1000 hour test.

As a result of the endurance test and its previous screening tests, catalyst MB-3 fulfills the criteria set forth earlier and is considered an acceptable catalyst for the thermal decomposition of sulfuric acid.

5.4.2.2 ALFA-4 ENDURANCE TEST RESULTS

Using the same test conditions as MB-3, catalyst Alfa-4 was then examined in the endurance test facility. These test conditions were 871°C at a space velocity of 10,000 hr⁻¹. A (simulated) 80 w/o H₂SO₄ feed was employed.

The average conversion rate was 52.6 percent with a span of ± 6.4 percent. The equilibrium conversion rate is ~87 percent, therefore the observed rate represents an efficiency of ~60 percent. There was no evidence of degradation in the conversion rate throughout the entire test.

These results, presented in Figure 5-12, are approximately equal to the conversion rates observed in the screening tests, and were maintained throughout the 1000 hour time period.

Figure 5-11. Endurance Test Results - Catalyst MB-3

Figure 5-12. Endurance Test Results for Catalyst ALFA-4

5.5 FUTURE WORK

In 1980 the major area of investigation will be an independent study of acceptable catalysts, specifically MB-3 and ALFA-4. The effects of parameters such as catalyst geometry, size, and catalyst bed geometry and size will also be investigated. Tests will also be conducted to provide the pertinent data needed to design a prototype reduction reactor. These tests will be tailored to determine reaction order, reaction rate constant, catalyst effectiveness factor, heat and mass transfer coefficients, etc. Additional tests determining the mode of operation, i.e., isothermal or adiabatic, of the reduction reactor may also be conducted.

In effect, sufficient data will be generated under atmospheric conditions, to permit selection of a reference catalyst for the hydrogen production process. Efforts beyond 1980 will direct towards catalyst evaluations under pressurized conditions.

5.6 REFERENCES

1. "The Study of Thermochemical Hydrogen Preparation. An Oxygen-Evolving Step Through Thermal Splitting of Sulfuric Acid," M. Kokiya, et.al, National Chemical Laboratory for Industry, Meguru-kui, Tokyo, Japan.
2. "Hdrogen Programme," Excerpt from Progress Report, January-June 1979, Commission of the European Communities, Joint Research Centre, Ispra Establishment.
3. "Solar Thermal Hydrogen Production Process," Annual Technical Progress Report, January-December 1978, Westinghouse Electric Corporation, Advanced Energy Systems Division, P. O. Box 10864, Pittsburgh, PA 15236.
4. "Sulfur Cycle Hydrogen Generation Process," Technical Progress Report, May 17, 1977 to December 31, 1977, Westinghouse Electric Corp., A.E.S.D., Pittsburgh, Pa. 15236.
5. "Hydrogen Generation Process", Annual Technical Progress Report, January-December, 1976, Westinghouse Electric Corp. A.E.S.D., Pittsburgh, Pa. 15236.
6. S. S. Lin, DRM NO: DA-0642, Westinghouse Electric Corporation, Advanced Energy Systems Division, Pittsburgh, PA 15236, (1979).

6.0 ACID VAPORIZER MATERIALS EVALUATION (R. L. Ammon, H. A. Irwin)

6.1 OBJECTIVE AND BACKGROUND

The objective of this task is to evaluate potential acid vaporizer structural materials. The acid vaporizer has been identified as a critical component with respect to structural materials since both the liquid and vapor phases of sulfuric acid are present in the vaporizer at elevated temperatures and pressures, with process parameters considered thus far ranging from 361°C (55 psia) to 452°C (300 psia).

The testing of materials in the presence of high temperature boiling sulfuric acid requires that a test vessel, inert to the acid environment, be utilized to contain the materials samples and the boiling acid. While there is an abundance of data and industrial experience with materials in handling sulfuric acid up to its boiling point, little is known about the behavior of materials when exposed to concentrated sulfuric acid at elevated temperatures and pressures. Gold, platinum, and quartz are resistant to the corrosive attack of concentrated sulfuric acid at high temperatures. However, gold and platinum, while suitable for small-scale purposes are prohibitively expensive for use in large scale hydrogen production. Quartz is both fragile and a poor heat transfer medium.

High silicon cast irons, namely Duriron, Durichlor 51, and Superchlor, are known to have low corrosion rates in boiling 98 w/o sulfuric acid at or near atmospheric pressure and have traditionally had wide industrial use in handling sulfuric acid. These alloys all contain 14.5 percent silicon. In addition, Durichlor 51 and Superchlor contain 4.5 percent chromium while Duriron contains 0.5 percent chromium. However, use of these alloys is limited by the fact that they are very hard and brittle, subject to thermal shock and have low tensile strength.

It is beyond the scope of this investigation to develop new materials for use in the Sulfur Cycle hydrogen production process. Instead, the investigation

is limited to identifying and procuring materials and developing and analyzing corrosion test data on materials that are commercially available at present or in the near future.

Table 6-1 outlines the acid vaporizer materials test program. The first phase of the program consists of static material screening with samples exposed to 98 w/o sulfuric acid for incremental time periods of 250 hours and total integrated times of 1000 hours. Initially, screening tests are run at 361°C which corresponds to an expected sulfuric acid vapor pressure of 3.7 atmospheres (55 psia). Additional screening tests are being run at 452°C, corresponding to an expected sulfuric acid vapor pressure of 20.0 atmospheres (300 psia).

The second phase of the test program, not yet initiated, will be materials endurance tests, with test parameters and procedure similar to the materials screening tests except that the incremental time periods will be 500 hours with total test times of 5000 hours.

The testing of materials in the presence of high temperature boiling sulfuric acid requires that a test vessel, inert to the acid environment, be utilized to contain the materials samples and the boiling acid. The initial test vessels were made of stainless steel with a removable internal gold liner⁽⁶⁻¹⁾. Because welds in the gold liner developed leaks in the presence of sulfuric acid vapor⁽⁶⁻²⁾, it was decided during 1978 to use a test vessel made of Duriron components. Chemically vapor deposited (CVD) silicon carbide vessels also were procured but because of small cracks both in the vessel and in the sealing area, the SiC vessels have not been used.

6.2 SUMMARY OF RESULTS

Since the acid vaporizer test program was initiated in 1977, nearly three dozen materials have been subjected to the screening tests. Table 6-2 provides a complete listing of these materials tested through 1979.

All screening tests at 361°C have been completed with samples tested for 1000 hours or until they were so severely attacked that one or more could not be placed back in test. Based on measurements of weight changes, the materials which

TABLE 6-1

ACID VAPORIZER MATERIALS TEST PROGRAM

Test Type	Test Environment	Sample Location	Temp (°C)	Pressure (Atmos)	Test Time
Materials Screening	98 w/o H ₂ SO ₄ (Refreshed) ⁴	Liquid, vapor Liquid-vapor Interface	361 452	3.7 (55 psi) 20.0 (300 psi)	250-hr increments 1000 hrs total
Materials Endurance	98 w/o H ₂ SO ₄ (Refreshed) ⁴	Liquid, vapor Liquid-vapor Interface	361 452	3.7 (55 psi) 20.0 (300 psi)	500-hr increments 5000 hrs total

TABLE 6-2

ACID VAPORIZER MATERIALS TESTS AT 361°C

1000 HOUR TESTS

Silicon Nitride, Reaction Bonded
 Silicon Nitride, Hot Pressed
 Duro Acid-Proof Brick
 Macor Machinable Ceramic
 Silicon, Polycrystal
 Durichlor 51
 Duriron
 Silicon Carbide, CVD
 Vitreous Carbon
 Alumina
 Aluminum Silicate

500 HOUR TESTS

SS 18-18-2
 SS 310
 Inconel 625
 Alonized Inconel 625
 Sialon 80
 Sialon 81
 Sialon 88
 Cartech Type 20Cb3
 Hastelloy G
 Carbon Steel (CS) 1018
 Alonized CS 1018
 Tungsten-Powder, sintered,
 swaged (PSS)

750 HOUR TESTS

Hastelloy C-276
 Incoloy 825
 Inconel 657
 Tungsten-Plate
 Tantalum, as received

250 HOUR TESTS

Titanium Diboride
 Hastelloy B2
 Stainless Steel (SS) 316
 Alonized SS 316
 Zirconium 702
 Tantalum, preanodized

NOTE: Samples were exposed to 98 w/o sulfuric acid at 361°C.
 Those that failed to achieve 1000 hours were taken out of test
 because they were so severely attacked that they could not be
 attached to the sample holder.

appear to have the best corrosion resistance are polycrystal silicon, CVD, SiC, and silicon nitride. The metallic materials which are most corrosion resistant are Duriron and Durichlor 51. Section 6.4 of this report provides a detailed discussion of the test results.

