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SOLAR THERMAL HYDROGEN PRODUCTION PROCESS

FINAL REPORT

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prepared for
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ABSTRACT

Under sponsorship by the United States Department of Energy, Westinghouse Advanced Energy Systems Division has investigated the potential for using solar thermal energy to split water into hydrogen and oxygen. A hybrid thermochemical/electrochemical process, known as the Sulfur Cycle, has been the focus of these investigations. Process studies have indicated that, with adequate and ongoing research and development, the Sulfur Cycle can be effectively driven with solar heat. Also, economic analyses have indicated that the cycle has the potential to produce hydrogen in economic competitiveness with conventional methods (e.g. methane/steam reforming) by the turn of the century. A first generation developmental system has been defined along with its critical components, i.e. those components that need substantial engineering development. Designs for those high temperature components that concentrate, vaporize and decompose the process circulating fluid, sulfuric acid, have been prepared. Extensive experimental investigations have been conducted with regard to the selection of construction materials for these components. From these experiments, which included materials endurance tests for corrosion resistance for periods up to 6000 hours, promising materials and catalysts have been identified.

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EXECUTIVE SUMMARY

This executive summary provides an overview of the results of the work performed under this contract and a road map to locate additional details on specific topics. To help serve this purpose, this executive summary uses the same numerical and verbal titles found in the main body of the report.

1.0 INTRODUCTION

Westinghouse began investigations of "thermochemical water splitting" in 1973 at its Research and Development Center. Initially, a large number of potential thermochemical cycles for hydrogen generation were investigated, and rather quickly, a judgment was made that a hybrid electrochemical/thermochemical cycle had good promise for development into a commercial process. Because this hybrid cycle uses sulfuric acid as a circulating fluid, it was designated as the Sulfur Cycle. Research and development proceeded under Corporate sponsorship and outside sources of funding. In 1977, the Solar Energy Division of the U. S. Department of Energy became interested in sponsoring development work on some aspects of the Sulfur Cycle for solar thermal applications. As a result, Westinghouse Advanced Energy Systems Division began work on the contract reported herein in January 1978. Initially, the schedule was for one year but contract amendments extended the scope of work and schedule through December 1982.

2.0 PROCESS AND SYSTEM STUDIES

2.1 Solar Hydrogen Economic Analysis

Because the ultimate viability of solar hydrogen will be based on its economic potential to compete with other methods for manufacturing hydrogen, an economic analysis was performed to gain some perspective on this issue. The major objectives of this analysis were to answer two key questions:

- Will solar hydrogen plants be able to compete economically with other techniques for making hydrogen?

- What bearing do key variables such as size of the projected market, plant capacity rating, and experience/cost relationships, have on the potential for solar hydrogen to successfully penetrate the projected market for hydrogen?

The results of the analysis indicated that, depending on the size of plants built, solar hydrogen does have the potential to become economically competitive with conventional hydrogen (steam/methane reforming) before the turn of the century. For example, if commercial status can be attained by 1995 with solar plants rated at 30,000 SCFH, then by 1997, 175 of these plants will have been built (assuming they represent only 6% of the total new hydrogen demand). Compared to new steam/methane plants at the same rating, both types of plants will generate hydrogen costing approximately \$70/MMBTU.*

In contrast, if much larger plants are built, say 1×10^6 SCFH, it will take somewhat longer for the plants to reach "economic maturity", i.e. for experience effects to permit substantial cost reductions to occur because of volume production. By the year 2004, however, these larger solar hydrogen plants should be competitive with steam/methane reforming plants of the same capacity. Because of economies of scale, hydrogen from these larger plants would cost approximately \$25/MMBTU (1980 dollars) or about one third of that from the smaller plants discussed in the preceding paragraph.

These economic analyses were based on best estimates of escalation over the next forty years as forecasted by Data Resources Inc. A conservative experience curve effect of 85% was used in projecting solar hydrogen cost reductions, i.e., a 15% cost reduction occurs each time accumulated production capacity doubles. The method for computing the cost of hydrogen (COH) was done consistently for both solar and conventional plants by adapting an approach published by Gregory, et.al. of the Institute of Gas Technology.

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*Costs are expressed in constant 1980 dollars rather than current dollars by using the implicit GNP deflator. The seemingly high values for steam methane reforming plants in the year 1997 are due to the projected real escalation of natural gas, i.e. escalation above that that can be attributed to general inflation.

The first commercial solar hydrogen plant is estimated to require a fixed capital investment of \$22 million assuming it follows a prototype plant of the same rating (30,000 SCFH). The prototype plant will require \$36 million fixed capital investments. This value includes \$24 million for the installed cost of equipment. The solar subsystem is estimated at \$13.7 million and the hybrid sulfur cycle at \$10.5 million. Direct equipment costs for the sulfur cycle represent \$3.1 million of the \$10.5 million while the electrolytic subsystem of the hybrid sulfur cycle represents less than \$1 million of the \$3.1 million equipment cost.

In evaluating costs over a range of plant sizes, appropriate scaling factors were used. On a plant basis, a conservative exponent of 0.8 was used. On an equipment basis, a linear scaling was used for the electrolyzer and the solar collector field.

Section 2.1 of this report presents detailed discussions of the economic analyses along with numerous tables, curves and assumptions that supported the analysis.

2.2 Pressurized Test Unit

A major milestone during the system process studies was the conceptual design definition of a developmental system designated as the pressurized test unit (PTU). The PTU configuration was chosen after comprehensive trade studies were performed and a rigorous selection process used to rank several candidate configurations. The selection process used a set of weighed criteria to rank six final PTU configurations that had been screened from a larger list of candidates.

The PTU was sized for a nominal 85 kW(t)* rate of hydrogen generation so that the hybrid sulfur cycle could be coupled with a distributed solar collector (or simulated solar heat source) of reasonable size. A high temperature heat

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*Based on hydrogen's HHV, ~60,000 Btu/lb

transport loop, e.g., helium at 1800°F, would provide the thermal interface between the heat source and the sulfur cycle process.

When its final design has been completed along with associated component development, the PTU can be constructed as a development test bed for the sulfur cycle. Subsequent operational testing of the PTU will validate component and subsystem design approaches and provide a data base for follow-on developmental systems, e.g., a pilot plant. Section 2.2 of this report describes the features of the PTU and reviews the design studies and selection process that led to the preferred PTU configuration.

2.3 Plant Operational Studies

Before the PTU design studies were performed, a set of plant operational studies was conducted to examine the operational aspects of an integrated solar/hydrogen/chemical plant. Specific issues 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 consideration on plant design.

A reference solar hydrogen/ammonia production plant was 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 were specified, and this information was used to aid in defining a set of plant operating modes. Six modes were indicated based on the premise that the plant should produce ammonia 24 hours/day. A sequence was 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. The detailed results of these plant operational studies are presented in Section 2.3.

2.4 Process Scoping Studies

The need to do the operational studies discussed above was identified during some initial process scoping studies. These studies were oriented toward identifying potentially attractive chemical or fuel processes that could be driven by solar energy and use the Sulfur Cycle as a source of hydrogen feedstock. Five chemical or fuel processes were evaluated: ammonia, methanol, hydrogen peroxide, direct reduction of iron ore, and coal liquefaction. All of these processes appeared to be technically feasible using high-temperature solar technology.

Capacity matching of the solar/hydrogen subsystem with end product process requirements was identified as a significant issue. For example, ammonia and methanol solar plant capacities defined during these studies are equivalent to small, older existing fossil-fueled plants while new fossil-fuel ammonia and methanol plants are five or six times larger. Some of the plant capacity discrepancies potentially can be resolved by using multiple solar central receivers and piping steam and acid to a central production plant. The detailed results of the scoping studies are contained in Section 2.4.

3.0 ACID VAPORIZER DESIGN AND DEVELOPMENT

As the pressurized test unit (PTU) configuration was being defined, initial sizing and scoping studies for all of its components were made. Also the components were rated into one of four categories: (a) established technology; (b) near term technology; (c) developmental; or (d) speculative. None of the components was judged to be speculative and many were rated as established or near term. A few were judged to be developmental and therefore represent those critical components that require substantial engineering development and supporting research. These critical components included the heat exchange equipment needed to concentrate and vaporize the sulfuric acid before it is decomposed into sulfur dioxide and oxygen.

Because of the absence of industrial experience in designing or building equipment that must contain boiling concentrated sulfuric acid at high pressure, an extensive evaluation was undertaken to identify materials that have adequate corrosion resistance. From this materials evaluation, which included corrosion

tests with about three dozen candidate materials, silicon carbide was selected to be the most attractive (or reference) material for acid vaporizer construction.

Design and analysis activities on silicon carbide acid vaporizers led to a design based on a tube and shell heat exchanger configuration. Because of the ceramic material used in this design, consideration was given to the fact that there are no existing ASME or ASTM standards (e.g. the ASME Pressure Vessel Codes) to cover this situation. This fact, along with considerations of recent advances in fabricability of silicon carbide, led to the incorporation of special sliding seals in the design to accommodate differential thermal expansion and thermal stresses during startup.

As the acid vaporizer design was detailed, appropriate stress analyses were performed along with technical discussions with qualified fabricators of silicon carbide. As a result of this work, the application of the sliding seals to silicon carbide was identified to be in need of experimental verification.

While the seals are commercially available for high temperature applications with metals, they have not been used heretofore with ceramic materials.

Accordingly, a seal test rig was designed and a test program was specified to verify the adequacy of the sliding seal feature. This test rig was procured with special silicon carbide components, commercially available Helicoflex^R sliding seals (Inconel coil springs with gold liners) and ancillary hardware. The rig awaits assembly and testing when additional development funding can be obtained. Details of the work on the acid vaporizer design, and analysis materials evaluation and selection and seal test rig can be found in Section 3.0 of this report.

4.0 REDUCTION REACTOR DESIGN AND ANALYSIS

The other critical component that requires substantial engineering development is the high temperature chemical reactor for cracking the acid vapor* into

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*More precisely, the sulfur trioxide constituent of the acid vapor.

sulfur dioxide and oxygen. This acid decomposition reactor (or hereafter referred to as the "reduction reactor") must operate at temperatures around 1,600°F under pressurized conditions and needs a suitable catalyst to ensure adequate reaction rates for sulfur trioxide cracking.

Following the design studies on the PTU, component design efforts on the reduction reactor were conducted in parallel with the work on the acid vaporizer. From these efforts, a reduction reactor design concept emerged that has some similarities, and some major differences, when compared with the acid vaporizer design. The reduction reactor is a shell-and-tube heat exchanger driven by 1,800°F helium on its tube side. The shell side accommodates the acid vapor stream which flows through two pellet beds in series. The first bed is a pre-heating region while the second bed serves as the catalyst for the cracking reaction. The catalyst bed uses a commercially available catalyst that has iron oxide deposited on an alumina substrate. Operating conditions for the reduction reactor permits the use of suitable superalloy metals (e.g. Hastelloy-X and alonized Incoloy-800) for much of the structure. However, silicon carbide is used for the tubing in the higher temperature regions and, like the acid vaporizer, the reduction reactor relies on sliding seals to accommodate differential thermal expansion.

Detailed performance and thermal/hydraulic analyses (using a special purpose digital computer program) were performed to ensure the proper selection of reduction reactor dimensions, operating temperatures and fluid flow rates. Also, stress analyses were performed to ensure that the design concept has no significant structural problems and has the potential to meet appropriate pressure vessel design codes (e.g. Section VIII of the ASME Boiler and Pressure Vessel code. A complete description of the reduction reactor design is contained in Section 4.2 and the supporting thermal, performance and stress analyses are discussed in Sections 4.3 and 4.4.

The catalyst was selected after extensive screening tests had been performed to compare the performance of a number of commercially available candidates. The selected iron oxide on alumina catalyst was comparable in performance to

another catalyst based on platinum on alumina. Cost considerations tipped the scale in favor of the iron oxide. The selection of this catalyst was confirmed by a successful 5,000 hour endurance test in the acid vapor environment at 1,600°F.

To support the selection of materials for the reduction reactor, a thorough materials evaluation effort was undertaken with emphasis on tests in the acid vapor environment. The initial phase of this evaluation involved a screening test program during which a total of forty two candidate materials were subjected to the expected acid vapor environment. A number of these materials were tested for periods up to 1,000 hours and eight to ten exhibited very good corrosion resistance. From this group four materials were selected for endurance tests for 6,000 hours. Two of these were stainless steels: Type 20Cb-3 and Type 444. The other two were alonized Incoloy 800 and alonized Hastelloy G (a relative of Hastelloy X).

From the materials samples placed on endurance test, only the Type 444 stainless steel failed to exhibit corrosion resistance early in the test. This material was removed from the test after 2,000 hours and the other three materials withstood the 6,000 hour test with varying degrees of success. Details on the catalyst and materials evaluations are found in Sections 4.5 and 4.6 respectively.

Planners and designers of solar hydrogen plants based on thermochemical cycles that use sulfuric acid must determine eventually how best to couple the solar receiver with the thermochemical cycle. The principal questions involve whether or not to have an integral solar receiver/reduction reactor or to separate these functions into two or more pieces of equipment. These issues were considered under this contract with a conclusion that the indirect method for heating the reduction reactor (via a hot gas loop) would be preferable overall. The deliberations that led to this judgment are discussed in Section 4.7.

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1.0 INTRODUCTION

The idea of "water splitting" via thermochemical cycles began to receive serious attention, both in the United States and Europe, during the early 1970's. Westinghouse Electric Corporation initiated investigation in 1973 and, after screening a number of thermochemical cycles, the Corporation's efforts focused on a hybrid thermochemical/electrochemical process. This process, known as the Sulfur Cycle, consists of two principal chemical reactions. The production of oxygen occurs via the thermal decomposition of sulfur trioxide obtained from sulfuric acid:

A catalyst is used to accelerate the rate of sulfur trioxide reduction to sulfur dioxide and oxygen. The cycle is completed by using the sulfur dioxide from the thermal reduction step to depolarize the anode of an electrolyzer using dilute sulfuric acid electrolyte. The overall reaction occurring electromechanically is:

The net result of Reactions 1 and 2 is the decomposition of water into hydrogen and oxygen and the sulfur oxides are involved solely 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 required for the thermal inputs are compatible with advanced high temperature solar receivers and nuclear reactors. The electrical power can be provided by a companion solar thermal electric plant, a solar photovoltaic plant, by fuel

cells fed with a portion of the hydrogen and oxygen produced in the process, or by power from an available grid.

Research and development on the Sulfur Cycle has proceeded at Westinghouse under Corporate sponsorship and outside resources of funding. In 1977, the Solar Energy Division of the U. S. Department of Energy became interested in sponsoring work on some aspects of the Sulfur Cycle for solar thermal applications. As a result, Westinghouse Advanced Energy Systems Division began work on the contract reported herein in January 1978. Initially, the work was scheduled for one year. Contract amendments, however, expanded the scope of work and schedule through December 1982. Work under this contract has focused on technology development and supporting research for the thermochemical portions of the process and on interfacing the process with solar heat. Research and development on the electrolytic subsystem proceeded in parallel with independent sources of funding. The Conservation and Energy Storage Division of the Department of Energy provided principal support for electrolyzer development.

2.0 PROCESS AND SYSTEM STUDIES

2.1 SOLAR HYDROGEN ECONOMIC ANALYSIS

2.1.1 BACKGROUND

The ultimate viability of solar hydrogen will depend on its potential to compete economically with other methods for producing hydrogen. An economic analysis was performed to evaluate a plant that uses a solar central receiver system with thermal storage to provide the heat to a hybrid thermochemical electrical process for producing hydrogen. The major objectives of this analysis were to answer two major questions:

- Will solar hydrogen plants be able to compete economically with other techniques for making hydrogen?
- What bearing do key variables such as size of the projected market, plant size and experience curve benefits have on the solar hydrogen market potential?

The general approach taken in this study was to determine the market growth potential and cost of hydrogen (COH) for conventional hydrogen production methods and to compare these projections with the COH estimated for solar hydrogen plants. Specific steps in these studies included the following:

- Estimate plant performance and capital costs for a prototype solar hydrogen plant in a size equivalent to conventional hydrogen plants.
- Determine the market potential for conventional and new hydrogen plants based on existing market surveys and estimate the market share for solar hydrogen.
- Define the projected COH for conventional and development systems.
- Estimate the commercial plant costs and the COH for solar hydrogen plants as a function of size and market growth and compare with conventional plant projections.

Major assumptions and key references for this study include the following:

- Plant performance and cost based on a cycle to produce the thermal input to the acid vaporizer and decomposition reactor from solar energy and thermal storage for base loaded (continuous) operation.
- Solar System performance and costs based on a gas cooled central solar receiver system prepared by the Boeing Co. (Ref. 2-1).
- Hydrogen market projections based on the HEST Report "Reference" Forecast (Ref. 2-2).
- COH projections based on an analysis by Gregory, et al (Ref. 2-3).

2.1.2 PLANT PERFORMANCE ESTIMATES

Estimates of plant performance were based on (1) synthesis of performance calculations for the solar supply system and sulfur cycle system in separate studies, and (2) scaling these estimates to the prototype plant size. The overall plant cycle is shown schematically in Figure 2-1. The prototype plant configuration is based on solar central receiver technology and Sulfur Cycle technology. It includes a field of heliostats that focus the solar heat on a central receiver mounted on a tower. The receiver is coupled thermally by helium to a thermal storage system and to the Sulfur Cycle where the heat is used by the decomposition reactor and acid vaporizer.

Inputs to the overall cycle are insolation to the solar system, and electrical power and feedstock water to the sulfur cycle. The outputs include hydrogen and by-products oxygen, process steam and hot water. In the overall plant analysis credit is given for steam production for cogeneration usage in addition to hydrogen production; however, credits for oxygen and hot water are neglected.

A prototype plant size was selected to produce 30,000 SCFH* of hydrogen. This size is representative of natural gas fired hydrogen production plants. Thermal storage is included to provide the capability for around-the-clock operation. The solar receiver is sized to provide the thermal needs for the high temperature components of the Sulfur Cycle. Electrical requirements for the sulfur cycle are supplied from the commercial grid.

Sulfur Cycle Performance

A flowsheet for the sulfur cycle system is shown in Figure 2-2. The flowsheet is representative of a large scale hydrogen production plant sized to produce 1.86×10^6 SCFH of hydrogen (173 MW_t). System performance is summarized in Table 2-1 for the large scale system. These performance estimates were scaled linearly with hydrogen production rate to obtain the estimate for the prototype plant size also shown in Table 2-1. As shown in this table, the Sulfur Cycle performance (useful power output) is based on hydrogen production with credit given for oxygen and steam production. Typical statepoints and fluid stream compositions are shown in Table 2-2 for the large scale plant.

Solar System Performance

A solar plant application developed as part of DOE's Solar Retrofit Program was used to estimate performance and costs for the solar equipment based on current solar central receiver technology. The particular application selected was a Gypsum Plant located in Sweetwater, Texas (Reference 2-1). This application was selected since it considered a gas cooled solar receiver system and because of its location in a typical southwest environment. Typical performance characteristics are summarized in Tables 2-3 and 2-4.

Although the gypsum plant application is for a lower receiver outlet temperature (1340°F) and uses air as the transport fluid, the solar system efficiency is 61% and associated facility costs were assumed to be typical for the Sulfur Cycle prototype plant. A SERI study (Reference 2-4) was used as a basis for

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*Standard Cubic Feet per Hour

Figure 2-1. Solar Hydrogen Plant Schematic

Figure 2-2. Sulfur Cycle Flowsheet

TABLE 2-1 .
SULFUR CYCLE SYSTEM PERFORMANCE

	<u>LARGE SCALE PLANT</u>	<u>PROTOTYPE PLANT</u>
Hydrogen Production		
SCFH	1,859,000	30,000
MW _t	172.9	2.9
Steam Production (MW _t)	85.3	1.4
Oxygen Production (SCFH)	930,000	15,000
Heat Input (MW _t)	285	4.6
Power Input (MW _e)	94.7	1.5
Process Water Input (lb/hr)	343,200	5,540
Thermal Efficiency		
Hydrogen Production	46*	46
Hydrogen/Steam Production	68	68

estimating efficiency and costs for thermal storage. This study indicated a 90% efficiency for a gas/rock system.