Because of difficulties encountered in maintaining a seal throughout the 250 hour test intervals at 361°C in the Duriron test vessels, sealed quartz capsules containing individual material samples and a suitable amount of sulfuric acid are being used for the 452° C screening tests which were initiated late in 1979. Four capsules for each sample are required to cover the 250, 500, 750 and 1000 hour time periods. The seven non-metallic samples in the initial set are chemically vapor deposited (CVD) silicon carbide, alumina, aluminum silicate, polycrystal silicon, hot pressed silicon nitride, Duro acid-proof brick, and silicon carbide graphite (SCG) composite. The initial measurements with this set will be made early in 1980.

6.3 EXPERIMENTAL PROCEDURE

Screening of materials for use in the acid vaporizer at 361°C was done in the Acid Vaporizer Materials Test Facility, the schematic of which is shown in Figure 6-1.

Samples were degreased and then cleaned by gently rubbing with cleanser on the wetted surface, rinsed in flowing tap water, then in flowing distilled water, and flushed with ethanol. They were then air dried using a heat gun on cool setting.

Samples which are designated as Alonized had a commercial aluminizing treatment applied by the Alon Corporation to the surfaces of the cleaned samples. The Ta sample previously annealed at 1200°C was electrochemically anodized.

During most of CY 1978 and thereafter, tests at 361°C were accomplished using Duriron test vessels which consist of short lengths of Duriron pipe clamped to blank end flanges. Gaskets made of 1.3 mm diameter gold wire to fit near the outside diameters of the vessel flanges were used.

Figure 6-1. Apparatus for Testing of Acid Vaporizer Materials

Samples were suspended from a gold sample holder made of 1.3 mm diameter gold wire using 0.25 mm platinum wires to attach the materials to the gold sample holder. Three samples of each material were used: the X sample is in the vapor phase only; the Y sample straddles the liquid-vapor interface; and the Z sample is in the liquid phase only. The nominal sizes of the samples are 19 mm x 19 mm x 1.6 mm for X and Z samples and 51 mm x 13 mm x 3.2 mm for the Y samples. All samples had two holes, one at the top and one at the bottom. In an effort to minimize the galvanic effect between metallic samples, any samples which were not insulators themselves were insulated from the platinum wire used to attach the samples to other samples of the same material and/or to the gold sample holder, by short lengths of small diameter quartz tubing. The attachment of the samples onto the sample holder is shown in Figure 6-2. The sample holder is placed in a pressure vessel which is half filled with 98 w/o sulfuric acid. The top blank end flange is then clamped on. Belleville spring washers are used on the clamping bolts to maintain compression on the gold seal during thermal exposure. Figure 6-3 shows the appearance of the test vessel just prior to its placement in the furnace for a thermal exposure. The system is slowly heated to temperature for incremental time periods of 250 hours, after which time the furnace is turned off and the vessel is allowed to slowly cool to room temperature. The samples are cleaned of excessive corrosion products by boiling in dilute sulfuric acid while still on the sample holder, flushing with distilled water, and drying in an 80°C oven. The samples are then removed for visual inspection, weighing, and thickness measurements, after which time they are returned to test using renewed sulfuric acid.

For each capsule used in the screening of materials to 98 w/o sulfuric acid at 452°C, two samples of each material are required, one in the vapor phase and one in the liquid phase. The samples, the corners and edges of which were rounded typically to a radius of ~0.8 mm have nominal dimensions of 10 mm x 10 mm x 2 mm x 15 mm x 15 mm x 2 mm for the liquid and vapor phase samples, respectively. The large sample rests on a quartz sleeve which slips inside the quartz capsule.

The cleaned samples are sent to Westinghouse Research and Development Center where they are placed in quartz tubes, and initially sealed. The quartz tubes

Figure 6-2. Acid Vaporizer Materials Sample Holder, Showing Manner in which Three Samples of Each Materials are Supported.

Figure 6-3. Duriron Test Vessel.

with the samples before and after the initial seal are shown in the schematics in Figures 6-4a and 6-4b, respectively. After the initial seal, sulfuric acid sufficient to cover the lower sample at 452°C is added, the quartz tube is then immersed in liquid nitrogen until the sulfuric acid is solidified, after which time the tube is evacuated and the neck of the quartz tube is sealed. Figure 6-4c is a schematic of the fully sealed tube. The sealed quartz tubes are placed in the secondary SS containment vessel, the SS vessel is sealed and the system is slowly heated to temperature, all the while maintaining a slight overpressure on the quartz tubes. After the thermal exposure period, the furnace is turned off and the vessel slowly allowed to cool to room temperature. The quartz tubes are then broken, the samples removed for visual inspection, cleaning, photographing, weighting and thickness measurements.

6.4 DISCUSSION OF RESULTS

6.4.1 TESTS AT 361°C

Initial tests at 361°C were run for 250 hour increments using 98 w/o H_2SO_4 . In early tests with the Duriron test vessel, leaks developed, apparently because of considerable reaction of the samples with the sulfuric acid, and, therefore, pressures considerably greater than anticipated⁽⁶⁻³⁾. In most of the earlier tests, virtually no liquid sulfuric acid was recovered. In the later tests, virtually all of the liquid sulfuric acid was recovered. This was probably due to two factors: (1) the more reactive (least corrosion resistant) materials were eliminated from testing, and (2) Belleville spring washers were used on the clamping bolts to maintain compression on the gold gaskets during thermal exposure. Testing at 361°C has been completed. All samples were tested for total test times of 1000 hours or until the samples were so severely attacked that one or more samples of each material could not be placed back in test.

The most corrosion resistant materials of those tested at 361°C were ceramic. Figure 6-5 shows one such set of samples consisting of reaction bonded silicon nitride from KBI, Inc., hot pressed silicon nitride from Ceradyne, Inc., Duro acid-proof brick, Macor machineable ceramic, and polycrystal silicon at 0 and 1000 hours exposure.

Figure 6-4. Schematic of Quartz Sample Holders for Acid Vaporizer Tests at 452 °C

0 Hours

1000 Hours

VAPOR
PHASELIQUID/VAPOR
INTERFACELIQUID
PHASE

Figure 6-5. Visual Appearances of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C.

While many of the acid vaporizer samples tested during CY 1979 had a large amount of corrosion product on their surfaces, very little corrosion product was found on the above set of samples. Weight change data for these samples is given in Table 6-3. All the materials except for Macor exhibited a high degree of resistance to attack by the sulfuric acid as indicated by weight change data. The metallic silicon displayed exceptional corrosion resistance in both phases.

The constant positive cumulative weight change data for the reaction bonded silicon nitride as compared to the hot pressed silicon nitride was attributed to the difference in densities. The reaction bonded material had a density of 1.9 gm/cm^3 or approximately 60 percent of theoretical. The weight gain for the reaction bonded silicon nitride is most likely due to trapped acid in the interstices of the less dense material. Macor contains a dispersion of mica particles to impart the machining characteristics to the ceramic material.

The reaction of the mica with the liquid phase is most likely responsible for the observed spalling and delamination. The acid-proof brick displayed a constantly increasing loss of weight when exposed in the liquid phase. The most encouraging results were displayed by the pure polycrystalline silicon metal samples. Weight change data indicate very little interaction of the silicon with the sulfuric acid environment. The results will be verified by metallographic examination.

Six other materials which were tested for 1000 hours were Duriron, Durichlor 51, chemically vapor deposited (CVD) silicon carbide, vitreous carbon, high purity alumina, and aluminum silicate M-120 from Duramic Products, Inc., a subsidiary of KBI, Inc.

Duriron and Durichlor 51 are both high silicon cast irons containing 14.5 w/o silicon. The w/o of chromium is 0.5 and 4.5 for Duriron and Durichlor 51, respectively. Both are known to have low corrosion rates in boiling 98 w/o sulfuric acid at or near atmospheric pressures and both have traditionally had wide industrial use in handling sulfuric acid.