As indicated in Table 2-3 the annual average site insolation for Sweetwater, Texas is 2.1 MWh_t/m². The heliostat area required to deliver 4.59 MW to the Sulfur Cycle System for the prototype plant is 34,900 m², and the number of heliostats for the prototype plant is 794.

Per Table 2-3, the rated receiver power output is 11.9 MW for a field with 469 heliostats at noon summer solstice. For the prototype plant the rated power output of the receiver is 20.2 MW_t. At this condition 4.6 MW_t goes to the Sulfur Cycle System and 15.5 MW_t will be sent to storage. For a 61% solar thermal system efficiency, the power incident on the heliostats is 33.1 MW_t.

Prototype Solar Hydrogen Plant Performance

The plant performance shown in Table 2-5 is based on a solar system sized to produce enough heat to sulfur cycle to produce 30,000 SCFH of hydrogen. In

TABLE 2-2
STATE POINT SUMMARY FOR LARGE SCALE PLANT

STREAM NO.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
TEMP, °F	213	213	213	195	195	671	671	671	740	845	1600	1538	1348	423
PRESSURE, PSIA	294	294	294	14.7	328	323	322.5	322.5	321	319	294	292.5	290.5	28
Flowrate $\times 10^{-3}$, lb/hr														
Composition:														
H ₂														
O ₂											76.678	76.678	76.678	76.678
SO ₂	7113.095	248.011	6865.08	253.526							306.886	306.886	306.886	306.886
SO ₃											225.208	225.208	225.208	
H ₂ O	22934.04	799.647	22134.39	8.519	437.982	437.982	131.598	306.384	131.598	131.598	268.547	268.547	268.547	217.872
H ₂ SO ₄	38634.69	1347.057	37287.63		745.753	745.753	745.721		745.721	745.721				275.883

STREAM NO.	15	16	17	18	19	20	21	22	23	24	25	26	27	28
TEMP, °F	162	162	90	90	90	90	90	80	80	77	195	245	212	213
PRESSURE, PSIA	285	285	284.5	284.5	294	294	295	294	294	294	14.7	294	310	297
Flowrate $\times 10^{-3}$, lb/hr														
Composition:														
H ₂														
O ₂	76.678		76.678		76.678			76.678						
SO ₂	184.306	122.581	44.059	140.247	0.004	44.055			0.004			253.526	7419.98	
SO ₃														
H ₂ O		217.872				353.147	353.147		86.397	86.397	353.147	8.519	23106.7	4426.98
H ₂ SO ₄		275.883				601.304	601.304				601.304		38164.82	7457.53

STREAM NO.	15	29	30	31	32	33	34	35	36	37
TEMP, °F		213	1790	1205	978	1400	420	422	375	375
PRESSURE, PSIA		294	300	295	310	293	14.7	315	190	185
Flowrate $\times 10^{-3}$, lb/hr										
Composition:										
H ₂		9.6678								
O ₂						76.678	76.678			
SO ₂										
SO ₃										
H ₂ O							306.4	343.2	343.2	
H ₂ SO ₄										
He			1015.786	1015.786	1015.786					

TABLE 2-3
GYPSUM PLANT DESIGN SUMMARY

PRIME CONTRACTOR: Boeing Engineering and Construction Co. (BEC)

SITE PROCESS: Gypsum Wallboard Drying

PROCESS FLUID: Air

PROCESS TEMP: 232-288°C (450-550°F)

TURINBE TYPE: None

SITE LOCATION: Sweetwater, Texas

DESIGN POINT: Noon, Summer Solstice

RECEIVER:

RECEIVER FLUID: Air

CONFIGURATION: Cavity

TYPE: Forced Circulation

OUTPUT FLUID TEMP: 724°C (1335°F) at Design Point

OUTPUT FLUID PRESS: 0.30 MPa (44.1 psia)

HELIOSTATS:

NUMBER: 469

INDIVIDUAL MIRROR AREA: 44 m²

COST: \$180/m² (Target Cost - Baseline)

TYPE: BEC Second Generation (Pre-Production Model)

FIELD CONFIGURATION: North

STORAGE: None

TOTAL PROJECT COST: \$8.65 Million (Baseline Design)

TOTAL PROJECT COST (@ \$230/m² Heliostat): \$9.0 Million

SITE INSOLATION (Direct Normal):

ANNUAL AVERAGE: 2.10 MWh_t/m²

SOURCE: DELSOL, Solmet and NOAA Data

SITE MEASUREMENTS: NOAA, Abilene, Texas Station
1940 On (% of Available Sunshine)

TABLE 2-4
GYPSUM PLANT DESIGN POINT PERFORMANCE

TABLE 2-5
PERFORMANCE SUMMARY FOR PROTOTYPE SOLAR HYDROGEN PLANT

Solar System (Design Point):

Heat to Collectors	33,100 kWt
Receiver Power Out	20,200 kWt
Heat to Thermal Storage	15,500 kWt
Solar Thermal Efficiency	61%
Storage Efficiency	90%

Sulfur Cycle System (24 Hour Operation):

Thermal Input	4,590 kWt
Electrical Input	1,530 kWt
Water Input	5,540 lb/hr
Hydrogen Output	30,000 SCFH (2855 kWt)
Oxygen Output	15,000 SCFH
Steam Output	1,380 kWt
Sulfur Cycle Thermal Efficiency (Hydrogen & Steam)	*68%
Sulfur Cycle Thermal Efficiency (Hydrogen)	46%

*Efficiencies are based on thermal input from solar system and electrical input from grid. If the thermal efficiency for electrical generating plant is considered (assume 35% for coal fired steam turbine) then the sulfur cycle efficiencies are 50% and 33%.

addition to the hydrogen output, credit is given to steam production for cogeneration usage. Performance credits for oxygen production and hot water usage (other than preheating process water) are neglected.

2.1.3 ESTIMATES OF PLANT INVESTMENT REQUIREMENTS FOR PROTOTYPE AND FIRST COMMERCIAL PLANT

Sulfur Cycle System Cost Estimates

As a starting point, an equipment list was prepared for the Pressurized Test Unit described in Section 2.2. Each piece of equipment was sized and cost estimates were made (in 1981 dollars) assuming that the technology would be mature in 1990. Published reports on cost in journals such as Chemical Engineering were used to estimate costs on the conventional equipment such as low temperature heat exchangers, tanks, pumps, compressors, and blowers. Cost estimates were made for the vaporizers, decomposition reactor and electrolyzer based on material costs with factors applied to cover fabrication and assembly labor. Similarly, cost estimates were prepared for a large scale 285 MW sulfur cycle system that might be dedicated to a large chemical complex such as an ammonia plant. These equipment costs are summarized in Table 2-6.

Cost estimates for the prototype plant were made by scaling from the larger plant cost as a function of the hydrogen production rate raised to a power:

$$\frac{C_p}{C_l} = \left(\frac{P_p}{P_l} \right)^n$$
$$n = \frac{\ln(C_l/C_{ptu})}{\ln(P_l/P_{ptu})}$$

where: C = cost
P = hydrogen production rate
l = large commercial plant
p = prototype
ptu = pressurized test unit

TABLE 2-6
COST ESTIMATES FOR SULFUR CYCLE EQUIPMENT

	PTU	LARGE PLANT	PROTOTYPE PLANT
Hydrogen Production (SCFH)	800	1,860,000	30,000
Costs	(Thousands of 1981 Dollars)		
Electrolyzer	22.8	23,284	582
Decomposition Reactor	41.0	9,272	517
Vaporizer I	20.9	3,794	238
Vaporizer II	15.7	700	97
Vaporizer III		1,975	249
Oxygen Heater	8.5	279	44
Flash Drums	16.2	218	55
Surge Tanks	10.6	455	62
Mixing Drum	32.6	4,536	328
Catholyte Tank	11.0	909	87
D.R. Catalyst	0.5	380	11
Pumps	87.9	10,709	830
Compressor	51.7	2,500	317
Blowers	8.3	718	67
Valves	5.4	863	58
Heat Exchangers	34.7	1,529	204
Absorbers	14.1	1,087	108
Oxygen Expander		787	66
TOTAL	381.9	64,069	3,917

The cost of each major equipment item in the sulfur cycle system was scaled individually from the large plant size to the prototype plant size using this approach and with the exponent selected as a function of the type of equipment. The results also are shown in Table 2-6.

Estimates for a first commercial plant (identical in size to the prototype plant) were projected from the prototype plant based on the following assumptions:

- 15% reduction in heat exchangers, pumps, compressors, etc. due to volume purchasing
- 25% reduction in decomposition reactor costs due to reduced labor and volume purchasing
- 52% reduction in electrolyzer costs due to following:

	\$/ft ²
- prototype costs	145
- 80% catalyst recovery	3.6
- 50% reduction in carbon	5.85
- 15% reduction in gas separator	0.45
- 15% reduction in auxiliary cell components	0.75
- 50% reduction in labor	59
- Total Reduction	69.65
- New Cost	75.35
- % of Prototype	52%

Table 2-7 summarizes the equipment costs for the prototype and first commercial plant based on these assumptions.

Installed costs were estimated for the sulfur cycle system based on Happell and Jordan factors (Reference 2-5) as shown in Table 2-8. Based on these factors, the total installed costs of the sulfur cycle system is shown in Table 2-9 for both the prototype plant and first commercial plant.

SOLAR EQUIPMENT COST ESTIMATE

Cost estimates for the solar system was based on costs taken from Reference 2-1 for the gypsum plant application. Cost estimates for the solar subsystems that

TABLE 2-7
SULFUR CYCLE EQUIPMENT COSTS
(1000 \$'s - 1981)

	<u>PROTOTYPE PLANT</u>	<u>FIRST COMMERCIAL PLANT</u>
Electrolyzer	582	303
Decomposition Reactor	517	388
Vaporizer I	238	202
Vaporizer II	97	82
Vaporizer III	249	211
Recuperative Heat Exchanges	44	37
Flash Drums (2)	55	46
Surge Tank (3)	62	52
Mixing Drum	528	279
Catholyte Tank	87	74
O. R. Catalyst	11	9
Pumps (7)	830	706
Compressor (2)	317	270
Blowers (2)	67	57
Valve	58	49
Heat Exchanger (5)	204	173
Absorbers (2)	108	91
Oxygen Expander	<u>66</u>	<u>56</u>
Total Equipment Cost	3,920	3,085

TABLE 2-8

HAPPELL AND JORDAN FACTORS FOR CAPITAL COST ESTIMATION

Equipment Cost	A
Installation of Equipment	15% of A
Insulation Installed	25% of A
Piping Installed	100% of A
Electrical I&C Installed	15% of A
Structures	4.8% of A
Painting and Cleaning	9% of A

TABLE 2-9

 INSTALLED COST* OF SULFUR CYCLE SYSTEM
 (Thousands of 1981 Dollars)

	<u>PROTOTYPE</u>	<u>1st COMMERCIAL</u>
Equipment	3,920	3,085
Installation of Equipment	588	463
Insulation (Installed)	979	772
Piping (Installed)	3,920	3,085
Electrical (Installed)	588	463
Structures	188	148
Painting and Cleaning	<u>353</u>	<u>278</u>
Total Installed Cost	10,536	8,294

---

 *Reference Happell and Jordan

would be in the solar hydrogen plant are summarized in Table 2-10. Prototype plant costs were obtained by scaling the gypsum plant as a function of received power output.

Collector subsystem costs were scaled linearly with power and the other subsystems were scaled to the 0.7 power. To obtain the estimate for the first commercial plant the following were assumed:

- Base collector costs on the \$100/m² cost goal versus \$230/m for the prototype
- Reduce receiver costs by 25% (15% volume purchases, 20% on labor assuming 50/50 split of labor and material)
- Reduce master control system costs by 70% (software is 2 to 3 times hardware cost)
- Reduce gas supply storage by 15%

The thermal storage cost estimate was based on the following equation taken from Reference 2-6,

$$C = (31.6 \text{ \$/KW})(P) + (0.66 \text{ \$/kWh})(P)(H)$$

where P equals the power supplied from thermal storage and H equals the number of hours of storage.

Assuming 72 hours of storage for a solar system per Reference 2-4 results in a cost of \$469,000 for the prototype. A 15% reduction in cost for volume purchases was assumed to obtain the first commercial plant cost estimate. These costs were combined with the gas supply estimate in Table 2-10.

FIXED CAPITAL INVESTMENT

The total installed plant cost and the total capital investment is shown in Table 2-11 for the prototype plant and the first commercial plant. The total installed cost is taken from Table 2-9 and 2-10 and includes the site facilities, solar equipment, control systems, thermal storage and the sulfur cycle

TABLE 2-10
SOLAR THERMAL SUBSYSTEM COST ESTIMATES
(Thousands of 1981 Dollars)

	GYPSUM * PLANT	PROTOTYPE PLANT	1st COMMERCIAL PLANT
Receiver Power Output (MW _t)	11.9	20.2	20.2
Costs			
Site Facilities	411	595	595
Collector Subsystem	5,074	8,599	3,739
Receiver Subsystem	990	1,432	1,074
Master Control Subsystem	275	398	119
Gas Supply and Storage System	1,821	1,634	2,239
Waste Heat Boiler	-	100	85
Total Direct Installed Cost	8,571	13,658	7,766

* Ref. 2.1

TABLE 2-11
SOLAR HYDROGEN PLANT COST FOR SUMMARY
(1000 \$'s - 1981 - 30,000 SCFH H₂ Production)

	PROTOTYPE	FIRST COMMERCIAL PLANT
Site Facilities	595	595
Collector System	8,599	3,739
Receiver and Tower System	1,432	1,074
Master Control System	398	119
Thermal Transport and Storage System	3,103	2,638
Sulfur Cycle System	10,530	8,296
Waste Heat Boiler System	100	85
Total Installed Cost	24,757	16,546
Contingency ¹	4,456	1,655
Total Direct Costs	29,213	18,201
Indirect Costs (6.5%)	1,899	1,183
Interest During Construction (16%)	4,674	2,912
Fixed Capital Investment	35,786	22,296

¹) 18% for prototype, 10% for 1st commercial.

system. The total installed costs are estimated to be \$24.8 million and \$16.6 million for the prototype and first commercial plants, respectively.

Estimates of fixed capital investment include allowances of contingency (18% for prototype, 10% for commercial) indirects (6.5%), and interest during construction (16%). A fixed capital investment of \$35.8 million for the prototype and \$22.3 million for the first commercial plant were estimated.

2.1.4 EVALUATION OF HYDROGEN DEMAND CHARACTERISTICS

The purpose of this section is twofold. First, to review recent projections of future hydrogen demand in the domestic United States market. Second, to estimate the timing and size of the market for the sulfur cycle system based on the total U. S. market projections. The estimates derived in this evaluation will be used to estimate the cost of hydrogen (COH) from the sulfur cycle and conventional systems.

Hydrogen Demand Forecasts

The approach used herein was to review published forecasts of future hydrogen demand and to select one such forecast as the basis for evaluating the sulfur cycle.

Table 2-12 summarizes hydrogen requirements for the U. S. market as estimated in references 2-2, 2-6, 2-7, 2-8, and 2-9. The quad to SCF conversion in some of these references was based on the lower heating value of hydrogen and this practice was followed in Table 2-12. These data are plotted in Figure 2-3. It was decided to use the JPL-HEST Report "Reference" forecast (as it is called in Reference 2-2 as the basis for subsequent market projections since it is moderately optimistic but does not over-optimistically assume conversion of all commercial aviation to hydrogen fueled transports.

Forecast of New Hydrogen Plant Additions

The sulfur cycle is assumed to be available in its commercial form as a solar driven hydrogen production plant, by 1995. Given this assumption, the total

TABLE 2-12

FORECAST OF U.S. HYDROGEN REQUIREMENTS
(In Quads/Yr or 10^{12} SCF/Yr)*

APPLICATION	1975	1985	2000	2020
Chemicals				
Ammonia	0.35	0.55	0.90	
Methanol	0.06	0.11	0.23	
Petroleum Refining	0.15	0.28	0.56	
Miscellaneous	0.02	0.04	0.08	
Subtotal (Industrial H ₂)	0.58 (2.11)*	0.98 (3.57)*	1.77 (6.44)*	
Upper Bound (Industrial H ₂) ⁽³⁾			3.00 (10.92)*	
Subtotal Including Transportation ⁽⁴⁾			14.00 (50.96)*	50.0 (182.00)*
"Reference" H ₂ Projection from (5)	1.0 (3.64)*	1.9 (6.92)*	5.5 (20.02)*	
"Expanded" H ₂ Projection from (5)	1.0 (3.64)*	3.8 (13.83)*	22.0 (80.08)*	

*Indicates conversion to SCR/yr based on 1 quad = 10^{15} Btu = 3.64×10^{12} SCF (LHV of H₂) as used in the indicated references.

TABLE 2-13

NEW HYDROGEN PLANT CAPACITY ADDITIONS, TOTAL - U. S. MARKET

YEAR	BEST "REFERENCE" FORECAST		CUMULATIVE NUMBER OF NEW HYDROGEN UNITS (BY RATING)* AT END OF INDICATED YEAR			
	TOTAL H ₂ REQUIRED, SCF/YR X 10^{12}	CUMULATIVE* NEW H ₂ CAPACITY REQUIRED, SCF/YR X 10^{12}	656.3 Mwt	300.0 Mwt	100.0 Mwt	4.725 Mwt
			(3.30×10^{10} SCF/YR) (4.167×10^6 SCF/HR)	(1.51×10^{10} SCF/YR) (1.904×10^6 SCF/HR)	(0.503×10^{10} SCF/YR) (0.636×10^6 SCF/HR)	(0.024×10^{10} SCF/YR) (0.030×10^6 SCF/HR)
1985	6.9	-	-	-	-	-
1990	11.2	-	-	-	-	-
1995	15.8	0-0-0-0-0 Δ = 0.0	0	0	0	0
2000	20.0	→ Δ = 4.2	127**	278	835	17,647
2005	24.7	→ Δ = 8.9	270	589	1,769	37,395
2010	29.0	→ Δ = 13.2	400	874	2,624	55,462
2015	33.5	→ Δ = 17.7	536	1,172	3,519	74,370
2020	38.0	→ Δ = 22.2	673	1,470	4,414	93,277

* Starting in 1995

+ Based on arbitrarily selected range stated in various units, Mwt shown is equivalent to the thermal input to a sulfur cycle which will produce the indicated SCF of H₂.

** Indicates cumulative number of new units of 656.3 Mwt rating installed in the U. S. from 1995 to 2000. The market shares of the solar driven sulfur cycle process is estimated at 6.25 percent of the cumulative number of plants, or in this case, $0.0625 \times 127 = 8$ plants.

Figure 2-3. Forecasts of U. S. Hydrogen Requirements (Various Sources)

Figure 2-4. Cumulative Number of New Hydrogen Unit Installations by Capacity and Year - Total U. S. Market (HEST "Reference" Forecast)

potential market for all types of new hydrogen production plants can be represented by the cumulative new capacity required by the HEST "Reference" forecast beginning in 1995 as shown in Table 2-13. The resulting number of new units by size that are needed to meet the cumulative new capacity requirement are shown in Table 2-13, and in Figure 2-4 for a wide range of sizes.

Market Share Assumptions

Two assumptions are necessary to apply "the experience curve effect" to the sulfur cycle solar hydrogen plant. First, a market share assumption is needed to relate the cumulative number of sulfur cycle units that could be installed to the total number of new installations of all types shown in Table 2-13 and Figure 2-4. Second, an experience curve percentage that is realistic for new technologies similar to the sulfur cycle system must be estimated. This assumption is discussed in Section 2.1.6.