TABLE 6-3
ACID VAPORIZER TEST RESULTS AT 361°C

MATERIAL	SAMPLE LOCATION	Δ WEIGHT/AREA mg/cm ²			
		250 Hours	500 Hours	750 Hours	1000 Hours
Silicon Nitride, KBI Reaction Bonded	X	27.6	30.7	24.4	29.3
	Y	25.4	8.08	24.6	25.2
	Z	20.3	27.1	24.5	24.9
Silicon Nitride, Ceradyne Hot Pressed	X	-0.51	-0.55	-0.57	-0.6
	(No Y)	-	-	-	-
	Z	-0.19	-0.21	-0.17	-0.2
Duro Acid-Proof Brick	X	0.50	0.30	0.06	1.0
	Y	-2.28	-1.51	-4.84	-7.3
	Z	-4.30	-3.41	-7.84	-11.9
Macor Machinable Ceramic	X	-9.53	-16.3	-26.5	-35.8
	Y	-23.1	-30.6	-53.9	-122. e,f
	Z	-23.2	-40.9	-61.8	-74.9 e,f
	Control Z	-16.8	-35.9	-91.8 d,f	
Silicon, Polycrystal	X	0	0	0	0
	Y	-0.02	-0.01	-0.02	-0.02
	Z	0.02	0.02	0.02	0.02
Durichlor 51	X	-0.70	-1.08	-1.28	-1.81
	Y	-0.23	-0.42	0.06	-1.16
	Z	-0.13	-1.33	-0.18	-1.20
Duriron	X	-1.51	-4.88	-8.19	-10.9
	Y	-0.55	-2.46	-4.23	-5.56
	Z	-0.78	-3.20	-5.51	-7.40
Silicon Carbide, CVD	X	0.02	-0.03	-0.20	-0.09
	Y	0.17	0.15	-0.11	-0.31
	Z	0.01	0.28	-0.24	-0.57
Vitreous Carbon	X	-0.62	-1.10	-2.08	-3.25
	Y	-0.77	-0.92	-4.04	-8.13
	Z	-0.83	-2.68	-5.24	-10.0

TABLE 6-3 (CONTINUED)
ACID VAPORIZER TEST RESULTS AT 361°C

MATERIAL	SAMPLE LOCATION	Δ WEIGHT/AREA mg/cm ²			
		250 Hours	500 Hours	750 Hours	1000 Hours
Alumina	X	-19.7	-50.8	-93.8	-123.
	Y	- 2.47	- 7.78	-28.5	- 42.7
	Z	- 1.17	- 7.01	- 9.67	- 13.3
Aluminum Silicate	X	- 1.07	+ 1.25	.79	- 4.39
	Y	- 1.20	+ 3.86	3.44	- 4.60
	Z	- 2.57	+ 3.08	.58	- 7.11
W - Plate	X	-30.6	-209.	-312.	
	Y	-77.0	-343.	-367.	
	Z	-56.4	-460.	-548.	
W - Powder, sintered, swaged	X	-101.	-106.		
	Y	- 65.3	- 84.3		
	Z	- 39.6	- 73.9		
Hastelloy C-276	X	-133.	-397. c	a	
	Y	-133.	-491. c	a	
	Z	- 1.38	-403. c	a	
Incoloy 825	X	76.6	-347. c	a	
	Y	-41.7	-464. c	a	
	Z	- 1.26	-339. c	a	
Inconel 657	X	-14.9	-161. c	-453.	
	Y	-73.8	-246. c	-610.	
	Z	-90.3	-241. c	-608.	
Inconel 625	X	-51.5	-499.		
	Y	-122.	a		
	Z	-173.	a		
Alonized Inconel 625	X	-31.9	-463.		
	Y	-93.8	-518.		
	Z	-152.	a		

TABLE 6-3 (CONTINUED)
ACID VAPORIZER TEST RESULTS AT 361°C

MATERIAL	SAMPLE LOCATION	Δ WEIGHT/AREA mg/cm ²			
		250 Hours	500 Hours	750 Hours	1000 Hours
Tantalum, as received	X	- 0.79	-11.2 c	- 13.2	
	Y	-77.2	-238. c	-333.	
	Z	-235.	-441. c	-510.	
Tantalum, Preanodized	X	0.21			
	Y	-367.8			
	Z	-528.8			
Sialon 80	X	-55.9	-130.		
	Y	-39.6	-85.2		
	Z	- 0.03	-79.3		
Sialon 81	X	-190.	-297.		
	Y	-70.4	-163.		
	Z	-10.1	-72.1		
Sialon 88	X	a			
	Y	-22.8	-139.		
	Z	- 2.12	-46.4		
	Control X	-148.			
	Control Y	-124.			
Titanium Diboride	X	a			
	Y	a			
	Z	a			
SS-18-18-2	X	-210.	-292. b	a, c	
	Y	-148.	-220. b	a, c	
	Z	-57.2	-87.9 b	a, c	
SS 310	X	-61.7	-157.	a, c	
	Y	-53.3	-229.	a, c	
	Z	- 4.5	-139.	a, c	
Cartech Type 20 Cb-3	X	-71.8	a		
	Y	-38.6	-945.		
	Z	- 5.86	a		

TABLE 6-3 (CONTINUED)
ACID VAPORIZER TEST RESULTS AT 361°C

MATERIAL	SAMPLE LOCATION	Δ WEIGHT/AREA mg/cm ²			
		250 Hours	500 Hours	750 Hours	1000 Hours
SS 316	X	-213.0			
	Y	-681.0			
	Z	a			
Alonized SS 316	X	-147.			
	Y	-440.			
	Z	-343.			
CS 1018	X	-313.	-344.		
	Y	-488.	-702.		
	Z	-434.	a		
Alonized CS 1018	X	-231.	-309.		
	Y	-243.	-510.		
	Z	-222.	a		
Zirconium 702	X	- 54.9			
	Y	-208.			
	Z	a			
Hastelloy B2	X	-300.			
	Y	-824.			
	Z	a			
Hastelloy G	X	- 36.3	a		
	Y	- 22.5	a		
	Z	- 1.47	a		

TEST CONDITIONS: 98 w/o Sulfuric acid at 360°C
3.7 atmospheres (55 psia)

SAMPLE LOCATION: X - Exposed to Vapor Phase Only
Y - Exposed to Liquid/Vapor Interface
Z - Exposed to Liquid Phase Only

NOTES: Negative values indicate weight loss per unit area.

- a. Sample completely consumed or disintegrated at the end of this test increment.
- b. Sample exposed for a total of 271 hours.
- c. Sample exposed for a total of 521 hours.
- d. Sample exposed for a total of 602 hours.
- e. Sample exposed for a total of 852 hours.
- f. Sample delaminated - weight of largest piece.
- g. Some weight loss due to a chip off the sample during run.

The test results, expressed as weight change per unit area are given in Table 6-3. From the data of Table 6-3 and the macrophotographs of the test samples in Figures 6-6 through 6-8, it is seen that the CVD silicon nitride showed excellent corrosion resistance in both phases. The Durichlor 51 and aluminum silicate also showed good corrosion resistance in both phases. The Duriron and alumina samples were more susceptible to attack in the vapor phase while the vitreous carbon sample was more susceptible to attack in the liquid phase.

In another test series, which was tested for a total of 750 hours, the materials included two alloys high in nickel and chromium but low in iron, Inconel 657 (Ni-48Cr-1.6Nb-1Fe), and Hastelloy C-276 (Ni-16Cr-16Mo); one alloy high in nickel and chromium and moderate in iron, Incoloy 825 (42Ni-22Cr-22Fe), and as-received tantalum. The test results are reported in Table 6-3. The visual appearances of the above six materials at 0, 250, 500 and 750 hours can be seen in Figures 6-9 and 6-10. All of the samples of Hastelloy C-276 and Incoloy 825 were completely consumed after 750 hours. Except for the tantalum X sample, which showed very little attack, all the rest of the samples were severely attacked, so much so that they could not be attached to the gold sample holder. Thus, further testing of these four materials was discontinued.

Tantalum samples were preanodized according to the procedure given in Section 6.3 of this report and given a 250 hour thermal exposure. The test results are reported in Table 6-3. As seen in Figure 6-11, the Z sample and that portion of the Y sample which was in the liquid phase was catastrophically attacked, while the vapor phase sample showed excellent corrosion resistance. While it may appear from the data of Table 6-3 that the as-received tantalum samples showed superior corrosion resistance to the preanodized tantalum samples, to draw such a conclusion would be erroneous. As reported earlier⁽⁶⁻⁴⁾, leaks, and therefore loss of the sulfuric acid, was a major problem in the early tests when testing of the as-received tantalum occurred. Such was not the case when the preanodized tantalum was tested.

0 Hours

1000 Hours

VAPOR
PHASELIQUID/VAPOR
INTERFACELIQUID
PHASE

Figure 6-6. Visual Appearances of Samples After
Exposure to 98 w/o Sulfuric Acid at 361°C

6-19

0 Hours

1000 Hours

VAPOR
PHASE

LIQUID/VAPOR
INTERFACE

LIQUID
PHASE

Figure 6-7. Visual Appearances of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C.