The market share assumption was developed using the following reasoning for the hydrogen plant market beginning in 1995:

- All types of hydrogen production plants including conventional steam reforming, and new electrolytic, coal gasification, and thermochemical units will be competing for the new capacity addition market.
- It is assumed that conventional steam reforming units will capture 75 percent of the market. The primary feedstock for these conventional units will consist of natural gas (methane) but other fuels such as naphtha, ethanol, methanol, etc., can also be used.
- The newer technologies including advanced electrolytic, coal gasification, and thermo chemical units will capture the remaining 25 percent of the market.
- Of the thermochemical units, the solar driven sulfur cycle will capture 25 percent of the new technology share of the market. This is $0.25 \times 0.25 = 0.0625$ or 6.25 percent of the total market for all new installations beginning in 1995.

The above market share assumptions should be conservative relative to the solar driven sulfur cycle given the following considerations. First, natural gas

supply, demand and price will be factors working against new or continued use of conventional steam reforming plants. Regulatory factors such as the Natural Gas Policy Act (NGPA) incremental pricing provision will also tend to reduce acceptance of the steam reforming process. The incremental pricing provision of NGPA seeks to limit natural gas price increases for residential and other small users by initially forcing the industrial user to absorb most of the higher cost of new gas. Even if feedstock materials other than natural gas are used (naphtha, methanol, etc., for steam reforming and coal for gasification units) these fuels will experience real cost escalation that will increase the cost of hydrogen that is produced. Escalating electricity prices will have a similar impact on the cost of hydrogen produced by electrolysis methods. However, the solar driven sulfur cycle which does not require fossil fuel as a feedstock and requires much less electricity per unit of hydrogen than the electrolysis process, will be much less affected by energy cost escalation. In addition, an extensive amount of solar-thermal equipment manufacturing and test experience will be available for application to the sulfur cycle process by the 1990's.

Based on the above reasoning, the market share achieved by solar driven sulfur cycle process is estimated at 6.25 percent of the total market for new unit additions beginning in 1995. This percentage should be applied to the cumulative number of new units in Table 2-13 or Figure 2-4 to compute the number new units of 200 MWt size by 2005 is 1,769. The sulfur cycle market share is then $0.0625 \times 1,769$ or about 110 units. If we refer to Figure 2-5, we can see that if the cumulative number of units is 110 by 2005 and we assume an experience curve of 85 percent, the cost of the 110th unit will be about 0.32 times the cost of the first unit in the production run. In this manner, the market share estimate and the timing limit the experience curve benefits that can be achieved. These constraints are applied to the cost of hydrogen calculations for the solar driven sulfur cycle that are described in Section 2.1.6.

Natural Gas Availability Considerations

Natural gas steam reforming is currently the most widely used and lowest cost method of producing hydrogen. While industrial uses of hydrogen are expected

Figure 2-5. Effect of Experience on Unit Cost

to grow rapidly, it is generally acknowledged that there are severe limitations on the increased use of natural gas. These supply demand considerations were examined briefly to provide additional insight into the potential for solar sulfur cycle penetration of the hydrogen plant market. Table 2-14 presents one set of natural gas supply and demand projections. If the reference (2-6) and (2-7) projections of 1.77 quads of hydrogen by the year 2000 is produced by the natural gas steam reforming, this process would require 3.22 quads of natural gas feedstock. Since the total industrial usage for natural gas is projected at 4.6 quads for 2000, the natural gas feedstock of 3.22 quads would represent 70 percent of all industrial natural gas use. Any increase in natural gas steam reforming in an attempt to satisfy the reference (2-8) forecast (3.0 quads of hydrogen by 2000) or the Best "Reference" forecast (5.5 quads of hydrogen by 2000) would substantially exceed the projected natural gas supply as shown in Figure 2-6. As a result, these projections indicate strong economic availability and regulatory pressures are likely to prevent the expansion and the continuation of natural gas steam reforming as we approach the year 2000.

Also, the reference (2-10) projection does not anticipate replacement of natural gas by coal gas (which reaches 0.9 quads by 2000) to a significant extent. Therefore, there should be significant market potential for solar driven sulfur cycles (and electrolysis units to a lesser degree) during the 1990's. This brief evaluation therefore supports the contention that a 6.25 percent market share for solar sulfur cycles is conservative.

2.1.5 EVALUATION OF COST OF HYDROGEN FOR CONVENTIONAL AND ALTERNATIVE DEVELOPMENT SYSTEMS

The economic viability of the commercial size, solar driven sulfur cycle plants will be determined by their cost of hydrogen (COH) relative to conventional and other developmental systems. Therefore, it is necessary to establish the COH of conventional and alternative developmental systems as a basis for evaluating the sulfur cycle. The COH data must also be defined as a function of time in order to: incorporate the effects of future escalation in feedstock and energy costs; to relate the evaluation to hydrogen demand projections, and to relate

TABLE 2-14

NATURAL GAS SUPPLY & DEMAND PROJECTIONS (Ref. 2-10)

Natural Gas Demand (Quadrillion Btu)

Sector	Long Term					% Annual Change	
	1980	1985	1990	1995	2000	1980	1990
						1990	2000
Residential & Commercial	7.6	8.7	9.3	10.1	10.9	1.6	1.6
Industrial*	8.7	7.5	6.4	6.0	4.6	-3.0	-3.2
Electric Utilities	3.8	3.0	2.6	2.1	1.9	-3.2	-3.1
Transportation	0.5	0.5	0.5	0.5	0.5	0.0	0.0
Total	20.6	19.7	18.8	18.7	17.9	-0.9	-0.5

Industrial use of
synthetic gas

from coal   0.0   0.1   0.3   0.6   0.9

*Excludes synthetic liquids used by industry.

Natural Gas Supply (Trillion Cubic Feet)

Source	Long Term					% Annual Change	
	1980	1985	1990	1995	2000	1980	1990
						1990	2000
Lower 48 Production	19.1	17.6	16.1	15.3	14.1	-1.7	-1.3
Alaska	0.0	0.0	0.4	1.0	1.2	--	11.6
SNG	0.2	0.3	0.5	0.8	1.1	9.6	8.2
Imports	0.9	1.5	1.7	1.8	2.0	6.6	1.6
Total Supply	20.2	19.4	18.7	18.9	18.4	-0.8	-0.2

Figure 2-6. Natural Gas Demand - Supply Forecasts Assuming Hydrogen Requirements are Satisfied by Steam Reforming of Natural Gas

TABLE 2-15

COMPARISON OF HYDROGEN PRODUCTION ALTERNATIVES

	Steam Reforming	Coal Gasification	Electrolysis	Thermochemical Decomposition
Appropriate Overall Thermal Efficiency	70%	60-65%	32% (SPE) 21-25% (KOH)	Upper Limit: 55%
State-of-the-Art	Well known technology	Mature technology available	Proven, reliable technology	Research stages, not a proven technology
Environmental Effects	Depletion of natural gas and other light hydrocarbons	Impacts of coal mining; air pollution likely to be less than via electricity from coal	Pollution problems with electricity generation	High efficiency means less resource use. Possible release of harmful chemicals.
Advantages	Currently the cheapest method in the U. S.	Cheapest and most secure near-term alternative to methane reforming; abundant coal reserves in U. S.	Small plant size, can use non-fossil sources	Can use non-fossil sources
Disadvantages	Scant long term potential due to limitations on methane supply	Ultimate limitation is exhaustion of coal resources, requires large plant size	High cost, low net energy efficiency	Materials problems in reactant containment; large complex plant expected
Estimated hydrogen production costs*, \$/10 ⁶ Btu product (1980 \$)	\$6.80	\$9.50	\$19.65	

* Figures are based on an 880-million-std-ft³/d plant on the Gulf Coast; 100% equity financing; and a 10% discounted cash flow return. Electricity is priced at 3¢/kWh, coal at \$0.96/10⁶ Btu, and natural gas at \$3.15/10⁶ Btu.

Source: National Research Council

the evaluation to the new hydrogen plant market projections described in Section 2.1.4.

Published COH Estimates

Representative technical and economic assessments of conventional and developmental systems for producing hydrogen have been published in References (2-2), (2-3), and (2-10). Table 2-15, from reference (2-10) as shown herein, presents an overview of the hydrogen production alternatives.

Reference (2-3) compared the hydrogen production alternatives as a function of raw material or feedstock cost but did not include thermochemical decomposition processes. Figure 2-7, from reference (2-3), illustrates these COH estimates. The published data indicates that conventional steam reforming of natural gas is at present the lowest cost method of producing hydrogen. Steam reforming will continue to be the lowest cost method of producing hydrogen until: natural gas costs cause it to exceed the COH of other production methods; and/or until progress results in lower hydrogen production costs from alternative new technologies. Therefore it was decided to focus on the steam reforming of natural gas as the basis for evaluating the economic viability of the solar sulfur cycle.

Several steps were required to estimate the present and future COH of steam reforming plants. They were:

- Formulation of economic assumptions for computing the COH given plant capital costs and projected escalation of energy, feedstock, and labor costs.
- Estimating the value of the steam by-product credit with the effect of energy costs escalation included.
- Estimating the steam reforming plant COH over a range of plant sizes.

Several steps were required to estimate the present and future COH of steam reforming plants. They were:

Figure 2-7. Effect of Raw Materials Cost on Product Price for 100×10^6 SCFD by Various Processes

- Formulation of economic assumptions for computing the COH given plant capital costs and projected escalation of energy, feedstock, and labor costs.
- Estimating the value of the steam by-product credit with the effect of energy costs escalation included.
- Estimating the steam reforming plant COH over a range of plant sizes.
- Projecting the steam reforming COH over the period from 1980-2020.

Economic Assumptions

References (2-3) and (2-13) both present a similar methodology for computing COH given capital investment, labor, maintenance, feedstock, utility and other costs and credits. The reference (2-3) format was used with the following differences:

- Facility investment, water, and labor costs were adjusted to end-of-year 1980 values using the GNP deflator.
- Feedstock (natural gas), labor, and electricity costs were escalation as a function of time using the reference (2-10) forecasts.
- The steam by-product credit was computed as a function of time using the reference (2-10) forecasts for energy and labor costs and the capital and maintenance cost data of reference (2-14), updated to end-of-year 1980 dollars.

The resulting economic evaluation guidelines are listed in Table 2-16.

Real, as opposed to apparent* escalation rates, from reference (2-10) were used for the projected future cost estimates for natural gas and electricity. The escalation rates for the 2000-2020 period were assumed to be the same as those for the 1990-2000 period. Real escalation rates are due to supply and demand considerations and are independent of inflation. Therefore, the projected

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*Apparent escalation includes both inflation and real escalation. Projected costs due to apparent escalation are usually stated in current dollars.

TABLE 2-16

ECONOMIC EVALUATION GUIDELINES FOR STEAM REFORMING HYDROGEN PRODUCTION PLANTS

PROJECT LIFE: 20 Years

OPERATING FACTOR: 330 Days/Year

PLANT SIZE: 100×10^6 SCF/DayANNUAL HYDROGEN PRODUCTION: $33,000 \times 10^6$ SCFCapital Investment (End of Year 1980 Basis)

Facilities Investment	= 56.2×10^6 \$ as obtained from Reference (2-2) and adjusted to End of Year 1980 Basis
Interest During Construction	= 15% of Facilities Investment
Startup Expense	= 2% of Facilities Investment
Working Capital	= 60 Days Feedstock Utilities and Cash Supply
Total Capital Investment	= Sum of the Above

Annual Operating Cost

Feedstock	
Natural Gas	3.4 \$/10 ⁶ Btu + Escalation of Figure 2-10
Utilities	
Raw Water	0.57 \$/10 ³ Gallon
Power	0.034 \$/kWh + Escalation of Figure 2-9
Cooling Water	0.06 \$/10 ³ Gallon
Fuel	Same Price as for Feedstock

Cash Supply

Operating Labor	\$20,600/Man-Year + Escalation of Figure 2-8
Operating Labor Supervision	15% of Operating Labor
Maintenance	
Labor	2% of Facilities Investment
Supervision	15% of Maintenance Labor
Materials	2% of Facilities Investment
Administrative and Support Labor	20% of All Other Labor
Payroll Extras/Fringe Benefits, Etc.	20% of All Other Labor

Insurance 2% of Facilities InvestmentGeneral Administrative Expenses 2% of Facilities Investment

Taxes (Local, State and Federal). (No Investment Tax Credit). 50% of Net Profit

Gross Revenue Required Sum of the AboveBy-Product Credits

Steam	5.4 \$/1000 Pound + Escalation of Figure 2-11
Net Revenue Required	= Gross Revenue Required - By-Product Credits
Hydrogen Price, \$/10 ³ CF	= $\frac{\text{Net Annual Revenue Required}}{\text{Annual Hydrogen Production}}$

costs given herein are stated in constant dollars relative to the base 1980 year.

The use of a constant dollar approach to the economic analysis minimizes the number of assumptions and the complexity of the calculations and it is adequate for a comparative analysis of competing methods of producing hydrogen.

Since the real escalation of future electricity and natural costs is expected to be greater than zero, the COH from the steam reforming plant will increase with time even if the COH estimate is stated in constant 1980 dollars. Real escalation for the facility investment capital cost and water costs were neglected. This is equivalent to assuming that the real escalation rate for these costs will not exceed the rate of general inflation. The projected future costs of labor, electricity, and natural gas based on the real escalation rates are shown in Figures 2-8, 2-9, and 2-10 in constant 1980 dollars.

BY-PRODUCT STEAM CREDIT

The cost of steam (or steam credit) based on the updated reference 2-14 data and the escalated costs of Figures 2-8, 2-9, and 2-10 is shown in Figure 2-11 for two different boiler sizes. Natural gas fired boilers with an efficiency of 85 percent were assumed. The 42 Megawatt thermal boiler provides steam at the rate equivalent to the by product steam rate of the 100×10^6 SCF/Day steam reforming plant. The cost of steam for a smaller plant and the projected cost of the natural gas fuel are also shown in Figure 2-11 for comparison. The cost of steam versus boiler output rating and year of operation is shown in Figure 2-12.

PLANT SIZE SCALING RELATIONSHIP

The facility investment (FI) cost of large systems generally conform to the following type of relationship when scaled as a function of size:

$$\frac{FI_{Large}}{FI_{Small}} = \left(\frac{P_{Large}}{P_{Small}} \right)^x$$

Figure 2-8. Labor and Operation and Maintenance Cost Projection Ratio

Figure 2-9. Electricity Price Projection (Industrial User)

Figure 2-10. Natural Gas Price Projection (Industrial User)

Figure 2-11. Projected Steam Credit for By-Product Steam from Steam Reforming Hydrogen Production Plants

Figure 2-12. Cost of Steam Versus Boiler Output Rating and Year of Operation - Natural Gas Fired Boilers

Figure 2-13. Estimated Capital Costs of Conventional Steam Reforming Hydrogen Production Plants

where P_{Large} is the rating of the large plant and P_{Small} is the rating of the smaller plant. The plant rating is expressed in standard cubic feet of hydrogen per hour.

A previous (W) study, which included the analysis of steam reforming system vendor quotations, indicated that the scaling exponent for these systems is $X = 0.54$. Then, using the following data from reference (2-2):

$$\begin{aligned} FI_{Large} &= 56.2 \times 10^6 \text{ (1980 \$'s)} \\ P_{Large} &= 4167 \times 10^3 \text{ SCF/HR (100} \times 10^6 \text{ SCF/Day)} \end{aligned}$$

the facility investment for smaller steam reforming plants was calculated and is shown in Figure 2-13. It should be noted that the reference 2-2 size of 100×10^6 SCF/Day is quite large in comparison with steam reforming plants now operating or under construction. For example, one vendor's listing of 25 plants shows a plant size range from 0.06 to 6×10^6 SCF/Day with an average size of 0.72×10^6 SCF/Day or 30,000 SCF/Hour.

COST OF HYDROGEN PROJECTIONS FOR STEAM REFORMING

The economic assumptions, projected costs, value of the steam credit, and the above scaling relationship were used to compute the COH of steam reforming systems as a function of time and plant size.

With the plant size fixed at 100×10^6 SCF/Day, the resulting COH for the steam reforming process is shown in Figure 2-14. The value of the steam by-product credit and the cost of natural gas are also shown as a function of time (or year of operation). The COH was computed both with and without the steam by-product credit to establish upper and lower limits. For 1980 operation the resulting COH range for this 100×10^6 SCF/Day plant is 6.5-7 $\$/10^6$ Btu of hydrogen. By comparison, the National Research Council estimate from Table 2-15 shows a COH of 6.8 $\$/10^6$ Btu for a larger 880×10^6 SCF/Day plant with slightly different economic assumptions.

Figure 2-14. Projected Cost of Hydrogen from the Steam Reforming Process, Constant 1980 Dollars

Figure 2-15. Projected Cost of Hydrogen from the Steam Reforming Process, Constant 1980 Dollars

For this 100×10^6 SCF/Day plant, it was found that the real escalation rates applied to electricity and labor costs had very little effect on the projected COH. Electricity costs, for example, represented a two percent of the COH. But the projected real escalation of natural gas had a very strong impact on COH since 62 percent of the COH is due to the natural gas cost.

Reference 2-11 predicts steam reforming COH costs based on assumed per year escalation rates of 6.5 percent for natural gas and 5 percent for electricity. These escalation rates are significantly higher than the real escalation rates (implicit in Figures 2-8 and 2-9) that are used herein. It is therefore assumed that the rates used in reference 2-11 are apparent escalation rates and that the resulting COH estimates are stated in current dollars. The reference 2-11 COH projections in current dollars for different plant sizes are compared with the constant dollar COH projection in Figure 2-15. When the current and constant dollar COH estimates for the 100×10^6 SCF/Day plant are compared for 1980 operation they are in agreement as would be expected. But for 2000 operation, the current dollar COH is 31 $\$/10^6$ Btu in 2000 dollars versus 20.5 $\$/10^6$ Btu in constant 1980 dollars. This difference is due to the addition of general inflation to the real escalation rates used in the constant dollar COH projections.

Constant 1980 dollar projections are necessary for consistent comparisons with the estimated costs and COH of the sulfur cycle system. Therefore the constant dollar COH projections for the steam reforming process were expanded to include a range of plant sizes. The resulting COH projections are shown in Figure 2-16 with the by-product steam credit included. Figure 2-17 presents the COH projections without the steam credit.

CONCLUSIONS REGARDING STEAM REFORMING

Cost of hydrogen (COH) projections are needed for the comparative economic analysis of a solar driven Westinghouse sulfur cycle hydrogen generation process in a commercial plant configuration. The CSHP (Commercial Solar Hydrogen Plant) is based on the (W) sulfur cycle process which is still in the

Figure 2-16. Cost of Hydrogen Versus Year of Operation Steam Reforming with By-Product Steam Credit

Figure 2-17. Cost of Hydrogen Versus Year of Operation Steam Reforming without By-Product Steam Credit

development stage. The economic viability of the CSHP will depend on its COH relative to the COH from conventional or other developmental processes.

Of the conventional hydrogen producing processes, steam reforming of natural gas yields the lowest present COH, and this process is widely used in many industries. Therefore, the COH from conventional steam reforming of natural gas is suggested as the basis for assessing the economic viability of the CSHP.

There is general agreement that the cost of natural gas will escalate in the future at a rate that exceeds the general rate of inflation in the U. S. economy. These natural gas cost escalation predictions are based on expected decontrol and supply and demand considerations. This type of escalation is called "real" escalation because it is independent of inflation. Projected costs due to real escalation are usually stated in constant dollars relative to some base year. "Apparent" escalation includes both inflation and real escalation. Projected costs due to apparent escalation are usually stated in current dollars.

Because of the expected natural gas cost escalation which will be in excess of general inflation, an estimate of the COH from the steam reforming process will increase with time even if the estimate is stated in constant dollars relative to a base year.