6-20

0 Hours

1000 Hours

VAPOR
PHASE

LIQUID/VAPOR
INTERFACE

LIQUID
PHASE

Figure 6-8. Visual Appearances of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C.

0 Hours

250 Hours

VAPOR
PHASELIQUID/VAPOR
INTERFACELIQUID
PHASELEGEND:

INC 657 - Inconel 657
 C276 - Hastelloy C-276
 825 - Incoloy 825
 TA - Tantalum
 (as received)

Figure 6-9. Visual Appearance of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C.

Figure 6-10. Visual Appearance of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C (The Incoloy 825 and Hastelloy C-276 were completely consumed by 750 hours.)

6-23

0 Hours

250 Hours

TiB₂

VAPOR
PHASE

LIQUID/VAPOR
INTERFACE

LIQUID
PHASE

Figure 6-11. Visual Appearances of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C.
(The TiB₂ was completely disintegrated after 250 hours exposure.)

Titanium diboride which was tested in the same run as the preanodized tantalum was completely disintegrated after 250 hours exposure. Its appearance before the test is shown in Figure 6-11.

Three Sialon compositions (Types 80, 81 and 88) were tested. The Sialon compositions are ceramic phases in the Si-Al-O-N systems and consist of one, two and three-dimensional arrangements of (Si, Al) (O, N₄) tetrahedra. These new oxynitrides include structure types based upon α and β silicon nitride, silicon oxynitride, aluminum nitride and silicon nitride eucryptite, spinel, melilite and apatite. These materials are being explored for potential use in gas turbines and other high temperature engineering applications⁽⁶⁻⁵⁾.

Because the Sialon materials showed only minor weight changes in the reduction reactor tests which are conducted in the vapor phase only (see Section 4.4 of this report), it was decided to further test Sialon 88 even though the X sample was completely consumed after 250 hours exposure. Also, the Sialon 88 Y sample had been considerably corroded at the top hole. Thus, two new control samples, Control X and Control Y were tested in addition to the Y and Z samples which had been exposed for 250 hours. New holes in the top of the Y samples of both Sialon 80 and Sialon 81 were made because the old holes were not expected to withstand the corrosive environment for another 250 hours. This was a valid assumption as indicated by the test results reported in Table 6-3. The visual appearances of the samples at 0, 250, and 500 hours can be seen in Figures 6-12 and 6-13. Test results indicate that the Sialon compositions are more resistant to the liquid phase than the vapor phase of sulfuric acid. Although the Sialons were not consumed after 500 hours, further testing was discontinued since at least one sample of each Sialon was so severely attacked that they could not be attached to the sample holder.

Two types of tungsten were tested. One was tungsten plate and the second was tungsten which was formed from powder and then sintered and swaged (PSS). The weight change data is given in Table 6-3. As seen in Figure 6-14, considerable delamination of the tungsten plate was observed at 500 hours and catastrophic delamination after 750 hours. The PSS tungsten showed no evidence of delamination and had better corrosion resistance based on weight

Figure 6-12. Visual Appearance of Samples Before Exposure to 98 w/o Sulfuric Acid at 361°C.

Figure 6-13. Visual Appearance of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C.

Figure 6-14. Visual Appearances of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C. (Testing of PSS Tungsten was discontinued after 500 hours exposure.)

change data. However, because of the considerable attack at the bottom hole (liquid portion) of the Y sample which straddled the liquid/vapor interface, the PSS tungsten samples could not be attached to the sample holder. Thus, testing of the PSS tungsten was discontinued after 500 hours. Testing of the tungsten plate was discontinued after 750 hours.

Inconel 625, Alonized Inconel 625, CS 1018 and alonized CS 1018, were given additional 250 hour exposures for a total exposure time of 500 hours. In all four samples the Z (liquid phase) samples were completely consumed and thus no further testing was done. SS 18-18-2, and SS 310 which had previously been tested for 521 hours⁽⁶⁻⁶⁾ was also given an additional 250 hours exposure at the end of which the samples in all phases were completely consumed. The weight change data is given in Table 6-3 and the visual appearances of the samples are shown in Figures 6-15 through 6-17.

At this time, based on weight change data, the materials which appear to have the best corrosion resistance are polycrystal silicon, CVD SiC, and silicon nitride. The metallic materials which are most corrosion resistant are Duriron and Durichlor 51.

6.4.2 TESTS AT 452°C

Sealed quartz capsules containing individual material samples and a suitable amount of 98 w/o sulfuric acid are presently undergoing acid vaporizer tests at 452°C. Four capsules for each material are required to cover the 250, 500, 750, and 1000 hour time periods. The seven non-metallic samples in the initial run in which samples are exposed for 250 hours, are chemically vapor deposited (CVD) silicon carbide, alumina, aluminum silicate, polycrystal silicon, hot pressed silicon nitride, Duro acid-proof brick, and silicon carbide graphite (SCG) composite from Duramic Products, Inc. This test will be completed early during 1980 and the results reported then.

Figure 6-15. Visual Appearance of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C.

0 Hours

500 Hours

VAPOR
PHASELIQUID/VAPOR
INTERFACELIQUID
PHASE

LEGEND:
 1018-CS 1018
 1018A-Alonized
 CS 1018

Figure 6-16. Visual Appearances of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C

6-31

Figure 6-17. Visual Appearance of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C.

LEGEND: 310 - SS 310
18-18-2 - SS 18-18-2

Efforts are continuing to procure a suitable containment vessel for carrying out compatibility testing at 452°C and 20.4 atmospheres. A concern exists with respect to the use of the Duriron vessels at the higher temperature and pressures. Under the previous contract, silicon carbide (SiC) vessels were procured from a vendor for this purpose. These vessels proved difficult to seal and underwent several modifications by the vendor in order to remedy the problem. A new vessel incorporating a major modification has been received and gold gaskets were received during December 1979. Tests will be made early in CY 1980 to determine if the vessel can be sealed.

6.5 FUTURE WORK

Screening tests at 452°C will continue as outlined in Table 6-1 on those materials which have exhibited the best corrosion resistance in the 361°C tests. Because materials with high silicon content appear to have better corrosion resistance than other more conventional alloys, effort will be directed toward procuring and testing metallic samples which have been coated with silicon and/or silicon compounds. Only those samples which display a superior degree of corrosion resistance will be used as substrate material for the siliconizing process. Also, advantage will be taken of the opportunity to utilize the Laboratory Model test loop for materials testing. Samples will be located in the acid vaporizer and reduction reactor at positions where temperature and environmental conditions are known. Compatibility results from these tests will be compared with results obtained in the independent reduction reactor test program.

During 1980, endurance tests of materials which survive the screening tests are planned. Endurance tests will utilize the same facilities in which the screening tests were conducted. Tests will be initiated at 360°C and 452°C with a target test time of 5000 hours as outlined in Table 6-1. Samples will be examined at incremental time intervals to assess the degree of interaction. The design of a dynamic test facility will be initiated. In the facility, sulfuric acid will be continually vaporized and condensed under conditions which simulate actual large system operation with respect to temperatures and pressures. The dynamic facility will permit the assessment of the selected structural materials under conditions which approach anticipated large-scale system operation.

6.6 REFERENCES

1. Westinghouse Electric Corp., Sulfur Cycle Hydrogen Generation Process - Technical Progress Report," DOE Contract No. EG-77-C-02-4378, Report C00-4378-4, May 17, 1977 to December 31, 1977.
2. Westinghouse Electric Corp., "Solar Thermal Hydrogen Generation Process - Annual Technical Progress Report," DOE Contract No. ET-78-C-02-4705, Report C00-4705-19, January-December 1978.
3. Ibid.
4. Ibid.
5. K. H. Jack, "Review Sialons and Related Nitrogen Ceramics," Journal of Materials Science, 11, 1135-1158, 1976.
6. Westinghouse Electric Corp., "Solar Thermal Hydrogen Generation Process - Annual Technical Progress Report," DOE Contract No. ET-78-C-02-4705, Report C00-4705-19, January-December 1978.

APPENDIX A

OPERATION OF ACID DECOMPOSITION TEST FACILITY

APPENDIX A

OPERATION OF ACID DECOMPOSITION TEST FACILITY

Prior to operation and testing of a catalyst, a quartz reaction tube is loaded with a prescribed catalyst volume. A series of crushed quartz tubing is placed immediately upstream of the catalyst bed. This serves to both create a more homogeneous gas stream and also to aid in a uniform heat distribution to the process stream.

The loaded reaction tube is then installed into a split tube furnace with the center of the catalyst corresponding to the center of the furnace. Several thermocouples are then fastened to the outside of the reaction tube to control and monitor the furnace temperature.

Immediately upon installation, an Ar flow is initiated and maintained throughout the test period.

The reduction reactor furnace and the acid vaporizer furnace are then brought up to their operating temperatures.

To begin a test the Ar flow is terminated and the sulfuric acid feed initiated. The sulfuric acid, of desired concentration, is fed into the acid vaporizer using a positive displacement peristaltic tubing pump. A calibration curve is used to set the desired flow rate.

The sulfuric acid is then dripped into the acid vaporizer, which is filled with quartz chips to provide a more effective means of heat transfer.

The vaporized sulfuric acid, now a steam-SO₃ mixture, enters the reduction reactor and passes through the catalyst bed. The product stream, SO₂, O₂, steam, and SO₃ exit the reduction reactor and flow into a water cooled condenser. Here the unreacted SO₃ and H₂O are knocked out as dilute sulfuric acid. Samples are collected here for later analysis using the specific gravity and acid-base titration methods.

The SO₂ and O₂, after passing through a CaSO₄ drying bed to remove any residual moisture, proceed to a three way solenoid valve. At this point the produce gases are either vented or sent to the analysis train.

To analyze for SO₂, the stream flow is diverted directly to the SO₂ analyzer where it is photometrically measured for SO₂ content. After leaving the analyzer, the flow is measured using a bubble flowmeter and then vented. Conversion rate is calculated using the SO₂ flow method.

If the oxygen content is to be measured, the flow is piped to a liquid nitrogen cooled cryogenic separator. Here the SO₂ is condensed out and the oxygen flow sent to its respective analyzer. Calculations are then performed as described in O₂ flow method for calculating conversion rates.

To prevent any contamination problems, the entire system is constructed of quartz and teflon. All delivery lines are heat traced and insulated to prevent any condensation of the sulfuric acid feed.

Figure A-1 is a photograph of the Acid Decomposition Test Facility. Figure A-2 is a schematic diagram for the same. Figure A-3 depicts a loaded reaction tube prior to evaluation.

Figure A-1. Photograph of Decomposition Test Facility

Figure A-2. Schematic of H_2SO_4 Decomposition Catalyst Facility

Figure A-3. Loaded Reaction Tube Prior to Evaluation
(Catalyst ALFA-4, 20% Fe_2O_3 on 3.2 mm Alumina
Process Stream Flows Left to Right)

APPENDIX B

DETERMINATION OF SPACE VELOCITY FOR THE H_2SO_4
DECOMPOSITION TEST FACILITY

APPENDIX B

DETERMINATION OF SPACE VELOCITY FOR THE H_2SO_4 DECOMPOSITION TEST FACILITY

For a known catalyst bed volume, the space velocity based on the H_2SO_4 feed for the H_2SO_4 Decomposition Test Facility is calculated as follows:

Basis: Feed = 1cc/min 80 w/o H_2SO_4 at 25°C

Reactor Temp = 1173°K (900°C)

System Pressure = 1.1 atm

Reaction: $\text{H}_2\text{SO}_4 \xrightarrow{\text{catalyst}} \text{H}_2\text{O} + \text{SO}_3 \xrightarrow{\text{catalyst}} \text{H}_2\text{O} + \text{SO}_2 + 1/2 \text{O}_2$

Data: $\rho = 1.7224$ at 25°C for 80 w/o H_2SO_4

molecular weight of $\text{H}_2\text{SO}_4 = 98.06$

molecular weight of $\text{H}_2\text{O} = 18$

Assume: 100% thermal decomposition of $\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_3$

All constituents are ideal gases.

Calculation of H_2SO_4 (gas) flow

$\dot{n}_A$ = molar flow rate of H_2SO_4 [=] mol/min

$$\dot{n}_A = (1 \text{ cc/min})(1.7224 \text{ g/cc})(.80 \text{ H}_2\text{SO}_4) \left(\frac{1 \text{ mole}}{98.06 \text{ g}} \right)$$

$$= 1.41 \times 10^{-2} \text{ mol/min of H}_2\text{SO}_4$$

However, 1 mole of H_2SO_4 decomposes into 1 mole of H_2O plus 1 mole SO_3 , therefore,

$$\dot{n}_{A_T} = 2 (1.41 \times 10^{-2} \text{ mol/min})$$

$$= 2.82 \times 10^{-2} \text{ mol/min H}_2\text{SO}_4 \text{ (as H}_2\text{O} + \text{SO}_3)$$

Calculation of H_2SO_4 (as steam) Flow

$$\dot{n}_W = \text{molar flow rate of } \text{H}_2\text{O} [=] \text{ mol/min}$$

$$\begin{aligned}\dot{n}_W &= (1 \text{ cc/min})(1.7225 \text{ g/cc})(.20 \text{ H}_2\text{O})\left(\frac{1 \text{ mole}}{18 \text{ g}}\right) \\ &= 1.41 \times 10^{-2} \text{ mol/min} \cdot \text{H}_2\text{O}\end{aligned}$$

Total molar flow, $\dot{n}_T$;

$$\begin{aligned}\dot{n}_T &= \dot{n}_{A_T} + \dot{n}_W \\ &= (2.82 \times 1.91) \times 10^{-2} \\ &= 4.72 \times 10^{-2} \text{ mol/min}\end{aligned}$$

To Calculate Volumetric Gas Flow, $\dot{V}_T$

$$\begin{aligned}\dot{V}_T &= \frac{\dot{n}_T RT}{P} \\ &= \frac{(4.72 \times 10^{-2} \text{ Mol/min}) \left(\frac{.082 \text{ L-atm}}{\text{Mol} \cdot ^\circ\text{K}}\right)}{1.1 \text{ atm}} \\ &= 4.13 \text{ L/min} [=] 4130 \text{ cc/min}\end{aligned}$$

To Calculate Space Velocity

$$\begin{aligned}\text{Space Velocity} &= \frac{\text{Total Gas Flow}}{\text{Catalyst Volume}} [=] \text{ hr}^{-1} \\ &= \frac{(4130 \text{ cc/min})(60 \text{ min/hr})}{10.00 \text{ cc}}\end{aligned}$$

$$\text{SV} = 24,780 \text{ hr}^{-1}$$

APPENDIX C

OPERATION OF THE LABORATORY MODEL

APPENDIX C

OPERATION OF THE LABORATORY MODEL

The operating procedure for the Laboratory Model is as follows:

Five thermocouples are installed at various heights throughout the reduction reactor. These serve to monitor the radial temperature profile of the catalyst bed. The reduction reactor is then loaded with a known volume of catalyst and installed in the system. All lines are then heated, heat traced and insulated to prevent any condensation of sulfuric acid.

Immediately after installation of the reduction reactor an argon flow is initiated and maintained whenever acid is not being delivered to the vaporizer.

Sulfuric acid, of known concentration is then loaded into the acid feed reservoir. Prior to loading, the specific gravity, temperature, and volume of acid loaded, are recorded.

The reduction reactor furnace and acid vaporizer furnace are then heated to their desired operating temperatures. The SO_2 cryogenic separator is then activated and maintained at $\sim -60^\circ\text{C}$.

To start the test, the argon flow is first terminated. The sulfuric acid feed is then initiated, using a positive displacement tubing pump, at the desired flow rate. A calibration curve is used to determine the pump speed.

The sulfuric acid, now is vaporized in the acid vaporizer and then flows into the reduction reactor and through the catalyst bed where the reduction of SO_3 to SO_2 occurs. The product stream, a mixture of SO_2 , O_2 and unreacted H_2SO_4 exists the reactor and enters a water cooled condenser. Here the unreacted H_2SO_4 is condensed out and the SO_2 and O_2 mixture then enter. The unreacted H_2SO_4 is collected and retained for analysis.

The SO_2 and O_2 then are delivered to the analytical train or vented. The analytical train operates as described in Appendix A.

Conversion calculations are then performed using one or all of the methods outlined in Section 5.3.2.