There are several recommendations resulting from this analysis which are:

- (1) The projection of the COH from steam reforming of natural gas described herein appears reasonable and conservative in comparison of other published estimates. It is also based on a detailed breakdown of the capital, labor, O&M, raw materials and utility costs for such plants. Therefore, the COH projections of Figures 2-16 and 2-17 should be used to evaluate the economic viability of the CSHP.
- (2) The evaluation of the CSHP should assume the same economic guidelines as the steam reforming plant illustrated herein. The same format for

the capital and operating cost breakdown should also be used for the CSHP.

- (3) The electricity, labor, and O&M cost projections described herein should also be used in estimating the future COH cost from the CSHP.
- (4) The cost of steam (COS) credit values defined herein should be used in the CSHP evaluation of steam output capacity to evaluate the CSHP over a range of sizes.

2.1.6 EVALUATION OF COST OF HYDROGEN FOR COMMERCIAL SIZE SOLAR HYDROGEN PLANTS

The objective of this evaluation is to estimate the cost of the hydrogen that could be produced by a commercial size solar hydrogen plant based on the sulfur cycle. An integrated evaluation involving the following tasks is required to meet the objective:

- A range of plant sizes must be defined for the CSHP and related to the timing and size of the potential market for new hydrogen plants that is defined in Section 2.1.4.
- The economic guidelines and assumptions for estimating the COH of the CSHP must be defined.
- An estimate of the potential experience curve effects in reducing plant investment requirements from the first commercial unit to mature units must be developed. The constraints due to the size and timing of the potential market must be reflected in these estimates.
- The COH of the CSHP must then be estimated over a range of plant sizes and as a function of year of operation and the state of commercial maturity for the CSHP.

CSHP Plant Sizes

The prototype plant size defined for the CSHP in Section 2.1.3 has a rating of 30,000 SCF of hydrogen per hour. In addition to the 30,000 SCFH CSHP rating, two larger sizes also were considered. They were a 600×10^3 SCFH unit and a 1000×10^3 SCFH unit. The input and output parameters for all three plant sizes are given in Table 2-17. Yearly inputs and outputs based on an operating

factor of 330 days per year are also shown in Table 2-17. The hydrogen thermal output values are based on the higher heating value of hydrogen.

The potential market for new hydrogen plant additions was identified in Table 2-13. Since one of our basic assumptions is that CSHP units will first become available for installations in 1995, we are interested only in new installations beginning in that year. Also in Section 2.1.4 we developed a market share estimate of 6.25 percent of the total market for CSHP units. Therefore we can convert the data of Table 2-13 into the market share for the CSHP as shown in Table 2-18.

Economic Guidelines and Assumptions

The economic guidelines and assumptions are those needed to compute the CSHP COH from the estimated plant investment. The plant investment requirements for the prototype plant size with a 30,000 SCFH rating are given in Table 2-11 for the prototype plant and the first commercial unit. Table 2-19 presents the Table 2-11 cost data in terms of end-of-year 1980 dollars, based on the estimated GNP deflator for 1980.

The economic evaluation guidelines for the CSHP are summarized in Table 2-20. Except for some simplification or changes necessary because of technical differences between the CSHP and the steam reforming plant, these guidelines are equivalent to those of Table 2-16. A fixed charge rate of 26.5 percent is used to compute the annual revenue required for taxes, depreciation, and return on the capital investment at the same rates as in the steam reforming plant.

Escalation in the labor rate (\$20,600/man-year) was neglected. As in the steam reforming case the impact on COH is not significant. Escalation in the process water cost was also neglected for the same reason.

Escalation in the oxygen dry-product credit was neglected and this assumption results in a conservative CSHP COH prediction. For example, an extensive coal gasification industry would increase the demand for oxygen and its value as a by-product credit.

TABLE 2-17
SOLAR/H₂ SYSTEM INPUTS AND OUTPUTS OVER CSHP SIZE RANGE

	30 x 10 ³ SCFH		600 x 10 ³ SCFH		1000 x 10 ³ SCFH	
	Ø Rating	Ø 330 Days/Year	Ø Rating	Ø 330 Days/Year	Ø Rating	Ø 330 Days/Year
Thermal Input (MW _t)	4.59	-	91.8	-	153	-
H ₂ Output	30 x 10 ³ SCFH	237,600 x 10 ³ SCF/Yr	600 x 10 ³ SCFH	4,752 x 10 ⁶ SCF/Yr	1000 x 10 ³ SCFH	7,923 x 10 ⁶ SCF/Yr
H ₂ Output	2,855 MW _t	77,220 x 10 ⁶ Btu/Yr	57.1 MW _t	1,544,400 x 10 ⁶ Btu/Yr	95.19 MW _t	2,574,315 x 10 ⁶ Btu/Yr
Steam Output	1,380 MW _t	37,325 x 10 ⁶ Btu/Yr	27.6 MW _t	746,500 x 10 ⁶ Btu/Yr	46.0 MW _t	1,244,416 x 10 ⁶ Btu/Yr
Electricity Input	1.53 MW _e	12.12 x 10 ⁶ kWh/Yr	30.6 MW _e	242.4 x 10 ⁶ kWh/Yr	51.0 MW _e	404.1 x 10 ⁶ kWh/Yr

TABLE 2-18
CSHP MARKET POTENTIAL - CUMULATIVE NUMBER OF INSTALLATIONS
CUMULATIVE NUMBER OF INSTALLED CSHP UNITS BY RATING AND YEAR*

By End of Year	30 x 10 ³ SCFH Rating (4.59 MW _t CSHP)	600 x 10 ³ 91.8 MW _t CSHP)	1000 x 10 ³ SCFH Rating (153 MW _t CSHP)
1995	1	1	1
2000	1103	55	33
2005	2337	117	70
2010	3466	174	104
2015	4648	233	140
2020	5830	292	175

*Based on a 6.25 percent share of the total market for new installations beginning in 1995. First commercial unit is purchased, but not yet installed, at end of 1995.

TABLE 2-19
CSHP PLANT CAPITAL COST ESTIMATES FOR 30,000 SCFH PLANT RATING - 1000\$'S

	PROTOTYPE		1st COMMERCIAL PLANT	
	1981 \$'s	1980 \$'s	1981 \$'s	1980 \$'s
TOTAL INSTALLED COST -	24,757	22,589	16,546	15,097
FIXED CAPITAL INVESTMENT -	35,786	32,652	22,296	20,343

The fixed capital investment represents the total installed cost plus contingency, interest during construction, and other indirect costs as defined in Table 2-11.

TABLE 2-20

ECONOMIC EVALUATION GUIDELINES FOR CSHP HYDROGEN PRODUCTION PLANTS

PLANT RATING	MW _t	DEFINITION THERMAL INPUT TO SULFUR CYCLE AS ESTIMATED
OPERATING FACTOR	Days/Year	330 days per year
ANNUAL H ₂ PRODUCTION	10 ⁶ SCF	as estimated
DIRECT CAPITAL COST	\$ x 10 ³	Total installed equipment cost, TIC
CONTINGENCY, IDC & OIDC ²	%	34.75% of TIF for commercial units, 44.5% for prototype
FIXED CAPITAL INVESTMENT	\$ x 10 ³	TIC plus contingency, IDC and OIDC
START UP COSTS	\$ x 10 ³	2% of TIC
WORKING CAPITAL ³	\$ x 10 ³	60 days cash supply
TOTAL CAPITAL INVESTMENT	\$ x 10 ³	Sum of the above
FIXED CHARGE RATE	%	26.5% includes taxes, depreciation and return on investment
ANNUAL REVENUE REQ'D FOR CAPITAL INVESTMENT	\$ x 10 ³ /year	26.5% of total capital investment
<u>FEEDSTOCK AND UTILITIES</u>	-	
ELECTRICITY	\$ x 10 ³ /year	Projected real escalation rate from Figure 3, Section 2.1.5
PROCESS WATER ¹	\$ x 10 ³ /year	0.572 \$/10 ³ gal. or 0.0685 \$/10 ³ lbs
<u>OPERATION AND MAINTENANCE</u>	-	
LABOR AND SUPERVISION	\$ x 10 ³ /year	4.2% of TIC, includes all admin. labor, fringe benefits, etc.
MATERIALS	\$ x 10 ³ /year	2.0% of TIC
INSURANCE	\$ x 10 ³ /year	2.0% of TIC
GEN. ADMIN. EXPENSES	\$ x 10 ³ /year	2% of TIC
GROSS REVENUE REQ'D	\$ x 10 ³ /year	Sum of the above annual costs
<u>BY-PRODUCT CREDITS</u>		
STEAM	\$ x 10 ³ /year	Projected real escalation rate from Figure 6, Section 2.1.5
OXYGEN ¹	\$ x 10 ³ /year	5.72 \$/10 ³ lbs.
NET REVENUE REQ'D.	\$ x 10 ³ /year	GROSS REVENUE - BY PRODUCT CREDITS
H ₂ COST	\$ x 10 ³ SCF	Net annual revenue required/annual H ₂ production
H ₂ COST	\$ x 10 ⁶ Btu	HHV of hydrogen

(1) Stated in constant, end of year 1980 \$'s, real escalation rate is assumed to be equal to general inflation rate.

(2) Includes contingency, interest during construction, and other indirect costs.

(3) Cash supply is for feedstock and utilities, labor and supervision and materials.

PLANT SIZE SCALING RELATIONSHIP

The total installed cost (TIC) for the CSHP is equivalent to the facility investment cost for the steam reforming plant. As discussed in Section 2.1.5, the cost/size relationship for large systems generally can be represented by:

$$\frac{TIC_{large}}{TIC_{small}} = \left(\frac{P_{large}}{P_{small}} \right)^x$$

where P is the size, or rating, of the plant. The scaling exponent x, is generally determined from experience with cost data over a range of plant size.

Since a body of such experience for the CSHP does not exist at present, we must select a value for x by analogy. Considering various values of x;

x = 0.6, this is a "rule of thumb" value used extensively in the power plant industry based on extensive experience.

x = 0.54, used for conventional steam reforming plants in Section 2.1.5, based on Westinghouse evaluation of vendor quotations for plant ratings from 100-600,000 SCF/hour.

x = 1.00, economy of scale due to plant rating is used for scaling the heliostat field in Section 2.1.3 and for scaling the electrolyzer in the sulfur cycle since they are modular in very small sizes relative to plant size.

x = 0.70, conservative estimate for scaling up developmental equipment in the CSHP other than the heliostat field.

For the commercially available CSHP equipment, which consists of pipes, valves, heat exchangers, pumps, etc., it would be reasonable to conclude that a value of x = 0.6 as used for similar equipment in power plants would be appropriate for scaling up the CSHP. However, given the above values for the heliostats and other development equipment in the CSHP, it was decided to use x = 0.8 for

scaling up the plant size. The resulting installed cost for the first commercial CSHP plant as a function of size is shown in Figure 2-18, with the previously discussed cost of commercial steam reforming units shown for comparison.

EXPERIENCE CURVE EFFECTS

Table 2-18 presented the CSHP market potential in terms of the cumulative number of plants as a function of the plant size and year of installation. Figure 2-18 presented the installed plant cost of the first production plants in this same plant size range. As with other new technologies, it is reasonable to expect that the cost per plant will decrease as manufacturing and installation experience accumulates. This type of cost reduction is generally referred to as the experience curve effect and its application to numerous technologies has been extensively analyzed and documented as in Ref. 2-15 and 2-16. The experience curve effect is based on the combined effects of: volume purchasing of raw materials; volume manufacturing; labor learning; design, manufacturing, assembly, installation and testing improvements; and material and component substitutions. The combination of these effects on the cost of a unit can be represented by the following equation:

$$C_N = C_1 N^a$$

where:

N is the number of units (or plants)

C_1 is the cost of the first production unit

C_N is the cost of the Nth unit.

For the exponent;

$$a = \ln \text{EXP} / \ln 2.0$$

and EXP represents the experience curve factor. An experience curve factor of EXP = 0.9 or 90 percent means that the cost per unit will decrease by 10 percent as the cumulative number of units produced is doubled. Similarly, an 85

Figure 2-18. Installed Plant Cost Versus Plant Size

Figure 2-19. Installed Plant Costs, Steam Reforming Plants and Mature CSHP Units

percent experience curve will result in a 15 percent cost reduction when the cumulative number of units is doubled. Figure 2-5 presents the ratio of Nth unit cost to first unit cost versus the cumulative number of units in a production run for a range of experience curve factors. Experience curves of this type are often used to establish cost goals and to track progress in meeting such goals.

As examples, experience curves of 60 percent are typical in the electronics industry, and aircraft manufacturing has exhibited experience curves of 80 percent. After reviewing historical examples of experience curves, it was decided to use a conservative 85 experience factor for projecting the installed cost of "mature" CSHP plants. Two additional factors must be considered in projecting the installed capital cost of the mature CSHP plants. First, the rate at which one can proceed down the experience curve is constrained by the market share available to the CSHP, the rate at which manufacturing capacity can be expanded, and the rate at which real cost reductions can be affected product and manufacturing design and development. Second, the extent to which one can proceed down this experience curve is limited by physical constraints. For example, it is certainly not realistic to use an experience curve to predict a plant cost that is lower than the cost of the raw materials needed to manufacture the plant. With regard to this last factor, at some point in the accumulation of experience, cost reductions will level off as the technology matures. Then no further significant cost reductions will occur unless there are drastic changes in the technology.

Given the above it was assumed that CSHP units, on an 85 percent experience curve, would reach maturity when 175 such units had been produced. The resulting mature CSHP plant cost as a function of size is shown in Figure 2-19 along with the first commercial CSHP and steam reforming plant cost. The time required for the CSHP plants to reach maturity is constrained by the available market share defined in Table 2-18. The cost reductions given the 85 experience curve and the market share constraints are summarized in Figure 2-20. At 175 units, Figure 2-20 indicated the earliest date when each CSHP plant size could reach maturity. These dates and the mature unit installed plant costs

Figure 2-20. Transition from First Production to Mature Solar Hydrogen Plants with Timing and Market Size Constraints

are as follows. For the smaller plant size reaching maturity is projected in two years; it should be pointed out that expansion of manufacturing capacity and the experience curve process of reducing cost through design improvements and manufacturing improvements may preclude reaching the cost reductions in such a short period.

<u>CSHP PLANT SIZE</u>	<u>MATURE UNIT INSTALLED COST</u>	<u>EARLIEST DATE FOR MATURE UNIT</u>
$0.30 \times 10^6 \text{ SCFH}$	$5.30 \times 10^6 \$$	1997
$0.60 \times 10^6 \text{ SCFH}$	$50.0 \times 10^6 \$$	2010
$1.00 \times 10^6 \text{ SCFH}$	$73.7 \times 10^6 \$$	2020

As shown in Figure 2-19, the mature CSHP units, with the required solar collection and thermal storage equipment, still have a much higher installed cost than the mature, conventional steam reforming plants. The above mature units costs for the CSHP are regarded herein as the minimum costs, in constant 1980 dollars, for the CSHP plant.

COST OF HYDROGEN PROJECTIONS FOR CSHP UNITS

The previously defined economic guidelines, electricity costs and steam credit projections, and the above installed costs were used to develop the cost of hydrogen (COH) projections for the CSHP units. Baseline COH estimates assuming operation at 1980 values of electricity and steam credits were derived as the first step. These baseline estimates, shown in Table 2-21, treat the first commercial units forward in time to 1995 with the higher projected cost of electricity and higher values for steam credits. This date is consistent with our prior assumption that the CSHP technology would be first available for commercial applications by 1995. After 1995, the experience curve results in a declining plant installed cost until CSHP maturity is reached. This experience curve was applied only to the installed direct capital cost while holding the following costs at the same level as in the first commercial units:

TABLE 2-21

COST OF HYDROGEN PROJECTIONS FOR FIRST COMMERCIAL CSHP UNITS
(In Constant 1980's with Operation at 1980 Values for Electricity Costs and Steam Credits)

	PLANT TYPE				
PLANT RATING (THERMAL INPUT)	MM _t	4.590	4.590	91.8	153
OPERATING FACTOR	DAYS/YEAR	330	330	330	330
ANNUAL H ₂ PRODUCTION	10 ⁶ SCF	237.6	237.6	4752.0	7923.0
DIRECT CAPITAL COST	\$ x 10 ³	22,589	15,097	166,067	249,931
CONTINGENCY, IDC & ODC	\$	44.55	34.75	34.75	34.75
FIXED CAPITAL INVESTMENT	\$ x 10 ³	32,652	20,343	223,775	336,782
START UP COSTS	\$ x 10 ³	653	407	3,321	4,999
WORKING CAPITAL	\$ x 10 ³	330	246	3,377	5,326
TOTAL CAPITAL REQUIRED	\$ x 10 ³	33,635	20,996	230,473	347,107
FIXED CHARGE RATE	%	26.5	26.5	26.5	26.5
ANNUAL REVENUE REQ'D. FOR CAPITAL INVESTMENT	\$ x 10 ³ /year	8,913	5,564	61,075	91,983
FEEDSTOCK & UTILITIES	-	-	-	-	-
ELECTRICITY	\$ x 20 ³ /year	412	412	8,240	13,740
PROCESS WATER	\$ x 10 ³ /year	1	1	20	25
OPERATION & MAINTENANCE	-	-	-	-	-
LABOR & SUPERVISION	\$ x 10 ³ /year	949	634	6,975	10,497
MATERIALS	\$ x 10 ³ /year	452	302	3,321	4,998
INSURANCE	\$ x 10 ³ /year	452	302	3,321	4,998
GEN. ADMIN. EXPENSES	\$ x 10 ³ /year	452	302	3,321	5,000
GROSS REVENUE REQ'D.	\$ x 10 ³ /year	597	597	4,554	6,533
BY-PRODUCT CREDITS	-	-	-	-	-
STEAM	\$ x 10 ³ /year	597	597	4,554	6,533
OXYGEN	\$ x 10 ³ /year	56	56	1,200	1,880
NET REVENUE REQ'D.	\$ x 10 ³ /year	10,978	6,864	80,519	122,828
H ₂ COST (1980 OPERATION)	\$ x 10 ³ SCF	46.2	28.9	15.94	15.50
H ₂ COST ( )	\$ x 10 ³ SCF	142.1	88.9	52.11	47.71

TABLE 2-22

COST OF HYDROGEN PROJECTIONS FOR COMMERCIAL CSHP UNITS (\$/10⁶ BTU IN CONSTANT 1980 DOLLARS)
- WITH STEAM CREDIT -

PLANT SIZE, SCFH x 10 ³	30	600	1000
<u>YEAR OF OPERATION</u>			
1995	87	51	47
1996	58	42	38
1997	46*	37	34
2000		27	27
2010		21*	21
2020			15*

*175th Mature Unit COH

START UP COST

LABOR AND SUPERVISION COSTS

MATERIALS

INSURANCE

GENERAL ADMINISTRATIVE COSTS

The resulting COH projections for the CSHP units are shown in Table 2-22 with by product steam credits included and in Table 2-23 without steam credits. The calculations were carried forward in time only to the point where 175 plants of each size are installed and the CSHP reaches maturity.

After this point the COH of the CSHP units without steam credits will increase with time (in constant 1980 dollars) due to the escalating cost of electricity. With the steam credits (which includes electricity and natural gas escalation) the CSHP COH will level out and may decline slightly with time after the point of maturity.

2.1.7 COMPARISON OF SOLAR HYDROGEN AND CONVENTIONAL HYDROGEN PLANTS

The cost of hydrogen projections for conventional steam reforming plants were developed in Section 2.1.5 and cost of hydrogen projections for the commercial size solar hydrogen (CSHP) units were estimated in Section 2.1.6. The objective in this section is to compare the conventional and solar hydrogen plants to determine the conditions for economically viable CSHP units. The cost of hydrogen projections for both types of units are based on the same economic guidelines and calculation methodology. Conservative assumptions were used in estimating the installed CSHP capital costs and in estimating the cost-size relationship of the CSHP units. COH comparisons were made with and without credits for the steam by-product for two reasons.

First, the value of the steam credit can be based on a wide range of different assumptions. In this analysis it was assumed that the value of the steam was equivalent to the cost of producing steam using a conventional natural gas fired boiler at the same output rate as the conventional steam reformer or the solar hydrogen plant. While this is a rigorous analytical approach it may

result in an optimistic steam credit projection. Future cost escalation and regulatory constraints may preclude or reduce the use of natural gas to produce steam. Under such circumstances coal, other fuels, solar energy, cogeneration systems and other methods could perhaps produce steam at a lower cost than a natural gas fired boiler. In addition, assignment of any value to the by-product steam includes an implicit assumption that there is a willing customer for the steam and this assumption may not be valid.

Second, on a per unit of hydrogen produced basis, the CSHP unit produces 4.6 times as much by-product steam as the conventional steam reforming plant. Therefore, a comparison without steam credits is necessary to avoid biasing the results and conclusions.

For both types of units it may be possible to use the by-product steam to generate electricity for on-site use to sell back to the utility at PURPA buy-back rates. This possibility was not explored in this analysis.

In addition to steam, the CSHP unit also produces by-product oxygen. But at current oxygen prices the oxygen by-product credit is only 10-30 percent of the steam by-product credit. In addition, the real future escalation of the oxygen value was conservatively estimated at zero.

The COH of the CSHP and the conventional plant, both with a rating of 1.0×10^6 SCFH, are compared in Figure 2-21 with steam credits included. The COH of the CSHP becomes lower than the conventional plant COH shortly after 2000. This crossover occurs at the 37th unit in the 175 unit CSHP production run. The installed capital cost of the 37th CSHP plant is 105 million dollars while the conventional plant cost is 26 million dollars, both in constant 1980 dollars.

The same 1×10^6 SCFH units are compared in Figure 2-22 without steam credits. In this case, COH crossover occurs at the 62nd CSHP plant in 2004. The installed capital cost of the 62nd CSHP plant is about 93 million dollars.

Figure 2-21. Cost of Hydrogen Comparison Versus Year of Operation, 1.0×10^6 SCFH Units - With Steam Credits

Figure 2-22. Cost of Hydrogen Comparison Versus Year of Operation, 1.0×10^6 SCFH Units - Without Steam Credits

The smaller 0.03×10^6 and 0.6×10^6 SCFH plants are added to the COH comparison in Figure 2-23. This comparison includes steam credits. The smaller CSHP plants crossover the conventional plant COH earlier than the large CSHP plant. The smallest 0.03×10^6 SCFH plant cross over shortly after the 1995 market introduction with the 15th such CSHP plant. This 15th CSHP plant has an installed capital cost of 10.5 million dollars. The conventional plant is about 4 million in constant 1980 dollars.

All plant sizes without steam credits are compared in Figure 2-24. Deleting the steam credits delays the crossover point for the 0.6×10^6 and 1.0×10^6 CSHP plants by 2-4 years. The crossover point for the smallest 0.03×10^6 SCFH plant is unaffected by the deletion of the steam credits.

The estimated year of operation when COH crossover occurs is shown in Figure 2-25 for the range of CSHP plant sizes. The smaller plant sizes, when only 10-20 units into the 175 unit production run, crossover the conventional plant COH shorter after market introduction. This is a significant result because it indicates that the CSHP will be commercially viable, even in small sizes, without assuming substantial economics of scale due to very large plant sizes. It also indicates that only a small share of the market for new hydrogen plant installations is needed for CSHP commercial viability. The market share assumption used in this analysis was approximately 6 percent of the new installations. Even if this assumption turns out to be optimistic, it would only delay CSHP commercial viability (COH crossover) by a short time. In addition, the COH crossover point is unaffected by the credit or non-credit for the by-product steam in the small CSHP plant size.

The characteristics of the CSHP plants at the COH crossover point are summarized in Table 2-23. Regardless of the CSHP plant size assumed, all of the sizes become commercially viable well before the end of the 175 unit production run on a conservative 85 percent experience curve. After the year of crossover, the conventional steam reformed hydrogen produced from natural gas becomes more expensive than the sulfur cycle solar hydrogen even with a CSHP installed capital cost 3-4 times greater than that of a steam reforming plant. Even with the experience curve cost reduction, the 0.03×10^6 SCFH CSHP plant

Figure 2-23. Cost of Hydrogen Comparison - With Steam Credits

Figure 2-24. Cost of Hydrogen Comparison Versus Year of Operation, All Plant Sizes - Without Steam Credits

Figure 2-25. Year of Operation Versus Unit Size when CSHP SOLAR/H₂ COH becomes Less than Conventional Steam Reforming COH

TABLE 2-23

CHSP CHARACTERISTICS FOR COH CROSSOVER WHEN SOLAR HYDROGEN COST BECOMES LESS THAN STEAM REFORMING HYDROGEN COST (COSTS ARE IN CONSTANT 1980 DOLLARS)

SIZE SCFH x 10 ⁶	WITH STEAM CREDIT	WITHOUT STEAM CREDIT	CSHP PLANT	YEAR OF CAPITAL COST PLANTS	CSHP	YEAR OF CAPITAL COST PLANTS	NUMBER OF INSTALLED PLANT CAPITAL COST \$ x 10 ⁶	NUMBER OF INSTALLED PLANT CAPITAL COST \$ x 10 ⁶	CONVENTIONAL
	CROSSOVER	INSTALLED			NUMBER OF CROSSOVER \$ x 10 ⁶				
		0.03		1996	15	10.5	1996	15	10.5
		0.60		1999	42	68.0	2003	85	58.0
		1.00		2000	37	105.0	2004	62	93.0
									26.0

will cross over in 2001-2002 and the larger CSHP plants will cross over before 2015 as can be seen by examining Figures 2-23 and 2-24.

2.2. PRESSURIZED TEST UNIT (PTU) DEFINITION

2.2.1 GENERAL BACKGROUND

The pressurized test unit (PTU) is expected to provide early demonstration of the solar driven sulfur cycle process as part of the long range development of the cycle. With ongoing technology development and system engineering, the technology of the sulfur cycle can mature to the point that a series of development systems can be designed, erected and tested. The PTU system should represent one of the early demonstrations of a workable system and be a major milestone in the development of the cycle.

The specific long range objectives of the PTU are as follows:

- To demonstrate the production of hydrogen from the solar-driven sulfur cycle.
- To demonstrate the integration of the thermochemical portion of the sulfur cycle with distributed solar collector technology.
- To provide validation of the design choices, materials selections, system configurations, process parameters, and other related aspects of the solar hydrogen production process made for the PTU.
- To provide data from which to make more accurate assessments of the development needs, performance requirements, and costing bases for future solar hydrogen systems, both for large-and small-scale systems.

In Section 2.2.2, a selected configuration for the PTU is described. This configuration was chosen after comprehensive trade studies had been performed and a rigorous selection process had been used to rank several attractive configurations for the PTU. The selection process, discussed in Section 2.2.4, used a set of

weighted criteria to rank the candidate PTU configuration. The criteria and their relative "importance" or weighting numbers were as follows:

<u>Criteria</u>	<u>Weighting Factor</u>
● Degree of risk	9
● Information payoff	9
● Experimental flexibility	7
● Performance potential	5
● Safety/environmental considerations	5
● Capital costs	5

Using these criteria, the PTU configuration described in Section 2.2.2 was selected from among six candidate configurations that are described in Section 2.2.4. That section also discusses the rationale for the selection process and associated constraints and assumptions.

In arriving at the six final contenders for the PTU, investigations of a number of key process variables such as pressure level and acid concentration also were performed. These studies are discussed in Section 2.2.3.

2.2.2 PTU DESCRIPTION

Basically the PTU is designed for a nominal 85 kW(t) energy input to the SO_3 decomposition reactor, which will permit the coupling of the thermochemical system to a single distributed solar collector of reasonable size. The PTU concept has been selected to demonstrate both technologies, to validate critical design choices, and to provide data to enhance system development.

The PTU system is based on the Sulfur Cycle Water Decomposition Process, which is a two-step hybrid electrochemical/thermochemical cycle for decomposing water into hydrogen and oxygen.

The process, in its most general form, consist 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.

The equilibrium for reaction (1) lies to the right at temperature above 1000K. Catalyst is required 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 a water electrolyzer. The overall reaction occurring electrochemically is:

This is comprised of the individual reactions:

The net result of reaction (1) and (2) is the decomposition of water into hydrogen and oxygen. Sulfur oxides are involved as recycling intermediates.

The PTU process flow sheet is shown in Figure 2-26, with the flow rate and composition of each stream identified in Table 2-24. Based upon process studies, an acid concentration of 63 weight percent was selected for the electrolyzer. The electrolyzer is assumed to operate at 212°F (100°C) and at an overall cell voltage 607 mV. The PTU represents a hydrogen production rate of 850 SCFH (4.5 lb/hr). The hydrogen is generated in the electrolyzer and leaves at a pressure of 294 PSIA (Stream 3).

The sulfuric acid produced in the electrolyzer (63 w/o), Stream 1, passes through a throttle valve where the pressure is reduced from 294 to 2.5 PSIA. Then it is sent to Flash Drum - 1, where the vapor phase (Stream 5) and liquid phase (Stream 6) are separated. Stream 6 is heated from 170°F to 225°F then enters Flash Drum - 2 in order to further expel the SO₂ dissolved in the acid solution. The SO₂ and steam in Stream 9 are compressed from 2.5 to 14.7 PSIA with a vacuum pump (PV-1), and cooled in a condensing heat exchanger (E-5) to condense most of the steam in the

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Figure 2-26. PTU Process Flow Sheet

TABLE 2-24

STATE POINTS FOR THE PTU CONFIGURATION

STREAM NO:	* 1	2	3	4	5	6	7	8	9	10	11	12	13	14
TEMP., °F	213	213	213	170	170	170	225	225	197	225	225	213	400	729
PRESSURE, PSIA	294	294	294	2.5	2.5	2.5	2.5	2.5	2.5	2.5	329	294	14.7	323.5
FLOW RATE, lb/hr														
COMPOSITION: H ₂			4.536											
O ₂														
SO ₂	6318.978	119.226		119.226	118.075	1.151	1.151	1.149	119.224	0.001	0.001	6199.752	119.224	0.001
SO ₃														
H ₂ O	19798.256	373.552		373.552	15.869	357.683	357.683	54.807	70.676	156.814	156.814	19424.707	70.676	156.814
H ₂ SO ₄	33707.735	635.995		635.995		635.995	635.995			329.281	329.281	83071.74		329.281
2-60 STREAM NO:	15	16	17	18	19	20	21	22	23	24	25	26	27	28
TEMP., °F	845	980	1620	1250	442	415	162	162	162	90	90	90	90	90
PRESSURE, PSIA	322	319	294	291	288	287	285	285	285	284.5	285	284.5	295	294
FLOW RATE, lb/hr														
COMPOSITION: H ₂														
O ₂		2.4	36.00	36.00	36.00	36.00	36.00	36.00		36.00	36.00			
SO ₂	0.001	9.6	144.161	144.161	144.161	144.161	144.161	87.433	56.728	87.433	20.901	66.532	0.001	20.90
SO ₃	55.8	135.6	88.642	69.052										
H ₂ O	168.8	190.0	217.293	212.88	197.345	197.345	197.345	0.544	196.801	0.544	0.06	0.484	146.069	146.124
H ₂ SO ₄	261.7	148.5		24.003	108.585	108.585	108.585		108.585				306.714	306.714

*Note stream numbers on
Figure 2-1.

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[illegible]

stream before being returned to the mixing drum. The SO_2 in the vapor (Stream 41) is then compressed from 14.7 to 294 PSIA to the mixing drum with a three stage (C-1) compressor with intercoolers. The sulfuric acid leaving Flash Drum - 2 (67.74 w/o) is pumped from 2.5 to 329 PSIA and is sent to the thermal decomposition system.

In the thermal decomposition system, the acid is first heated to 729°F in a shell and tube type heat exchanger, Vaporizer-I, resulting a two phase mixture Stream 14. The two phase mixture is sent to Vaporizer-II for final vaporization and then sent to a recuperative heat exchanger for preheating before entering the decomposition reactor. The thermal inputs to the decomposition reactor (Q1) and Vaporizer-II (Q2) can be provided by indirect solar heating from a parabolic dish type solar collector using helium as a heat transport medium. A gas phase mixture of steam, SO_2 , SO_3 and unreacted SO_3 leaves the decomposition reactor at a temperature of 1600°F and is recuperatively cooled against the incoming acid streams in the recuperative heat exchanger, Vaporizer-I and E-1.

Stream 20 leaving E-1 is cooled in a condensing heat exchanger (E-3), where the steam and sulfuric acid are condensed and removed in Surge Tank-1. The gas phase mixture of SO_2 and O_2 leaving Surge Tank-1 is further cooled in a condensing heat exchanger (E-4) where bulk SO_2 is condensed and removed in Surge Tank-2. The gas phase mixture (Stream 25) leaving Surge Tank-2 is sent to a absorption tower (Absorber-1) and is scrubbed with 68 weight percent sulfuric acid drawn from Flash Drum-2. Based upon solubility and equilibrium considerations, an absorption tower with seven ideal stages will remove substantially all the SO_2 in Stream 25, although it is given a precautionary backup scrub in Absorber-2 against the incoming process makeup water. The oxygen stream leaves Absorber-2 at 294 PSIA (Stream 31). The liquid streams leaving Surge Tank-1, 2, 3, and Absorbers-1, 2 are all returned to the mixing drum and recycled back onto the electrolyzer.

All heat rejection from the plant will take place through a cooling tower capable of providing a 80°F supply of cooling water to the plant. Therefore, the demand for temperature levels unattainable with 80°F cooling water is avoided in the entire process.

Table 2-25 lists the major equipment for the PTU, and the plant electrical requirements are summarized in Table 2-26. The external heat requirements, Q_1 , Q_2 and the thermal energy required to make the electricity (assuming 39.5% conversion) are shown in Table 2-27. Defining overall process efficiency as the higher heating value of the hydrogen produced divided by the total thermal energy input to the plant, a calculated overall efficiency for the PTU is 31%. This fairly low value is based on the assumption that none of the rejected process heat is utilized for power generation or for any other useful purpose. In point of fact, much of the "waste heat" in the PTU configuration can be used to generate low grade (350°F) steam and hot water (210°F). Therefore it is reasonable to think in terms of a dual purpose plant that makes hydrogen and process heat as useful products. This can be considered as a variation on the usual concept of cogeneration, which normally produces electricity and process heat.

As a dual purpose or cogeneration plant, the PTU configuration provides an overall efficiency greater than 60%. In fact, it is possible to attain efficiencies approaching 80% by preferentially varying the product mix toward more process heat and less hydrogen. This mix is easily varied by modifying the concentration of sulfuric acid in the cycle. These effects are discussed in some detail in Section 2.2.3.5.

Since the PTU is designed for indirect coupling with a solar heat source, it permits the assembly and complete testing of both the electrolytic and thermochemical portions of the system in an integrated fashion prior to delivery to the collector site. It separates the design of the process system and that of the solar thermal receiver into discrete tasks. Such indirect coupling implies the capability for operation of the PTU using an alternate (e.g. combustion) heat source, which can be provided at the development site or at the collector sites for 24-hour-a-day operation in place of (or alternating with) the solar collector.

2.2.3 INVESTIGATION OF KEY PROCESS VARIABLES

2.2.3.1 General

A series of integrated cycle performance analyses have been carried out, with consideration given to such factors as steam separation, use of thermal storage,

TABLE 2-25

PTU MAJOR EQUIPMENT LIST*

Item	Title	Function/Remarks
1.	Electrolyzer	Operated at 100 mA/cm ² and 212°F.
2.	Tank	Retention tank for circulating catholyte.
3.	Valve (V-1)	Throttle valve or valves to reduce the system pressure from 20 ATM. to 0.17 ATM.
4.	Flash Drum -1 and Flash Drum -2	For separating the vapor phase (SO ₂ , H ₂ O) and the liquid phase (H ₂ SO ₄ solution).
5.	Vaporizer I	Shell and tube heat exchanger type vaporizer.
6.	Vaporizer II	Boiler type vaporizer for the final vaporization of the acid.
7.	Recuperative Heat Exchanger	To preheat the acid vapor before entering the decomposition reactor.
8.	Decomposition Reactor:	To decompose H ₂ SO ₄ vapor and SO ₃ .
9.	Surge Tank -1	To separate the vapor phase (SO ₂ , O ₂) and the liquid phase (H ₂ SO ₄ solution).
10.	Surge Tank -2	To separate the vapor phase (SO ₂ , O ₂) and the liquid phase (Liquid SO ₂).
11.	Absorber -1	Using sulfuric acid as an absorbent to reduce the SO ₂ concentration in the gas phase. Seven ideal stages required.
12.	Absorber -2	Using the process make up water to further reduce the SO ₂ concentration in the gas phase and to eliminate the acid mist. 1.3 ideal stages required.
13.	Surge Tank -3	To separate the vapor phase (SO ₂ , Steam) and the liquid phase (Water).
14.	Mixing Drum	To mix the returning streams to form sulfuric acid solution and saturated with SO ₂ at 20 atmospheres and 212°F.
15.	E-1	Heat exchanger to heat the acid solution from 170°F to 225°F. Heat load is 8.4 kW.
16.	E-2	Heat exchanger to cool the acid solution from 225°F to 90°F. Heat load is 9.5 kW.
17.	E-3	Condensing heat exchanger to cool the process stream from 415°F to 162°F. Heat load is 43.4 kW.
18.	E-4	Condensing heat exchanger to cool SO ₂ /O ₂ stream from 162°F to 90°F. Heat load is 3.5 kW.
19.	E-5	Condensing heat exchanger to condense the water vapor. Heat load is 29.2 kW.
20.	PV-1	Vacuum pump. 0.17 ATM. to 1.0 ATM.
21.	C-1	Three stage compressor with intercoolers.

TABLE 2-26

PTU AUXILIARY POWER REQUIREMENTS (REFER FIG. 1)

<u>Component</u>	<u>Power kW(e)</u>	<u>Component</u>	<u>Power kW(e)</u>
Electrolyzer	33.2	P-3	0.8
PV-1	4.3	P-4	0.01
C-1	3.2	P-5	0.01
B-1	0.2	P-6	0.02
B-2	0.1	P-7	0.2
P-1	0.1	Helium Circulator	13.0
P-2	0.1		
Total:		55.2	

TABLE 2-27

EXTERNAL ENERGY REQUIREMENTS

<u>Item</u>	<u>Heat Requirement, kW(t)</u>
Q1 (SO ₃ Decomposition Reactor)	85
Q2 (Acid Vaporizer - II)	41
Auxiliary Electric Power (Assuming 40% conversion from heat to 55 kW(e) of electricity)	<u>138</u>
Total	264

system pressure level, acid concentration. SO_2 stripping, SO_2/O_2 separation alternatives and direct contact acid vaporization. As a result of these studies of key process variables, a reference process configuration evolved, primarily from performance considerations. Alternatives to this reference PTU configuration also were defined based on consideration of the PTU objectives and key system criteria encompassing performance, costs, risks, etc. Some of these alternatives were suitable for consideration as potential configurations for the PTU. Others were found to be unsuited to the specific power level or operational limitations imposed by design choice made for the PTU.