APPENDIX D

CATALYST TEST DATA

APPENDIX D
CATALYST TEST DATA

This Appendix contains 10 tables of summarized test results from the catalyst screening tests, H_2SO_4 decomposition tests, and the catalyst endurance tests. The raw data from which these tables were prepared is contained in the following Westinghouse Permanent Record Books:

SO_3 Reduction Catalyst Screening Tests:

Book Numbers:	148245	157307
	157946	158752
	154473	158748
	154474	157958

H_2SO_4 Decomposition Tests:

Book Numbers:	158744
	158745
	158746
	157959

SO_3 Reduction Catalyst Endurance Tests:

Book Numbers:	158751
	157304
	157945

Acknowledgement:

Appreciation is expressed for the efforts of; Ms. Michelle Kaloz for her efforts in constructing, operating, and maintaining the test facilities, for conducting the tests, and for assimilating and reducing the raw data;

Mr. George Yatsko for his technical assistance in constructing the test facilities, and to Messrs. R. L. Ammon, R. W. Buckman, Jr., G. H. Farbman, and G. H. Parker for their support and technical management of the program.

TABLE D-1

ANHYDROUS AND WET TEST RESULTS FOR CATALYST CE-1

ANHYDROUS			
Temperature °C	CE-1		Equilibrium Conversion
	1000 hr ⁻¹	5000 hr ⁻¹	
650	9.5%	-	63.0%
700	21.0%	3.1%	71.5%
750	31.0%	10.7%	79.5%
800	44.9%	25.2%	86.5%
850	51.8%	40.3%	91.5%
900	57.5%	50.2%	94.5%

WET			
Temperature °C	CE-1		Equilibrium Conversion
	1000 hr ⁻¹	5000 hr ⁻¹	
650	5.3%	1.6%	48.5%
700	9.0%	2.5%	60.0%
750	20.7%	7.3%	69.0%
800	35.6%	19.6%	78.0%
850	38.9%	32.3%	85.0%
900	42.7%	38.2%	90.5%

SPACE VELOCITY	FLOW RATES, cc/min		
	Ar	SO ₃	STEAM
1000 Anhydrous	154	13	-
1000 Wet	105	18	43
5000 Anhydrous	766	67	-
5000 Wet	525	92	217

The steam - SO₃ ratio simulates an 80 w/o H₂SO₄ feed.
Catalyst CE-1 - Fe₂O₃ powder, >10, <20 mesh.

TABLE D-2
ANHYDROUS AND WET TEST DATA FOR CATALYST ALFA-2

ANHYDROUS			
Temperature, °C	CONVERSION %		
	1000 hr ⁻¹	5000 hr ⁻¹	Equilibrium
650	31.8	36.5	63.0
700	37.2	44.3	71.5
750	45.2	51.5	79.5
800	50.6	57.3	86.5
850	55.0	61.8	91.5
900	57.8	64.2	94.5

WET			
Temperature, °C	CONVERSION %		
	1000 hr ⁻¹	5000 hr ⁻¹	Equilibrium
650	33.1	37.1	48.5
700	40.4	44.7	60.0
750	47.4	52.0	69.0
800	53.9	58.5	78.0
850	59.5	63.9	85.0
900	64.0	68.0	90.5

SPACE VELOCITY	FLOW RATES, cc/min		
	Ar	SO ₃	Steam
1000 Anhydrous	173	15	--
1000 Wet	188	21	49
5000 Anhydrous	865	75	--
5000 Wet	595	104	245

The Steam/SO₃ Ratio represents an 80 w/o H₂SO₄ concentration.
Catalyst ALFA-2 = 0.5% Pd on 3.2 mm cylindrical alumina substrate.

TABLE D-3

INTERNAL CATALYST BED TEMPERATURES FOR CATALYST ALFA-2

SV = 1000 hr⁻¹, Wet Environment

Prior to Reduction Reaction	During Reduction Reaction	After Reduction Reaction
690°C	647°C	649°C
693	691	693
742	739	741
798	796	798
853	850	852

Ar Flow = 118 cc/min

Steam Flow = 49 cc/min

SO₃ Flow = 21 cc/minSV = 5000 hr⁻¹, Wet Environment

Prior to Reduction Reaction	During Reduction Reaction	After Reduction Reaction
649°C	644°C	648°C
698	692	698
746	741	746
804	798	804
868	863	868

Ar Flow = 595 cc/min

Steam Flow = 245 cc/min

SO₃ Flow = 104 cc/min

Catalyst Volume - 11.28 cc

Bed Length - 12.2 cm

Catalyst Mass - 55.25 g

TABLE D-4

ANHYDROUS AND WET TEST RESULTS FOR CATALYST ALFA-3

ANHYDROUS			
Temperature, °C	CONVERSION %		
	1000 hr ⁻¹	5000 hr ⁻¹	Equilibrium
650	22.8	12.1	63.0
700	36.8	27.4	71.5
750	42.1	44.8	79.5
800	49.7	57.9	86.5
850	45.9	-	91.5
900	41.6	75.7	94.5

WET			
Temperature, °C	CONVERSION %		
	1000 hr ⁻¹	5000 hr ⁻¹	Equilibrium
900°C	51.4	52.6	90.5

SPACE VELOCITY	FLOW RATES, cc/min		
	Ar	SO ₃	STEAM
1000 Anhydrous	154	13	-
1000 Wet	105	18	43
5000 Anhydrous	766	67	-
5000 Wet	525	90	217

The SO₃ - Steam Ratio simulates an 80 w/o H₂SO₄ feed.

Catalyst ALFA-3 - 15% Cr₂O₃ on 6.0 mm alumina pellets

TABLE D-5

OBSERVED CONVERSION RATES FOR CATALYST ALFA-4

ANHYDROUS TEST RESULTS

TEMP. °C	1000 hr ⁻¹	5000 hr ⁻¹	CONVERSION % 10,000 hr ⁻¹	20,000 hr ⁻¹	25,000 hr ⁻¹	Equi.
650	15.4	8.8	7.7	5.6	4.6	63.0
700	28.1	19.3	12.2	8.1	7.3	71.5
750	38.0	30.3	20.3	15.3	15.1	79.5
800	46.7	44.0	37.1	30.1	28.3	86.5
850	52.5	51.0	47.3	43.5	41.5	91.5
900	57.2	55.3	53.8	50.0	49.3	94.5

WET TEST RESULTS

TEMP.	1000 hr ⁻¹	5000 hr ⁻¹	CONVERSION % 10,000 hr ⁻¹	20,000 hr ⁻¹	25,000 hr ⁻¹	Equi.
650	12.3	5.8	2.7	1.2	0.5	48.5
700	29.4	22.6	15.4	13.4	-	60.0
750	38.2	30.8	24.6	-	-	69.0
800	43.8	39.1	36.2	-	-	78.0
850	45.7	-	-	-	-	85.0
900	48.3	47.6	44.5	42.2	35.3	90.5

FLOW RATES, cc/min

COMP.	1000 hr ⁻¹		5000 hr ⁻¹		10,000 hr ⁻¹		20,000 hr ⁻¹		25,000 hr ⁻¹	
	DRY	WET	DRY	WET	DRY	WET	DRY	WET	DRY	WET
Argon	153	110	154	105	308	210	615	420	767	525
Steam	-	43	-	44	-	87	-	173	-	217
SO ₃	12	17	13	19	26	37	53	73	67	92

TABLE D-6

LAB MODEL TEST RESULTS FOR CATALYST ALFA-4

TEMPERATURE °C	CONVERSION %	
	TEST	EQUI.
815	74.8	80.8
890	84.0	89.5
920	86.6	91.3
940	89.4	92.1

Feed: 4.1 cc/min H_2SO_4 (80 w/o)

$$\text{SV} = 750 \text{ hr}^{-1}$$

NOTE: Temperatures represent an average of five thermocouples located in the catalyst bed.