2.2.3.2 Steam Separation During Acid Vaporization

This alternative system configuration was developed during the early stages of the Sulfur Cycle process study as a means of minimizing waste heat rejection. Steam (which forms the bulk of the vapor phase over sulfuric acid) is separated from the acid solution before the acid is sent to the SO_3 decomposition reactor. The increased concentration of the acid substantially reduces the thermal input requirements to the reactor. Separated steam can be subsequently used to generate clean (i.e., acid-mist free) steam in another heat exchanger. The clean steam thus generated can be used to drive a turbine-generator set, and improve the overall process efficiency with respect to the non-separation case. For a large (380×10^6 SCFD) hydrogen plant, steam separation under optimum efficiency conditions could be carried out at a concentrator acid feed concentration of 63 percent, with steam separation to give 85 percent acid. For these conditions, overall process efficiency was calculated to be 44 percent. (Overall process efficiency is defined as the high heating value of hydrogen produced divided by the total thermal energy input to the process. As stated previously, electricity required from off-site sources is evaluated on the basis of 39.5% efficiency for the electrical power generating source). For a hydrogen generation plant having the limited power level of the PTU, the amount of heat rejected from the process by steam separation at conditions equivalent to those discussed above is insufficient to be utilized for electrical power generation with existing turbines. Steam removed from a 2-step acid vaporization process must therefore be condensed directly and recycled to the mixing drum to maintain the correct inlet acid concentration for the electrolyzer. Under these conditions, the overall process efficiency for a steam separation configuration (assuming day/night operation

with chemical storage for continuous hydrogen production) in a PTU-size plant is calculated to be 30.3%; for the single-stage vaporization (no steam separation) the day/night PTU design efficiency is 31.2%. Figures 2-27 and 2-28 are process flowsheets for the PTU with steam separation. Figures 2-29 and 2-30 are process flowsheets for the PTU without steam separation. None of the heat rejected from the process ($Q_3 + Q_4 + Q_5$) has been credited to the efficiency calculations in determining the efficiency values stated above.

Therefore, it is concluded that steam separation provides no advantage from a performance standpoint unless some means of using the heat rejected in condensing the acid mist/steam mixture is applied.

2.2.3.3 Thermal Storage for Electrolyzer Operation

Since the Sulfur Cycle Hydrogen Production Process has available process heat, thermal storage may result in an increase of thermal efficiency when continuous hydrogen production is required.

From preliminary studies, it was assumed that the electrolyzer would be operated at 125°C (275°F). A detailed energy balance around the electrolyzer was performed to determine if thermal storage is needed to maintain the temperature of returning acid at 125°C during nighttime operation. The study indicated that the heat from the electrolyzer maintained the temperature of returning acid at 125°C, provided that heat losses were insignificant in the remainder of the system. Thus, thermal storage will not be required for the PTU to maintain the temperature of the electrolyzer during nighttime operation.

2.2.3.4 System Pressure Level

The effect of system pressure level on cycle performance has been assessed assuming the use of single-pressure process system. Pressure levels were varied from 5 atmospheres and 20 atmospheres. The lower pressure level was defined based on experimental results with sulfuric acid electrolyzers in tests which indicated that cell voltage was minimized at ~5 atmospheres, with no significant decrease in cell voltage attributable to pressure increases beyond this level. Theoretically, it is expected that electrolyzer performance should be enhanced

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Figure 2-27. PTU Process Flow Sheet (Steam Separation), Daytime Operation (9 Hrs.)

Figure 2-28. PTU Process Flow Sheet (Steam Separation), Nighttime Operation (15 Hrs.)

Figure 2-29. PTU Process Flow Sheet (Steam Separation), Daytime Operation (9 Hrs.)

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Figure 2-30. PTU Process Flow Sheet (No Steam Separation), Nighttime Operation (15 Hrs.)

by an increasing electrolyzer operating pressure to the limit of SO_2 solubility in the electrolyte. These results were achieved by others with a slightly different electrolysis process at a temperature of 10°C , and thus were not directly comparable to the proposed operating conditions for the Westinghouse electrolyzer.

Sulfur dioxide solubility calculations based on Henry's Law constants taken from Reference 2-18 indicate that SO_2 solubility in subazeotropic solutions of sulfuric acid at 100°C should continue to increase with increased SO_2 partial pressures to 27 atmospheres, as shown in Figure 2-31. Further increases in pressure result in SO_2 condensation and formation of a liquid SO_2 phase in the electrolyzer, thus degrading cell performance.

From an economic standpoint, there is a strong incentive to decrease the size of the reduction reactor. This can be achieved by an increase in process design pressure. An upper limit of 20 atmospheres was selected on the basis of mechanical design considerations for the (potentially) non-metallic components of the system such as the acid vaporizer and reduction reactor. The majority of parametric cases have been done with the 20 atmosphere level. Figures 2-32 and 2-33 are process flowsheets for the PTU system operated at 5 atmospheres, in the day/night mode which can be compared to the 20 atmosphere cases in Figures 2-29 and 2-30. The calculated process efficiencies are 30.9 percent in 5 atmosphere operation versus 31.2 percent for operation at 20 atmospheres. (These results are based upon a simplified modeling of the energy requirements for acid recirculation and gas compression). The apparent conclusion is that performance does not change significantly with an increase in pressure.

A dual-pressure-level system was then investigated, with a high-pressure electrolyzer and a lower-pressure reactor. The conversion efficiency of SO_3 is reduced by $1/\sqrt{P_{\text{tot}}}$ as pressure is increased, and more thermal energy must be provided to completely vaporize the acid feed to the reduction reactor at higher pressures. A dual-pressure-level system with 20 atmospheres in the electrolyzer and 10 atmospheres in the decomposition reactor was studied. The result revealed that the overall process efficiency for the dual pressure system is approximately 1% higher than that of the single pressure (20 atmospheres) system. However, the size of the decomposition reactor and the catalyst required for SO_3 decomposition would be doubled for the dual pressure system at the conditions studied.

SO₂ SOLUBILITY, GRAMS OF SO₂/100 GRAMS OF H₂SO₄ SOLUTION

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Figure 2-31. Pressure Vs. SO₂ Solubility in Various Concentrations of H₂SO₄ Solution at 100°C

Figure 2-32. PTU Process Flow Sheet (No Steam Separation), Daytime Operation (9 Hrs.)

Figure 2-33. PTU Process Flow Sheet (No Steam Separation), Nighttime Operation (15 Hrs.)

2.2.3.5 Acid Concentration

A key part of the analysis effort was the study of the effect of acid concentration on overall process efficiency. Six cases were investigated which considered concentrations ranging from 30 to 70 percent sulfuric acid feed to the electrolyzer. A pressure level of 20 atmospheres was assumed throughout the electrolytic and thermochemical subsystems. A summary of the basic conditions and performance figures for each acid concentration is contained in Table 2-28. Figure 2-34 shows how the overall process efficiency varies with acid concentrations. When only the high heating value of the hydrogen is credited to the efficiency calculation, overall process efficiency reaches a maximum at 31.8% with 63 weight percent acid. The cell voltage for each case was based on calculations that assumed an operating temperature of 100°C at 100 mA/cm². (Ref. 2-23).

If all heat rejected from the process system is utilized to generate 350°F saturated steam and 210°F hot water, the maximum process efficiency occurs at 30 weight percent acid conditions with 77.6 percent efficiency. This value assumes that both steam and water thermal energy is credited to the efficiency calculation. Figure 2-35 plots the amounts of hydrogen and process heat available per kilowatt of thermal energy input as a function of acid concentration.

In order to take credit for the thermal energy extracted from the process systems, as well as the hydrogen produced, it must be possible to integrate the small-scale solar hydrogen plant with a facility or process requiring both hydrogen and process heat; or as at a minimum, co-site the hydrogen plant with a process plant requiring thermal energy in the temperature ranges at which the reject heat appears. Table 2-29 is a listing of thermal energy requirements by temperature range, and electrical requirements of selected industrial plant types. The majority of plants are seen to need thermal energy in the 350°F (and lower) temperature range. Concurrent use of the hydrogen (and oxygen) product is not generally required. The specific energy levels may be matched by provision of a set of distributed collectors/hydrogen systems for the case of solar hydrogen plants of about PTU power rating; the temporal characteristics of solar thermal energy delivery are of course normally incompatible with the design mode of operation of most industrial plants.

TABLE 2-28

SUMMARY OF SIX CASES STUDIED

Case Number	1	2	3	4	5	6
Wt. Percent H_2SO_4 at Electrolyzer Inlet	29.82	49.74	52.74	59.74	62.74	69.74
Wt. Percent H_2SO_4 at Electrolyzer Outlet	30	50	53	60	63	70
Cell Voltage, Volt	0.380	0.468	0.492	0.570	0.607	0.723
Solar Thermal Input ($Q_1 + Q_2$), kWt	127.9	120.59	111.41	108.20	103.43	100.08
Electrical Input to Electrolyzer, kWe	10.85	17.71	18.96	23.3	25.29	31.30
Total Energy Input, kWt	164.52	173.15	166.97	174.43	174.52	186.12
Hydrogen Production, SCF/hr	445.2	589.6	601.1	637.7	649.5	675.2
Available Thermal Energy to Produce 134.63 PSIA, 350° F Steam (200° F Return), Kwt	49.6	31.0	23.8	21.5	17.8	17.5
Available Thermal Energy to Produce 210° F Hot Water, kWt	101.9	62.0	53.5	51.9	42.4	30.3
Overall Efficiency Based on Hydrogen Production Only, %	22.8	28.9	30.5	31.2	31.8	30.6
Overall Efficiency Based on Hydrogen and Steam Production, %	49.4	44.8	43.2	42.2	40.9	38.9
Overall Efficiency Based on Hydrogen Steam and Hot Water Production, %	77.6	60.7	59.0	57.8	53.5	45.0
* System Pressure, Atmospheres	20	20	20	20	20	20
Oxygen Production, SCF/hr	222.6	294.8	300.5	318.9	324.8	337.6

* System pressure is nominal pressure

Figure 2-34. Sulfur Cycle Thermal Efficiency Vs. Acid Concentration

Figure 2-35. Acid Concentration Vs. Hydrogen Production Rate per KW_t Energy Input, and Available Energy per KW_t Energy Input for Producing Hot Water and Steam

TABLE 2-29

1974 CHARACTERISTICS OF SELECTED INDUSTRIAL PLANTS

A. PLANT ENERGY REQUIREMENTS							
INDUSTRY	Plant Thermal Energy Requirements (10 ⁶ Btu/hr)						Plant Electric Requirements (MW)
	<212°F	212-350°F	350-500°F	500-1000°F	1000°F	TOTAL	
Cane Sugar Refining	45	250	-	18	13	329	1.28
Beet Sugar	279	910	-	-	57	1247	3.78
Distilled Liquors	16	93	-	-	-	110	5.06
Finishing Plants Cotton	59	66	-	-	-	125	1.44
Finishing Plants Synthetic	75	34	-	-	-	109	1.34
Paper and Pulp Mills	49	153	71	-	26	300	9.11
Alkalies and Chlorine	-	543	-	-	-	543	82.7
Non-Cellulosic Fibers	295	-	-	-	-	295	26.8
Cyclic Crudes and Intermediates	-	-	-	-	-	91	10.1
Petroleum Refining	40	41	-	1107	436	1626	17.8
Paving Mixtures	-	810	-	-	-	810	5.18
B. DAILY AND ANNUAL OPERATING CHARACTERISTICS							
INDUSTRY	Size of Plant		Estimated Shift Operations/Day		Annual Operation (Hours/Yr)		
Cane Sugar Refining	Large		2-3		5500		
Beet Sugar	Medium		1-2		4000		
Distilled Liquors	Large		2-3		4500		
Finishing Plants, Cotton	Large		2-3		5800		
Finishing Plants, Synthetic	Large		2-3		5800		
Pulp and Paper Mills	Large		3		7500		
Alkalies and Chlorine	Large		3		5600		
Non-Cellulosic Fibers	Large		2-3		5500		
Cyclic Crudes and Intermediates	Large		3		6200		
Petroleum Refining	Large		3		7500		
Paving Mixtures	Large		1-1.5		2600		

Source: General Energy Associates (From Reference 6)

Plant design with thermal storage capability and 24-hour-per-day hydrogen production can probably be provided to match the source/sink requirements in this area.

2.2.3.6 Sulfur Dioxide Stripping

Sulfuric acid leaving the electrolyzer contains a high concentration of sulfur dioxide, which must be stripped from the acid stream for the following reasons:

- SO_2 in the reduction reactor would hinder SO_3 conversion.
- A portion of the acid solution leaving the electrolyzer can be utilized as a scrubbing liquor for SO_2/O_2 separation purposes. A low SO_2 concentration is therefore necessary.

Stripping of the residual SO_2 from the electrolyzer acid effluent to be used for the thermochemical feed stream, catholyte makeup stream and SO_2/O_2 separator liquor can be achieved by flash separation at a controlled pressure and temperature. Pressure reduction across a control valve or orifice will result in part of the acid stream flashing from the liquid to the vapor state. Since the flashing process occurs under essentially adiabatic conditions, the latent heat of vaporization is taken from the sensible heat content of the acid stream, and its temperature falls as a consequence of this process. Product liquid and vapor fractions are considered to be in equilibrium with one another owing to the intimate contact which prevails in the flashing mixture. Assuming an acid composition of 63 weight percent with 11.8 percent SO_2 in solution dissolved in it at 20 atmospheres and 100°C , four cases were studied with flashing occurring at a different pressure level for each case. The results of the equilibrium calculations for the process are as follows:

Case	1	2	3	4
Pressure, Atm.	3.00	1.00	0.34	0.17
Resulting Temp., $^\circ\text{F}$	205.00	195.00	187.00	170.00
Resulting H_2SO_4 conc., w/o	63.09	63.26	63.85	64.00
SO_2 solubility, (g SO_2 /100g acid)	1.88	0.65	0.2	0.117

Case 4 was selected for further study owing to the low SO_2 solubility in acid. It is desirable that the acid used as an absorbent for SO_2/O_2 separation be practically SO_2 free. Since a further reduction in pressure appears impractical the stream must be stripped at a higher temperature. By stripping the stream from Case 4 at 225°F , 67.7 w/o H_2SO_4 will result with an SO_2 concentration less than 3 PPM (by weight). This concentration will be suitably low for all the required purposes. Preheating of the electrolyzer effluent can be carried out in a regenerative preheater using rejected process heat from the thermochemical system.

2.2.3.7 Sulfur Dioxide/Oxygen Separation

It is required that the separation of sulfur dioxide and oxygen produced in the sulfur trioxide decomposition step be carried out efficiently, since high levels of SO_2 in the oxygen are not acceptable for most process uses, nor from an emissions control standpoint. Loss of SO_2 from the recirculating process stream also imposes an additional materials makeup cost on the plant, although this appears to be insignificant even for levels at which the SO_2 concentrations exceed those allowed by 40CFR60 for sulfuric acid production facilities when calculated on the basis of amount of acid produced in the sulfur cycle. Presumably, the design and operation of the PTU and its SO_2/O_2 separation subsystem will provide separation performance data for the responsible authorities to use in codifying emissions limits for this type of solar hydrogen facility. The process design studies for the PTU are based upon the premise that the residual SO_2 in the oxygen efflux be reduced to values which are as low as practicable, consistent with the overall objectives of PTU operation. There are two major means to achieve separation, cryogenic separation and absorption in an acid liquor. The results of evaluations for both processes are discussed in the following subsections.

Cryogenic Separation

Sulfur dioxide may be condensed from a cooled mixture of SO_2 and O_2 vapors. Figure 2-36 displays the results of calculations showing condensing temperature versus the weight percent of SO_2 not condensed (and the resulting volume percent of SO_2 in the exit gas stream). For a condensing temperature of $+40^\circ\text{F}$, which is compatible with the temperature of chilled water provided by a lithium bromide absorption chiller unit operated from the available 350°F saturated steam generated by the process, 8 percent SO_2 by volume remains in the gas exit stream. At -40°F , attainable with a refrigeration unit but with significantly increased electrical energy requirements, 0.88 percent SO_2 by volume remains in the gas exit stream. Further reduction of SO_2 concentration beyond this value can be achieved by scrubbing the gas in an absorption tower in which the absorbing solution can be either acid or makeup water. Since this final scrubbing can provide only equivalent performance to a system using series absorption towers, with a significant energy penalty due to the requirement for chillers or refrigerators, cryogenic separation is considered to be infeasible certainly for the PTU and most probably for larger plants as well.

Absorption in Acid Solution

Removal of SO_2 from the decomposition reactor exit stream can be carried out by use of a set of absorption towers utilizing SO_2 -free acid and/or process makeup water as the absorbents. This type of separation system is compatible with a minimum cooling water temperature of 80°F .

The result of the studies indicates that the SO_2/O_2 separation can be adequately achieved (to less than 35 PPMV of SO_2 in the exhaust) by absorption in a plate tower with seven ideal stages using three times the minimum absorbent rate. The sulfuric acid solution available from the process is used as an absorbent. It is desirable that subsequent to the first tower an additional plate tower be installed to remove any entrained mist of the sulfuric acid from the first tower although the second tower is not effective for reducing the SO_2 concentration. The second tower can reduce the SO_2 concentration in the exhaust to 25 PPMV in 1.6 ideal stages using the amount of the process makeup water as an absorbent. Further study to size the first tower revealed that in order to maintain proper vapor velocities for obtaining high plate efficiencies, the diameter of the

Figure 2-36. Condensing Temperature Vs. Mole-Percent of SO_2 not Condensed, and Volume-Percent O_2 Remaining in the Stream

tower should be in the range of 1.8 to 2.0 inches. Apparently, it is too small to be considered for a plate tower. Thus, study on packed towers to replace plate towers was warranted.

The advantages of packed towers over plate towers are that the packed tower is cheaper to build, especially for corrosive liquids. It has less pressure drop; it has a smaller liquid holdup; and it can be built in small size. The mass transfer coefficients of $\text{SO}_2\text{-H}_2\text{SO}_4$ solution, and $\text{SO}_2\text{-H}_2\text{O}$ are calculated based on the methods of references 3 and 4. Also, it is assumed that the towers are packed with 1/4 inch Raschig Ring. The result of the studies shows that to reduce the SO_2 concentration to the level as described in previous plate tower system, the size of the first tower which uses H_2SO_4 solution as an absorbent is 3.9 inches in diameter and 12.0 feet in height. The size of the second tower which uses process makeup water as an absorbent is 2.6 inches in diameter and 5.8 feet in height.

2.2.3.8 Direct Contact Acid Vaporization

To alleviate the material problem of using shell and U-tube type acid vaporizer, an alternative concept was created using a tray tower or packed tower direct acid concentrator to evaporate the water by direct contacting the acid and the hot gases leaving the decomposition reactor. The schematic is shown in Figure 2-37. This configuration provides some other beneficial effects to the overall system effectiveness:

- The pinch point problem encountered in the acid concentrator cold end is relaxed to some degree by the removal of the pressure boundary heat transfer resistance of the shell-and-tube type heat exchanger. More process heat from the hot gas stream leaving the SO_3 decomposition reactor can be utilized to heat the incoming acid stream.
- The interior trays of the concentrator can be designed from materials which provide increased corrosion to the hot acid streams (particularly in the presence of stream phase changes which can enhance corrosion on active heat transfer surfaces). If a suitable material cannot be developed to provide a life-time comparable to that required for a commercial system, tray replacement will be considered since it is simple and inexpensive compared to retubing or replacing a heat exchanger unit;

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Figure 2-37. Schematic of the Direct Contact Acid Evaporation

or a packed tower can be used in lieu of tray tower. Although the shell of such a unit still need be designed for the system lifetime, it can be easily done by installing a layer of ceramic material lining.

- With this type of concentrator, no H_2SO_4 is recirculated since no free SO_3 combines with water and condenses in the evaporator section.

The result of the analysis shows that the incoming acid at 67.7 w/o and 225°F can be concentrated to approximately 95 w/o and below its boiling point, while the vapor phase leaving the tower is at roughly 500°F depending upon the design of the tower. The 95 w/o acid leaving the tower is then sent to a vaporizer (boiler) for final vaporization. It must be noted that although this configuration can solve some of the material problem and the overall process efficiency is comparable to that of the indirect contact acid vaporization scheme, there are some technical difficulties associated with this configuration:

- Requires a pump to circulate the high temperature acid. The pump may not be available.
- Problem of high temperature acid flow control.
- Difficulty in the design of the tower which has to transfer large amount of heat and mass between the two phases.

2.2.4 SELECTION PROCESS

2.2.4.1 Selection Logic and Criteria

The PTU for the solar-driven sulfur cycle hydrogen production process is to serve as a first generation developmental system for a small-scale commercial solar hydrogen plants, compatible with distributed solar collector technology. The PTU is also envisioned as a source of data for the evaluation of large-scale solar hydrogen plants, which most probably will use central receivers. The development of the PTU must therefore factor in important aspects of system design which are characteristic of both types of projected commercial solar hydrogen systems.

Prior Westinghouse work on development of the sulfur cycle has included materials testing, components testing, and bench scale operation of the

sulfur cycle with an electrical heat source, in addition to process and design studies for both small-and large-scale solar hydrogen production plants. Using these results a large number of potential PTU design concepts can be proposed. This extensive set of concepts can be reduced to a few candidate concepts, by application of constraints and assumptions, and by requiring that certain desirable features be provided in the PTU design. The PTU selection logic is shown in Figure 2-38.

The final selection of the PTU concept will be achieved by application of a matrix evaluation technique. In this technique, a comparison between candidate PTU concepts is made by figures-of-merit which are derived by evaluating the various concepts using selection criteria. The criteria reflect the relative importance of effectiveness, cost, and risk issues and the concept exhibiting the best figure-of-merit is considered to be the configuration most worthy of selection for the next phase - PTU preliminary design.

The criteria appropriate for assessment of the candidate PTU concepts have been grouped in three major issues: effectiveness, cost, and risk. Within each of these issues, several specific criteria can be itemized.

- EFFECTIVENESS

- Efficiency

- Information Payback

- COST

- Capital Costs

- RISK

- Safety and Emissions Control

- Developmental Requirements

While these three major issues can apply nearly universally to the analysis of complex systems, the criteria within each issue can vary depending on the type of application. For the PTU, key criteria such as safety and efficiency will be selected from the above and used as the basis for comparison. For some criteria (e.g., - efficiency) the comparison between two candidate concepts may be made with respect to a quantifiable value. In others (e.g. - safety) the capability for quantification is limited and the comparison among concepts

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Figure 2-38. PTU Selection Logic

relies more upon the judgment of the assessing parties than upon calculational basis. In either case, a comparison among concepts can be made performed on a relative basis and the final selection, done on the basis of figures-of-merit, can be made in an objective manner.

2.2.4.2 Constraints and Assumptions

The parametric studies for assessing cycle performance of the PTU, and characterizing the special configurations and parameter ranges for the PTU were based upon the following assumptions:

- (a) The PTU process system will be designed for 85 kW_t solar energy input to the SO₃ decomposition reactor.
- (b) The permissible range of acid concentration at the electrolyzer outlet is 30 to 70 weight percent.
- (c) Allowable system pressures are 5 to 20 atmospheres.
- (d) Single pressure level operation are assumed for the early studies.
- (e) SO₃ conversion at the specified temperature, pressure, and acid concentration are assumed at equilibrium.
- (f) SO₃ decomposition occurs at a fixed temperature of 1144K (1600°F).
- (g) Electrolyzer voltage is based upon a temperature of 100°C and a current density of 100 mA/cm². For certain analysis, a slightly higher electrolyzer temperature of 125°C was assumed.
- (h) All electrical power required beyond that generated by the process system itself is provided from the grid. For efficiency calculations, the external electrical generator is assumed to operate at 39.5 percent efficiency.

From the field of potential PTU concepts. A smaller group of candidate concepts has been selected by application of a list of constraints and desirable features for such a unit.

The following constraints and assumptions apply to the choice of candidate PTU configuration:

- The PTU must be compatible with distributed solar collector technology. This implies that the thermochemical portion of the system should be designed based on the capabilities of the collectors at the Jet Propulsion Laboratory Parabolic Dish Test Site, since this is the largest distributed collector facility available for testing that have the required temperature capability.
- The PTU shall be designed to provide a capability for investigating the effect of process parameter variation on critical performance areas such as hydrogen production, efficiency, product purity, SO₂ emissions levels, etc.
- The PTU shall be designed to provide ease of access for component inspection, removal and replacement. This is compatible with its use as a development tool for specific component designs and materials.
- The PTU design shall address the critical issue of SO₂ and oxygen separation by providing a processing system capable of meeting some maximum acceptable level of emissions of SO₂ and acid mist. No codified emission level exists for this type of plant. (40CFR60, subpart H, addresses the requirements for sulfuric acid production plants.) One of the major areas in the development of the PTU will be the evaluation of acid mist and SO₂ emissions potential, and the specification of proposed limits for these emissions.
- The PTU design shall provide remote operating capability for ease of integration with the potential solar heat source, and for maximum operator safety.

The features listed below are characteristics of the PTU that appear desirable. These features can be evaluated for their acceptability by use of the rating/selection system discussed in Section 2.2.4.1 as variations in the PTU concept

- The PTU should be designed for indirect coupling with the solar heat source. This permits the assembly and complete testing of both the electrolytic and thermochemical portions of the system in an integrated fashion prior to delivery to the collector site. It separates the design of the process system and that of the solar thermal receiver into discrete tasks. The disadvantage of requiring this approach is that the promising combination of a directly heated reduction reactor with distributed collector technology is a priority not considered. For this reason, it is listed as desirable rather than required.
- The PTU should be designed to operate with a minimum cooling water temperature compatible with that provided by an atmospheric cooling tower. This implies the presence of a refrigeration unit

in the overall PTU configuration if temperatures lower than 90°F are necessary to achieve acceptable levels and SO₂ and O₂ separation. In any event, a full-scale commercial plant has no recourse but to meet this requirement; a PTU (small-scale) can utilize an outside source of chilled water if necessary.

- The PTU should be designed to use the grid for all its electrical power requirements. Preliminary process studies on PTU-sized (85 kWt) units have shown that the quality and amount of waste heat available from the thermochemical systems is not sufficient to drive even the smallest of steam turbine generators. Other means of providing electrical power are conceivable - photo-voltaic cells, organic Rankine cycle turbine plants operating off PTU waste heat, or fuel cells using a portion of the hydrogen and oxygen produced by the process. Each of these has advantages and disadvantages both for the PTU as a developmental tool, for a full-scale commercial plant.
- The PTU design should permit the mounting of most major components on a single base, or skid, to provide for maximum transportability and compactness. The PTU can thus be assembled and partially pretested prior to shipment to the collector test site.
- The PTU should be designed for operation with a continuous thermal input. This implies a design that does not include chemical storage for 24-hour-a-day hydrogen production. The application of a commercial system will dictate the requirement for or against such round-the-clock capability. While the transient thermal input handling capability of the PTU systems is a critical issue and must be investigated fully, it is clear that the Sulfur Cycle process itself can be better understood if operating data can be taken from a continuously-operating process. This desirable feature is somewhat coupled to the selection of a process configuration using indirect coupling to the solar heat source. Such indirect coupling implies the capability for operation of the PTU using a combustion heat source, which can be provided at the development site or at the collector for 24-hour-a day operation in place of or alternative with the solar collector.
- Portions of the PTU process systems should be designed to permit operation with substantial variation of critical parameters, such as acid concentration, electrolyzer pressure, SO₃ decomposition reactor temperature. This feature is compatible with the development function of the PTU. Since diurnal and cloud-cover induced variations in solar flux imply varying operating conditions in the process system, it is important to have data on the effects of parametric variations upon PTU performance.

2.2.4.3 Candidate Configurations

Reference PTU Configuration

The reference configuration for the PTU shown in Figure 2-26 integrates the basic Westinghouse Sulfur Cycle with a solar heat source of 85 kWt input to the SO_3 decomposition reactor. The configuration has been developed as a result of the process cycle performance trade offs reported on in Section 2.2.3.

In addition to the specification of a given configuration, the reference process parameters and calculated performances form the basis for comparison with all other candidate PTU concepts. Some of these parameters, and the process information consistent with them are as follows:

- Solar thermal input to the decomposition reactor is limited to 85 kWt.
- Acid concentration in the electrolyzer is 63 weight percent.
- Nominal pressure is 20 atmospheres.
- Electrolyzer operating conditions: 100°C at 100 mA/cm^2 .
- No thermal or chemical storage capability is provided.
- Absorption towers using SO_2 -free acid and water are provided to effect SO_2/O_2 separation.

Table 2-24 lists the flowrate and composition of each stream for the reference configuration. A detailed description of the reference process is given in Section 2.2.2.

Alternatives to the Reference Process Configurations

Alternatives proposed to the reference process configuration described above are as follows.

For the use of an indirect heat source, there are three additional process configurations proposed. (Let the reference process be considered as Configuration 1).

- Configuration 2 - Using a single pressure for both electrolytic and thermochemical sections of the process system, this configuration substitutes a direct contact acid concentrator as shown in Figure 2-37 for the shell-and-tube type concentrator/evaporator of Configuration 1. Final evaporation of the concentrated acid must still be carried out by the introduction of thermal energy from the main heat source.
- Configuration 3 - Similar in most respects to Configuration 1, but uses a dual-pressure process, with electrolyzer pressure higher than decomposition reactor pressure.
- Configuration 4 - Dual-pressure process version of Configuration 2.

In addition to these four basic configurations, two additional configurations using a directly heated SO_3 reduction reactor concept are proposed. These configurations place the SO_3 decomposition reactor at the focal point of the solar collector to maximize the utilization of collected solar energy. These configurations are not as easily realizable as those with indirect coupling, nor do they easily permit full scale testing of the process away from the collector site. They will be considered to evaluate potential characteristics for commercial solar hydrogen systems using direct solar heating.

- Configuration 5 - Directly-heated SO_3 reduction reactor, using a single-pressure process. The electrolytic and SO_2/O_2 separation systems remain essentially the same as for the reference configuration.
- Configuration 6 - Identical to Configuration 5 but utilizing a dual pressure process, with electrolyzer pressure higher than decomposition reactor pressure.

2.2.4.4 Results of Evaluation Process

For the selection of a final PTU configuration for development, an evaluation process which considered certain basic selection criteria, and how well each candidate system met these criteria, was used. The process was based on classical systems optimization techniques, and used a combination/comparison of numerical values representing the "standing" or relative worth of each candidate

PTU configuration in each criterion, and on an overall basis, to aid in final selection of the most appropriate PTU configuration for further development.

Simply stated, the process used a "figure-of-merit" comparison to delineate the most worthy candidate configuration. The "figure-of-merit" (FOM) for the N^{th} configuration (FOM(N)) was defined as

$$\text{FOM}(N) = W_1 C_{1N} + W_2 C_{2N} + \dots + W_{I-1} C_{(I-1)N} + W_I C_{IN} =$$

$$\sum_{K=1}^I W_K C_{KN}$$

where

$W_K \equiv$ Numerical weighting factor for K^{th} criterion in find criterion set, single-valued for each K

$C_{KN} \equiv$ Normalized numerical value representing the worth of each configuration N in each criterion area K ; thus, a single discrete value of C must be derivable for each pair (K, N)

The set of K criteria and their respective weighting factors W_K were derived through an interactive process in which management and technical personnel familiar with advanced systems in general, and solar hydrogen processes in particular, were participants. The criteria will be further defined in the Appendix E.

The most worthy candidate concept was defined as that concept which, when evaluated with respect to the specified criterion set, resulted in the highest figure-of-merit. Thus, for three configurations A, B, and C, the relationships

$$\text{FOM}(A) > \text{FOM}(C)$$

$$\text{FOM}(B) > \text{FOM}(C)$$

$$\text{FOM}(B) > \text{FOM}(A)$$

would indicate that configuration "B" was most worthy of development in the PTU program.

Experienced technical and management personnel interacted to delineate appropriate criteria for PTU evaluation, and to assign weighting factors according to the perceived importance of the criteria to the final choice of PTU configuration. The appropriate criteria were selected so that they represented the three major issue areas which are generally common to the evaluation of nearly all complex systems, that is, the areas of effectiveness, cost and risk as described previously.

Classical systems engineering evaluation techniques always prescribe the utilization of evaluation criteria from all three areas in order to achieve a balanced viewpoint with regard to the specific system being evaluated. A further constraint on the selection of evaluation criteria is that they specifically address the prescribed mission or missions of the system being evaluated. Without such a constraint, the evaluation process can be rather pointless. The "success" of the PTU as a demonstration of the Sulfur Cycle hydrogen process, driven by a solar heat source, is tied directly to the capability of the selected configuration to achieve the previously-stated PUT Task Objectives. These objectives, from which the evaluation criteria must be derived, are as follows:

- (1) To demonstrate the production of hydrogen from a solar-driven Sulfur Cycle
- (2) To demonstrate the integration of the Sulfur Cycle thermochemical portions with distributed solar collector technology
- (3) To validate design choices, materials selections, process parameter ranges
- (4) To provide fundamental data on the overall process which can permit a more accurate assessment of development needs, performance requirements, and costing methods for future solar hydrogen systems, both large - and small scale.

Within the defined major issues areas, and with reference to the mission objectives previously specified, the following six (6) criteria were selected for the PTU evaluation process:

In the Effectiveness Area

- Information payoff potential (3,4)
- Experimental Flexibility (2,3,4)
- Performance Potential (1,4)

In the Risk Area

- Degree of Risk in Demonstration Technology (1,2,3,4)
- Safety and Environmental Considerations (3,4)

In the Cost Area

- Capital Costs of PTU equipment (less solar collector system costs) (3,4)

(Numbers in parentheses indicate which specific mission objectives each criterion bears a direct relation to).

The set of six criteria finally chosen limits the complexity of the selection process but provides full coverage with respect to the main task objectives.

Each criterion was assigned a weighting factor, as described previously, which related to its perceived importance in the scheme of PTU program development. These factors were chosen on a subjective scale of 0-10, with 10 representing a criterion of highest importance. The final weighting of each criterion, and the range of values before the achievement of a consensus, were as follows:

<u>Criterion</u>	<u>Final Weighting</u>	<u>Initial Range of Values</u>
Degree of Risk	9	6-10
Information Payoff	9	7-9
Experimental Flexibility	7	5-8
Performance Potential	5	1-6
Safety/Environmental Considerations	5	0-6
Capital Costs	5	3-5

The final weighting factors were also normalized, and the final form of the figure-of-merit then became for the Nth candidate configuration

$$\begin{aligned} \text{FOM}(N) = & 0.225 {}_1N + 0.225 C_{2N} + 0.175 C_{3N} \\ & + 0.125 C_{4N} + 0.125 {}_5N + 0.125 C_{6N} \end{aligned}$$

The six configurations described in Section 2.4.3 were chosen for the evaluation process. The basic selection process consists of evaluating the C_{jN} 's for each configuration N and criterion J, summing each set as appropriate, and choosing the highest-valued FOM.

The overall figures of merit for the six configurations were as follows:

<u>Configuration</u>	<u>FOM</u>	<u>Rank</u>
1	.832	1
2	.796	3
3	.833	1
4	.792	4
5	.608	5
6	.608	5

Since the third digit in the figure of merit has no real significance, the ranking provided no rationale for a choice between configurations 1 and 3. Configuration 1 was subsequently selected because of its greater simplicity related to a single operating pressure level.

The detailed numerical evaluation and the detailed listings of the C_{jN} 's are described in Appendix E.

2.2.5 COMPONENT SCOPING EVALUATION

Although detailed design of the PTU process equipment is not within the scope of work, a preliminary configuration design and sizing of PTU equipment was performed. In addition, each piece of equipment was rated in terms of its developmental status and a risk measure using a equipment application rating matrix. This matrix assigns equipment into four different classifications:

- A - Established technology
- B - Near Term
- C - Developmental
- D - Speculative

Table 2-30 illustrates the matrix and elaborates on these categories. The results of the equipment rating studies are summarized as follows:

Electrolyzer: Rating - C

The electrolyzer was scoped and sized based on the operating conditions of 20 atmospheres, 212°F (100°C) and a cell voltage of 0.6 volt. The module consists of a stack of 230 cells, each approximately 1.6 feet (49 cm) x 1.6 feet (49 cm), supported, together with the electrolyte distribution piping and minifolds, inside a pressure vessel. The anolyte and catholyte recirculation rates are shown in Table 2-24. It is recognized that the ultimate electrolyzer design will be based on the data of future pressurized cell tests and trade-off studies which will involve simultaneous optimization of anolyte and catholyte recirculation rates, cell voltages, current densities, inlet and outlet port dimensions and placement, and manifold dimensions.

HEAT EXCHANGERS (E1, E2, E3, E4 and E5)

The heat exchangers was sized for specific construction materials which should withstand the corrosive conditions. Further study is required to see if the materials are the most durable and economical available. Tubes were sized to

TABLE 2-30

EQUIPMENT APPLICATION RATING CRITERIA

APPLICATION RATING	EQUIPMENT STATUS EQUIPMENT STATUS	PERFORMANCE DATA BASE	EXTRAPOLATION FROM PERFORMANCE DATA BASE	WORK REQUIRED	R&D PROGRAM CHARACTERISTICS	
					RATIONALE	SUCCESS PROBABILITY
Established (A)	Firm selections can be made. Equipment is commercially available in form required.	Sufficient	None	Minimal, routine applications engineering	Not Applicable	Not Applicable
Near Term (B)	A number of equipment candidates are identified. Candidates are commercial or near commercial.	Incomplete	Short extrapolations from existing data base are involved.	Confirmatory testing and minimal R & D	Straight-forward	Virtually Certain
Developmental (C)	Equipment not previously designed, but engineering data base exists for design.	Incomplete; important gaps exist.	Large extrapolations from existing data required.	Considerable R & D is required.	A credible rationale exists. Alternative avenues are evident.	Good to excellent.
Speculative (D)	Equipment not previously designed with major materials, design or manufacturing uncertainties.	Sparse or Absent	Highly speculative or not possible.	Extensive R & D is required.	Rationale is not clear, or requires a break-through or serendipity.	Fair to Poor.

ensure turbulent flow, and the heat transfer coefficients were calculated for each stream based on its thermal properties. The following table lists the results:

HEAT EXCHANGER	MATERIAL	HEAT TRANSFER AREA (ft ²)	RATING
E1	Tantalum	1	B
E2	Teflon Clad Steel	5.1	A
E3	Tantalum	6.4	B
E4	Teflon Clad Steel	5.1	A
E5	316 Stainless Steel	5.2	A

Vaporizer I: Rating - C

Since the sulfuric acid solution leaves the tube side as a two phase fluid, the thin and long-tube vertical type evaporator was selected to minimize the two phase flow-separation. Also, due to high temperature and the corrosive nature of the fluids in both tube and shell sides, silicon carbide was selected for the material of construction. The total heat transfer area required is 6.33 ft².

Proposed Configuration: Tube and Shell

- Tube Side
- Triangular pitch, 0.75 inch center to center
  - 1/4 inch inner diameter
  - 1/2 inch outer diameter
  - 11 tubes, 5 feet in length

- Shell Side
- 2 5/8 inch inner diameter
  - 3 1/8 inch outer diameter

Vaporizer II: Rating C

The same type as Vaporizer I was selected. The total heat transfer area required is 3.95 ft².

Proposed Configuration:

- Tube Side
- 1/4 inch inner diameter
  - 1/2 inch outer diameter

Triangle pitch with center-to-center 5/8 inch.

- Shell Side
- 2 1/2 inch inner diameter
  - 3 inch outer diameter

Number of tubes - 12

Length - 3 1/2 feet plus heads

Recuperative Heat Exchanger: Rating - B

Based on the results of the ongoing material test program, Incoloy 800 (alloyed) was selected to contain the hostile gases. The total heat transfer area is 5.1 ft².

Proposed Configuration:

- Tube Side
- 3/8 inch inner diameter
  - 5/8 inch outer diameter

Triangle pitch with center-to-center 3/4 inch.