TABLE D-7

H₂SO₄ DECOMPOSITION TEST RESULTS FOR CATALYST ALFA-4
USING AN 80 W/O H₂SO₄ FEED

TEMP.	SPACE VELOCITY	AVERAGE CONVERSION	EQUILIBRIUM CONVERSION	EFFICIENCY
700°C	13,000 hr ⁻¹	19.5%	60.0%	32.5%
750	15,000	36.6	69.0	53.0
800	15,000	69.5	78.0	83.3
850	18,000	81.6	85.0	91.8
900	18,000	87.8	90.5	97.0

TABLE D-8

ANHYDROUS AND WET TEST RESULTS FOR CATALYST ALFA-5

ANHYDROUS

TEMPERATURE, °C	CONVERSION %		
	1000 hr ⁻¹	5000 hr ⁻¹	Equilibrium
650	-	-	63.0
700	-	-	71.5
750	-	-	79.5
800	-	-	86.5
850	-	-	91.5
900	25.9	32.1	94.5

Feed: 92% (by volume) Ar
8% (by volume) SO₃

WET

TEMPERATURE, °C	CONVERSION %		
	1000 hr ⁻¹	5000 hr ⁻¹	Equilibrium
650	-	-	48.5
700	-	-	60.0
750	-	-	69.0
800	-	-	78.0
850	-	-	85.0
900	7.7	6.6	90.5

Feed: 66% (by volume) Ar 11% (by volume) SO₃ where steam - SO₃ ratio simulates an 80 w/o H₂SO₄ feed.
23% (by volume) Steam

TABLE D-9

ENDURANCE TEST RESULTS FOR CATALYST MB-3

Temperature = 871°C

SV = 10,000 hr⁻¹Feed = 80 w/o H₂SO₄ (Simulated)

Time, hrs	Conversion %
1	64.7
21	66.0
46	68.0
66	70.0
90	71.8
155	74.9
240	72.1
305	72.9
408	70.5
473	70.5
525	75.4
575	75.1
666	78.3
716	72.3
738	71.2
841	73.1
906	74.1
983	77.0
1002	75.3

TABLE D-10

ENDURANCE TEST RESULTS FOR CATALYST ALFA-4

Space Velocity = 10,000 hr⁻¹

Temperature = 871°C

Feed = 80 w/o H₂SO₄ (Simulated)

TIME (HOURS)	CONVERSION (%)
1	47.6
20	61.4
67	60.7
157	45.2
186	50.0
206	56.6
300	62.3
372	51.1
468	63.7
516	51.3
540	53.4
564	50.3
642	52.4
704	46.5
726	45.2
750	46.1
774	47.1
847	45.1
872	55.3
893	49.1
925	46.5
949	46.7
1014	50.4

APPENDIX E

REDUCTION REACTOR MATERIALS TEST DATA

TABEL E-1

REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - INLET CONDITIONS
RUN RR 482HI3

SAMPLE	Δ Weight/Area, mg/cm ²											Visual Appearance after 1000 hrs
	78 hrs	155 hrs	225 hrs	302 hrs	401 hrs	502 hrs	600 hrs	696 hrs	797 hrs	895 hrs	1000 hrs	
Hastelloy G	-1.03	.27	.12	.11	.11	.11	.16	.23	.28	.30	.35	Gray-black with rust edges and cream patches
CS 1018	7.47	12.3	14.5	-3.59	-5.33	-2.93	-.46	-.46	1.94	2.74	3.90	Flaky rust with white patches
Alonized SS 316	.29	1.43	1.43	1.41	1.40	1.41	1.47	1.50	1.52	1.53	1.54	Gray with yellow hues
Alonized CS 1018	-.11	.68	.71	.64	.64	.71	.81	.81	.82	.83	.84	Gray with rust and yellow hues
SS 316	.45	.73	.90	.83	1.01	1.06	1.45	1.68	1.83	1.84	1.96	Gray-black with rust patches
Tantalum	-.99	.29	.35	.59	-2.46	-2.33	-2.33	-2.63	-4.61	-7.26	-13.0	Completely white

TEST CONDITIONS:

Furnace Temperature	-	482°C
SO ₃ Flask Temperature	-	53°C
SO ₃ Flow Rate	-	25 scc/min
Steam Flow Rate	-	58 scc/min
Argon Flow Rate	-	78 scc/min

NOTE: NEGATIVE VALUES INDICATE WEIGHT LOSS PER UNIT AREA

TABLE E-2
REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - INLET CONDITIONS
RUN RR 482HI4

SAMPLE	Δ WEIGHT/AREA, mg/cm ²										VISUAL APPEARANCE AFTER 1000 HOURS
	100 Hours	210 Hours	348 Hours	397 Hours	496 Hours	594 Hours	692 Hours	793 Hours	891 Hours	1000 Hours	
Sialon 81	.03	.03	.10	.10	.10	.10	.10	.10	.16	.21	Green
Al ₂ O ₃	.14	.10	.18	.18	.18	.22	.18	.22	.22	.22	Like as received
Zirconium 702	-	.71	.88	.90	1.18	1.39	1.58	1.83	2.10	2.31	Dark gray corrosion
Hastelloy B2	.20	.58	1.37	1.43	2.80	3.22	5.21	5.58	6.50	9.44	Black corrosion
Sialon 88	.09	.09	.18	.21	.21	.21	.32	.21	.16	.21	Gray
Sialon 80	.09	.14	.17	.22	.22	.22	.22	.22	.19	.21	Green corrosion
TiB ₂	*										

TEST CONDITIONS:

FURNACE TEMPERATURE - 482°C
SO₂ FLASK TEMPERATURE - 53°C
SO₂ FLOW RATE - 25 scc/min
STEAM FLOW RATE - 58 scc/min
ARGON FLOW RATE - 78 scc/min

*The TiB₂ sample was completely disintegrated by the first interruption at 100 hours and was replaced by Zirconium 702. Therefore, subtract 100 hours from the column values to get the exposure times for Zirconium 702.

TABLE E-3
REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIROMENT - INLET CONDITIONS
RUN RR 482HI5

SAMPLE	Δ WEIGHT/AREA, mg/cm ²											VISUAL APPEARANCE AFTER 1000 HOURS
	75 Hours	196 Hours	237 Hours	336 Hours	432 Hours	547 Hours	650 Hours	721 Hours	840 Hours	966 Hours	1000 Hours	
Duro Acid-Proof Brick	.55	.62	1.62	1.67	1.71	1.69	3.55	2.40	2.38	3.20	2.66	Like as-received.
Duriron	1.01	1.39	1.54	2.03	2.17	2.43	3.04	1.74	1.30	1.39	1.74	Gray and black with spots of yellow residue.
Vitreous Carbon	-21.3	-83.5	-95.3	-127.	-	-	-	-	-	-	-	Gray, pitted, almost completely disintegrated ^a .
Durichlor 51	.21	.44	.08	.21	.23	.28	1.51	.13	.26	.44	.64	Like as-received with large spot of yellow residue.
Tungsten - powder, sintered swaged	.79	1.34	1.53	1.95	2.19	2.34	3.61	2.80	2.97	3.31	5.16	Completely covered with adherent green corrosion layer.
Aluminum Silicate	1.63	1.85	3.31	3.22	3.13	3.09	4.45	4.00	3.98	4.14	3.66	Like as-received with large spots of white residue on each side.
Inconel 617	-	-	-	-	-	.17	1.08	1.46	1.74	1.86	2.69	Black corrosion layer with some yellow residue ^b .

TEST CONDITIONS: FURNACE TEMPERATURE - 482°C
SO₃ FLASK TEMPERATURE - 53°C
SO₃ FLOW RATE - 25 scc/min
STEAM FLOW RATE - 58 scc/min
ARGON FLOW RATE - 78 scc/min

NOTES: Negative values indicate weight loss per unit area.

^aThe vitreous carbon sample was taken out of test after 336 hours.

^bTesting of Inconel 617 began after the interruption at 432 hours. Therefore, subtract 432 hours from the column values to get the exposure times for Inconel 617.

TABLE E-4

REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - INLET CONDITIONS
RUN RR 871H11

SAMPLE	Δ WEIGHT/AREA, mg/cm ²										VISUAL APPEARANCE AFTER 1000 HOURS
	58 Hrs	180 Hrs	228 Hrs	329 Hrs	491 Hrs	596 Hrs	695 Hrs	805 Hrs	903 Hrs	1000 Hrs	
Silicon	.07	.07	.07	.11	.14	.21	.23	.28	.25	.32	Dull, transparent coating
Inconel 625	1.01	.56	.42	.19	-.10	-.03	-.35	-.57	-.51	-.85	Yellowish coating
Anionized Inconel 625	-.26	-.27	-.28	-.28	-.30	-.30	-.31	-.30	-.33	-.32	Black corrosion patches
Silicon Nitride	.04	.13	.06	.06	.08	.24	.12	.10	.01	.10	Gray with very light cream and beige corrosion
Inconel 657	3.66	3.27	2.81	2.10	1.54	.95	.58	.35	.04	-.41	Green corrosion layer
Silicon Carbide	0	.06	0	-.02	.06	.06	.08	.06	.08	.09	Like as-received but lacks original sheen

TEST CONDITIONS:

FURNACE TEMPERATURE - 871°C
 SO₃ FLASK TEMPERATURE - 53°C
 SO₃ FLASK TEMPERATURE - 25 scc/min
 STEAM FLOW RATE - 58 scc/min
 ARGON FLOW RATE - 78 scc/min

NOTE: Negative Values Indicate Weight Loss Per Unit Area

TABLE E-5

REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - INLET CONDITIONS
RUN RR 871H12

SAMPLE	Δ WEIGHT/AREA, mg/cm ²									VISUAL APPEARANCE AFTER 1000 HOURS
	96 Hours	194 Hours	298 Hours	425 Hours	511 Hours	631 Hours	740 Hours	Hours	1000 Hours	
Durichlor 51	2.20	2.44	2.56	1.58	1.13	.12	.03	-.65	-.65	Spalling black corrosion layer
Alumina	0	.03	.14	.07	.05	.09	.09	.09	.09	Like as-received with black specks
Hastelloy G	.71	.83	.89	.86	.80	.82	.77	.75	.74	Black corrosion layer
Duro Acid-Proof Brick	.29	.29	.77	.19	.04	.70	.52	-.75	.28	Like as-received
Duriron	4.66	7.56	8.62	15.4	20.0	26.6	33.2	34.2	40.0	Heavy spalling, gray-black corrosion layer
Aluminum Silicate	-.13	-.16	.26	-.23	-.39	-.10	-.16	-.44	-.39	Like as-received

TEST CONDITIONS:

FURNACE TEMPERATURE - 871°C
 SO₃ FLASK TEMPERATURE - 53°C
 SO₃ FLOW RATE - 25 scc/min
 STEAM FLOW RATE - 58 scc/min
 ARGON FLOW RATE - 78 scc/min

NOTE: Negative values indicate weight loss per unit area

TABLE E-6
REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - INLET CONDITIONS
RUN RR 871HI3

<u>SAMPLE</u>	<u>WEIGHT/AREA, mg/cm²</u>		<u>VISUAL APPEARANCE AFTER 108 HOURS</u>
	<u>67 Hours</u>	<u>108 Hours</u>	
Inconel 671	.73	.78	Gray corrosion
Alonized Inconel 671	.53	.69	Light green corrosion
Incoloy 800	.47	.72	Brown corrosion
Alonized Incoloy 800	.21	.70	Silver and white

TEST CONDITIONS:

Furnace Temperature	-	871°C
SO ₃ Flask Temperature	-	53°C
SO ₃ Flow Rate	-	25 scc/min
Steam Flow Rate	-	58 scc/min
Argon Flow Rate	-	78 scc/min

TABLE E-7

REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - OUTLET CONDITIONS
RUN RR 650H01

SAMPLE	Δ WEIGHT/AREA, mg/cm ²										VISUAL APPEARANCE AFTER 1000 HOURS
	101 Hours	200 Hours	299 Hours	398 Hours	496 Hours	612 Hours	708 Hours	805 Hours	904 Hours	1000 Hours	
Silicon	.09	.05	.12	.09	.12	.14	.09	.14	.21	.21	Gray
Silicon Nitride	.17	.09	.10	.06	.64	.04	.01	.06	.04	.01	Like as-received
Alonized Inconel 625	.14	.99	.93	.79	.84	.83	.37	.56	.60	.65	Cream color corrosion layer
Silicon Carbide	.05	-.03	0	0	.03	.13	.03	.04	.03	.04	Like as-received with minute amount of white residue
Inconel 625	.10	.27	.45	.57	.77	1.35	1.01	1.08	1.13	1.18	Some rust-colored spots with green and white corrosion
Inconel 657	.11	1.34	3.08	4.53	5.62	8.12	9.11	11.2	10.8	10.4	Green and white corrosion

TEST CONDITIONS:

FURNACE TEMPERATURE - 650°C
 SO₃ FLASK TEMPERATURE - 53°C
 SO₃ FLOW RATE - 25 scc/min
 SO₂ FLOW RATE - 47 scc/min
 O₂ FLOW RATE - 23 scc/min
 STEAM FLOW RATE - 169 scc/min

NOTE: Negative values indicate weight loss per unit area.

TABLE E-8

REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - OUTLET CONDITIONS
RUN RR 650H02

SAMPLE	Δ WEIGHT/AREA, mg/cm ²										VISUAL APPEARANCE AFTER 1000 HOURS
	93 Hours	186 Hours	281 Hours	383 Hours	481 Hours	575 Hours	699 Hours	798 Hours	896 Hours	1000 Hours	
Aluminum Silicate	2.19	2.54	2.62	2.65	2.62	2.70	2.76	2.76	2.79	2.79	Like as-received with small rust spot on one side.
Durichlor 51	1.57	3.75	5.51	7.85	6.79	6.86	7.85	7.56	7.69	8.52	Maroon-rust corrosion.
Hastelloy G	3.69	4.20	1.72	1.84	2.81	3.13	3.62	3.64	3.13	3.64	Black and rust corrosion layer.
Hastelloy B2	-	87.0	159.	217.	230.	-	-	-	-	-	Heavy black, beaded corrosion with small greenish areas ^a .
Duriron	3.01	7.93	15.6	21.1	21.1	23.7	24.6	25.9	27.7	31.8	Rust-like corrosion layer.
Alumina	.22	.38	.41	.41	.41	1.04	.74	-.63	.91	.85	Like as-received.
Vitreous Carbon	-126.	-	-	-	-	-	-	-	-	-	Gray, pitted, almost completely disintegrated. ^b
Zirconium 702	-	-	-	-	-	-142.	-	-	-	-	Completely covered with white, powdery corrosion. ^c
Stainless Steel 310	-	-	-	-	-	-	3.88	.36	-6.29	-4.76	Maroon-rust corrosion ^d

TEST CONDITIONS:

FURNACE TEMPERATURE	- 650°C
SO ₃ FLASK TEMPERATURE	- 53°C
SO ₃ FLOW RATE	- 25 scc/min
SO ₂ FLOW RATE	- 47 scc/min
O ₂ FLOW RATE	- 23 scc/min
STEAM FLOW RATE	- 169 scc/min

NOTES: Negative values indicate weight loss per unit area.

^aTesting of Hastelloy B2 began after the first interruption at 93 hours. Therefore, subtract 93 hours from the column values to get the exposure times for Hastelloy B2.

^bThe vitreous carbon sample was taken out of test after the first interruption at 93 hours.

^cTesting of Zirconium 702 began after the interruption at 481 hours. It was taken out of test after the interruption at 575 hours for a total test time of 94 hours.

^dTesting of SS 310 began after the interruption at 575 hours. Therefore, subtract 575 hours from the column values to get the exposure times for SS 310.

TABLE E-9

REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - OUTLET CONDITIONS
RUN RR 650H03

<u>SAMPLE</u>	<u>Δ WEIGHT/AREA, mg/cm²</u>			<u>VISUAL APPEARANCE AFTER 336 HOURS</u>
	<u>127 Hours</u>	<u>216 Hours</u>	<u>336 Hours</u>	
PSS Tungsten	28.9	44.0	60.7	Thick, flaky green corrosion
Sialon 88	.24	.24	.28	Like as-received
Cartech Type 20 Cb 3	.77	4.10	5.08	Black and rust corrosion
Sialon 80	-.51	-1.40	-2.69	Light grey
Sialon 81	-.17	-.88	-1.25	Light grey
Hastelloy C-276	1.03	1.53	3.74	Black corrosion

TEST CONDITIONS:

FURNACE TEMPERATURE - 650°C
 SO₃ FLASK TEMPERATURE - 53°C
 SO₃ FLOW RATE - 25 scc/min
 SO₂ FLOW RATE - 47 scc/min
 O₂ FLOW RATE - 23 scc/min
 STEAM FLOW RATE - 169 scc/min

NOTE: Negative values indicate weight loss per unit area.

TABLE E-10
REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - OUTLET CONDITIONS
RUN RR 871H01

<u>SAMPLE</u>	<u>Δ WEIGHT/AREA, mg/cm²</u>					<u>VISUAL APPEARANCE AFTER 417 HOURS</u>
	<u>120 Hours</u>	<u>164 Hours</u>	<u>259 Hours</u>	<u>360 Hours</u>	<u>417 Hours</u>	
Incoloy 800	1.71	1.69	1.76	2.20	2.06	Brown-rust corrosion
Alonized Incoloy 800	-.49	0	.13	.63	.47	Yellow-brown corrosion
Inconel 671	4.89	4.59	4.97	5.88	4.63	Yellow corrosion
Alonized Inconel 671	2.51	2.66	2.68	2.96	2.67	Gray

TEST CONDITIONS:

FURNACE TEMPERATURE - 871°C
SO₃ FLOW - 25 scc/min
SO₂ FLOW - 47 scc/min
O₂ FLOW - 23 scc/min
STEAM FLOW - 169 scc/min

NOTE: Negative values indicate weight loss per unit area.