- Shell Side
- 2 5/8 inch inner diameter
  - 3 1/8 outer diameter

Number of tubes - 11

Length - 3 feet plus heads.

Decomposition Reactor: Rating - C

A shell and tube heat exchanger type reactor was selected. The heat source, hot helium, flows through the shell side. The first section of the reactor is a preheat section, where the shell side is filled with 5/32 inch diameter quartz pellets. The second section is the SO₂ reduction section, where the shell side is filled with the catalyst of 1/8 inch diameter Fe₂O₃ pellets (Iron oxide on alumina substrate, 20% Fe₂O₃). The material of construction will be alloyed Incoloy 800.

Proposed Configuration:

<u>Tube Side</u>	• 7/16 inch inner diameter • 11/16 inch outer diameter	Triangle pitch with center-to-center 15/16 inch.

<u>Shell Side</u>	• 4 7/8 inch inner diameter • 5 5/8 inch outer diameter

Number of tubes - 24

Total Length - 17 feet

Catalyst Section - 5 feet

Absorption Columns 1 and 2: Rating - A

The SO_2 absorption should be conducted in packed columns for the PTU system because the plate column diameters at permissible velocities are less than two (2) inches for the flow rates specified. This is unfeasible for a plate column.

The column diameters for the 2 beds backed with 1/4 inch Raschig Rings at a vapor velocity of one half of the flooding velocity is calculated using the "Generalized Correlation for Flooding and Pressure Drop".

In differential contact columns the tower height is the product of the number of transfer units and the height of a transfer unit. Since the mass transfer coefficient of the $\text{SO}_2/67\% \text{H}_2\text{SO}_4$ system is unavailable; empirical relationships based on the properties of the sulfuric acid solution were used to estimate the height of a transfer unit for Absorber-1. This is unnecessary for Absorber-2 because the mass transfer coefficient of the SO_2/water system is available.

The transfer units needed to make the required separation is determined for each column to calculate and depth of packing. The column dimensions are specified in the following table:

Surge Tank - 1, 2, 3, Flash Drums - 1,2 and Mixing Drum: Rating - A

All the tanks and drums for the PTU were sized to retain incoming liquid for twenty (20) minutes except mixing drum.

SURGE TANK-1:

Material of Construction: KYNAR PVDF - lined steel
Volume: 1.53 ft³ (14.43 gal.)
Configuration: 8" diameter, 4'4" in height with two heads.

SURGE TANK-2:

Material of Construction: KYNAR PVDF - lined steel
Volume: 0.27 ft³ (2.03 gal.)
Configuration: 4" diameter, 3' in height with two heads.

SURGE TANK-3:

Material of Construction: KYNAR PVDF - lined steel
Volume: 0.38 ft³ (2.84 gal.)
Configuration: 4" diameter, 4'5" in height with two heads

FLASH DRUM-1:

Material of Construction: KYNAR PVDF - lined steel
Volume: 3.44 ft³ (25.7 gal.)
Configuration: 10" diameter, 5'5" in height with two heads

FLASH DRUM-2:

Material of Construction: KYNAR PVDF - lined steel
Volume: 1.77 ft³ (13.2 gal.)
Configuration: 8" diameter, 5'1" in height with two heads

MIXING DRUM: Based on 10 minute retention time of incoming liquid flow.

Material of Construction: KYNAR PVDF - lined steel
Volume: 104.2 ft³ (780 gal.)
Configuration: 3' diameter, 14'8" in height with two heads

Throttle Valve: Rating - B

It is to reduce the pressure of the process stream from 294 psia to 2.5 psia at a flowrate approximate 5500 gallons per hour of 63 w/o H_2SO_4 solution. It may require several valves in parallel to accomplish thw work.

Blowers (B-1 and B-2): Rating - A

B-1 has to handle 29.2 ACFH of O_2/SO_2 gases and overcomes a head up to 28 inches of water. B-2 must handle 22.6 ACFH of O_2/SO_2 gases with up to a head of 14 inches of water.

Vacuum Pump (PV-1), Compressor (C-1) and Helium Circulator: Rating - B

The vacuum pump is to compress the SO_2 and H_2O VAC from 2.5 psia to 14.7 psia, and the power requirement is 5.75 horsepower. The vacuum pump must have internal cooling system.

The compressor is to compress the SO_2 and H_2O vapor from 14.7 psia to 294 psia, and the power requirement is 4.25 horsepower. It is proposed that a three stage centrifugal compressor with inter-coolers be employed.

The helium circulator is to circulate 514.4 pound per hour of helium. The power requirement is 17.4 horsepower.

Pumps (P-1, 2, 3, 4, 5, 6 and 7): Rating - A

All pumps for the PTU are teflon diaphragm with the balance of material being Hastelloy-C except P-5 and P-6. The discharge pressure is at least 330 psig.

- P-1: 38 gallons per hour (gph), 0.18 horsepower (hp)
- P-2: 38 gph, 0.154 hp
- P-3: 4,678 gph, 1.07 hp
- P-4: 380 gph, 0.02 hp
- P-5: Water pump, steel construction, 5 gph, 0.02 hp
- P-6: 316 S. S. Construction, 9 gph, 0.04 hp
- P-7: 35gph, 0.004 hp

The maximum capacity of a currently available pump is not sufficiently large for serving as P-3, thus several pumps in parallel will be required. To manufacture a larger capacity pump for P-3, some developmental work is required.

From the design and process studies that led to the selection of the PTU Configuration, the component scoping, sizing and rating studies described above were made. From these results, it is evident that those four components that were rated in category C (or developmental) represent those pieces of equipment that need more technology development than other components in the PTU.

Therefore, the on-going technology development efforts have emphasized this particular set of components, the electrolyzer, Vaporizer I, Vaporizer II, and the decomposition reactor. The electrolyzer is unique in that its development has been sponsored by a separate contract from DOE/STOR. Therefore, efforts under the Solar Hydrogen Program focused on the high temperature components, two of which interface with solar receivers.

2.3 PLANT OPERATIONAL STUDIES

Early, process studies 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 scoping economic assessments were made. Those results are presented in Section 2.4.

The plant operational studies, presented herein, were performed to gain 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.

2.3.1 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 earlier 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, these 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 2.3.5, Economic Assessment). This cost is approximately the same as the costs estimated during earlier scoping studies.

However, due to changes in the plant process flowsheet, this 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 earlier 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.

2.3.2 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 2-39. 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 2-40, and a process flow sheet is shown in Figure 2-41.

The plant is composed of a number of major and secondary subsystems, as indicated on the block schematic, Figure 2-40 and listed below.

- Group A - Solar Thermal Electric Plant

- A-1 - Steam Receiver Subsystem
- A-2 - Steam Cycle Equipment
- A-3 - Thermal Storage Subsystem

Figure 2-39. Solar/Hydrogen/Chemical Plant Arrangement

Figure 2-40. Plant Block Schematic

Figure 2-41. Process Flow Sheet for Solar Hydrogen Plant Daytime Operation

- 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

The major components, functions, and operating requirements of each of the major subsystems are shown in Table 2-31.

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.

2.3.3 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:

TABLE 2-31

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.

MODE

MAJOR CHARACTERISTICS

1	● Steam receiver supplying HP turbine and TES ● Hot air receiver operating normally ● Sulfur dioxide storage charging
2	● Storage subsystems all in standby because insolation insufficient to charge ● Hot air receiver operating normally
3	● Steam receiver and TES supplying HP turbine ● Hot air receiver operating normally ● Sulfur dioxide storage discharging ● Supplemental electric power (grid) required
4	● Steam receiver in standby ● Hot air receiver in standby ● TES supplying HP turbine ● Sulfuric acid storage charging ● Supplemental electric power (grid) required
5	● Steam receiver charging TES ● Hot air receiver charging SO₂ storage ● Electrolyzer in standby
6	● All subsystems shutdown

The individual operating modes of the various subsystems during the six plant operating modes are shown in Table 2-32.

TABLE 2-32

SUBSYSTEM OPERATING MODES

Subsystem	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5	Mode 6	
A-1 Steam Rec.	0	0	0	S	0	S	0 = Operating S = Standby C = Charging D = Discharging
A-2 H.P. Turb./Gen.	0	0	0	0	S	S	
A-3 Thermal Stor.	C	S	D	D	C	S	
B-1 Electrolyzer	0	0	0	0	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.	0	0	0	S	0	S	
D-2 Acid Decomp.	0	0	0	S	0	S	
D-3 L.P. Turb./Gen.	0	0	0	S	0	S	
D-4 O ₂ Turbine	0	0	0	S	0	S	
D-5 SO ₂ /O ₂ Sep.	0	0	0	S	0	S	
E-1 Ammonia Plt.	0	0	0	0	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 2.3.5), 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.

2.3.4 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 heliostat 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:

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

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, $\frac{\text{watts}}{\text{m}^2}$

a = 0.14 per kilometer altitude

c = 0.357

s = 0.678

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 2-42. 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 2-42 are measurements at Albuquerque on day 183 (July 2, 1976) as reported by Sandia Laboratories. 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 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 2-43.

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).

Figure 2-42. Solar Flux Versus Time-of-Day for Three Days of the Year

Figure 2-43. Heliostat Field Layout with Representative Heliostat Locations

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.

The results of these calculations are presented in Figure 2-44. 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, along with results of calculations performed with the MIRVAL computer code. Estimated values for the solar hydrogen plant are shown in Table 2-33.

Receiver Collection Efficiency

The receiver collection losses include spillage due to reflected rays missing the target (aiming losses), receiver reflectivity, receiver radiation

Figure 2-44. Calculated Solar Field Cosines

TABLE 2-33
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%

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 and these values are shown in Table 2-34. The spillage, reflectivity, and piping thermal losses are assumed 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:

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

The results for a steam external solar receiver and a hot air cavity receiver are shown in Figures 2-45 and 2-46. 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 2-45 and 2-46) 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 2-40). 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

TABLE 2-34

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			

Figure 2-45. Thermal Power Absorbed in Steam Receiver
Versus
Time-of-Day and Time-of-Year

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 2-45 and 2-46. Integration 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 2-45 and 2-46 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 2-47. 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 2-45). 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 2-35. 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 2-46. Thermal Power Absorbed in Hot Air Receiver Versus Time-of-Day and Time-of-Year

Figure 2-47. Power Absorbed in Receiver Versus Time

TABLE 2-35

STEAM RECEIVER

DESIGN DAY	RECEIVER Watts/m ²	DESIGN POINT 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

2.3.5 ECONOMIC CONSIDERATIONS

The system designs shown in Table 2-35 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 earlier 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 2-36. A breakdown of the production costs is given in Table 2-37.

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 2-48. 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 2-36
CAPITAL COST SUMMARY (MILLIONS OF 1978 DOLLARS)

DESIGN DAY	Winter Solstice		Winter Solstice		Summer Solstice			
Receiver Design (Reference Time)	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 2-37

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 2-48. 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 that had been made previously.

2.4 PROCESS SCOPING STUDIES

The Sulfur Cycle Water Decomposition Process requires electric power and high temperature ($\sim 1600^{\circ}\text{F}$) thermal energy; both of which may be obtained from solar radiation. The resultant hydrogen may then be used as a feedstock for a chemical or synthetic fuel process. Thus, solar-derived fuels and chemicals may be produced from an integrated solar/hydrogen/chemical complex, with hydrogen production as an intermediate process. The objective of the studies described herein was to identify specific solar/hydrogen/chemical processes and approaches which appear to have the greatest promise with respect to technical and economic feasibility and ultimate market acceptance.

These studies were performed in the following steps:

- Establishment of general guidelines
- Solar/hydrogen process definition and tradeoffs
- Chemical and fuel process scoping studies
- Flowsheet preparation
- Economic scoping

2.4.1 GENERAL GUIDELINES

The Sulfur Cycle requires thermal energy input for acid vaporization/decomposition and for electric power generation. Maximum temperature requirements are approximately 1600°F for the acid portion and $900\text{--}1000^{\circ}\text{F}$ for the steam-electric system. These temperatures require high solar concentration ratios which can be obtained most readily with central receiver-type solar systems. Using this rationale, the following general guidelines and groundrules were established for conducting the process studies:

- Hydrogen plant process heat is to be solar-derived.

- Technology base for the high-temperature solar receiver is to be consistent with a Black and Veatch study.⁽²⁻²⁴⁾ Other means for obtaining the required solar-thermal energy are to be investigated.
- The solar portion of the process is to be limited to 350 - 400 MWt absorbed in the receiver at noon, winter solstice. This is in keeping with present projections for commercially-sized solar central-receiver plants (approximately 100 MW_e).
- Hydrogen production is to be in the range 10 - 30 million SCFD. This is limited by the solar-thermal plant size, and is dependent on modes of operation and energy storage.
- Technology base for the hydrogen production plant is to be consistent with a 1977 Westinghouse report to DOE⁽²⁻²⁵⁾ with updated technical factors as determined through the continuing development of the process.
- Initial considerations are to be given to continuous (24-hour) plant operation, using intermediate chemical energy storage, and intermittent operation of the subsystems depending upon insolation. Batch operation of the hydrogen plant or the end-product process will be given secondary considerations.
- Technology bases for the end-product processes (chemical and/or synthetic fuel) are to be determined as the processes are more specifically identified.
- Site-peculiar conditions are to be based on an Albuquerque, New Mexico site. This includes characteristics of available energy sources (i.e., solar, coal, and electric).

2.4.2 SOLAR/HYDROGEN PROCESS DEFINITIONS AND TRADE-OFFS

A number of concepts were analyzed to evaluate the feasibility of integrating the Sulfur Cycle with the solar heat source and the end-product process. From this evaluation, five generalized system design options were selected; their characteristics are given in Table 2-38. The general approach is based on use of two central receiver "power towers" - one for sulfuric acid decomposition and one for electric power generation. A sketch of a typical solar/hydrogen/chemical plant arrangement is shown in Figure 2-49. Sulfuric acid from the electrolyzer is vaporized and decomposed within the solar receiver/decomposition reactor. Electric power is generated from steam produced in the steam receiver tower. Feed-water heating is supplied by waste heat from the acid decomposition tower.

TABLE 2-38
SYSTEM DESIGN OPTIONS

<u>Option</u>	<u>Electric Power Generation Type</u>	<u>Energy Source For Electric Power</u>	<u>Energy Source For Acid Decomposition</u>	<u>Storage Means For Electrical Power</u>	<u>Storage Means For Acid Decomposition</u>
1	High Pressure Steam Turbine	Steam Solar Receiver Tower	Solar Receiver Tower/Decomposition Reactor	Thermal (Oil/Rock)	Chemical (SO ₂)
2	Fuel Cells + Low Pressure Steam Turbines	H ₂ + O ₂ Acid Regen. Waste Heat	Two Solar Receivers --	Chemical (H ₂ + O ₂) None	Chemical (SO ₂) --
3	Purchased Power + Low Pressure Steam Turbines	Purchased Acid Regen. Waste Heat	Solar Receiver --	None None	Chemical (SO ₂) --
4	High Pressure Steam Turbines (Daytime Operation Only)	Steam Solar	Solar Receiver	None	None
5	High Temperature Helium Gas Turbines (Daytime Operation Only) + Low Pressure Steam Turbines	Helium Solar Receiver Tower Acid Regen. Waste Heat	Solar Receiver --	None None	None --

Figure 2-49. Solar/Hydrogen/Chemical Plant Arrangement

Sizing of the solar collector fields and receivers was based on previous studies⁽²⁻²⁶⁾ employing the MIRVAL computer code, developed at Sandia Livermore. The collector fields were sized based on annual average values for the field cosine angle, shadow and blocking losses, etc. Direct normal solar radiation was taken as 1045 watts per square meter for nine hours per day. Actual average annual insolation was accounted for in the determination of the plant capacity factor.

The steam-electric plant design and performance was based on studies performed for DOE for 100 MW_e solar thermal power systems^(2-27, 28, 29). The receiver chosen was of the McDonnell-Douglas external receiver-type. Turbine-generator performance was taken as 34.7 percent conversion of thermal input to electric power (heat rate = 9840 Btu/KW-Hr). Thermal energy storage was based on the oil/rock sensible heat-type. All heat rejection was by dry cooling towers.

The proposed receiver/decomposition reactor conceptual design was based on reviews of high-temperature central receivers being studied under existing DOE contracts. Specifically, the Boeing closed-cycle helium receiver⁽²⁻³⁰⁾ and the Black and Veatch open-cycle air receiver were reviewed. The design chosen was a downward facing cavity with a 360° collector field. The solar flux is transferred directly into the vaporized sulfuric acid through silicon carbide tubes (similar to the proposed Black and Veatch air receiver).

A significant result of the receiver evaluation was a decision to use separate steam and acid receivers. The proposed cavity-type acid receiver requires a rather small, efficient aperture and a corresponding tightly-packed heliostat field. Large capacities (i.e., 100 MW_e equivalent) result in high field losses and extremely tall towers. Therefore, it was decided to limit the solar heat input to the high-temperature acid receiver to approximately 175 MW_t.

The Sulfur Cycle process design and flowsheet configuration were adopted from a previous Westinghouse study for DOE⁽²⁻²⁵⁾. However, some modifications were

required for compatibility with the solar heat source. Study of the solar receiver equipment arrangement within the acid receiver tower indicated an option of pumping liquid sulfuric acid to the tower top (~ 660 ft) or transporting heat to the ground for ground-level vaporization. It was determined that the pumping power would be approximately 500 HP (for a 13×10^6 SCFD H_2 plant) greater for vaporization at the tower top than on the ground. This was considered insufficient to justify a secondary heat transport loop for ground-level vaporization, and further work was based on vaporization, as well as decomposition, conducted in the solar receivers at the top of the tower. In related work, the acid vaporization/decomposition system design was revised to eliminate a regeneratively-heated decomposition reactor and to perform final vaporization with solar heat. This simplified the receiver circuitry and permitted a once-through design.

Several sulfuric acid concentrator operating schemes and acid concentrations were analyzed to determine their effects on the overall solar/hydrogen process efficiency. Flash evaporation and thermal acid concentration with steam separation were studied and found to offer little or no efficiency improvement over straight thermal vaporization. All process flowsheets were based on 80 w/o acid and straight thermal vaporization. Electrolyzer performance was based on a total cell voltage equal to 600 mV with a current density of 200 mA/cm^2 and a system pressure of 20 atm.

2.4.3 SELECTED CHEMICAL AND FUEL PROCESSES

Scoping studies were performed to identify potential end-product processes for the production of chemicals or synthetic fuels. Emphasis was placed on processes that had hydrogen capacity requirements compatible with the proposed solar/hydrogen plant output (10-30 million SCFD) and that could be integrated into a stand-alone solar/hydrogen/chemical or fuel complex. Smaller user applications (e.g., hydrogenation of edible fats and oils) were dismissed. Likewise, large potential users requiring complex integration and other extensive plant processes (e.g., petroleum refining) were deferred for future study.

Five processes were selected for further analysis: chemical processes for producing ammonia, methanol, and hydrogen peroxide; an iron ore direct reduction process; and a coal liquefaction plant. Each process was configured as follows:

2.4.3.1 Ammonia Production Plant

The ammonia production plant is a process for synthesizing anhydrous ammonia (NH_3) from hydrogen and nitrogen. Ammonia manufacture is the largest single hydrogen user in the United States. The ammonia synthesis plant flowsheet is shown in Figure 2-50. Mass flowrates are given in Table 2-39. Nitrogen is obtained from the cryogenic separation of air. The solar/hydrogen plant provides both hydrogen feedstock and electric auxiliary power.

2.4.3.2 Methanol Synthesis

Methanol is manufactured by a synthesis process similar to ammonia. The main difference is the requirement of a carbon feedstock (as CO or CO_2). Present process designs and catalysts require CO or a mixture of CO and CO_2 . However, several opportunities exist for employing a solar/hydrogen/methanol plant without a direct fossil fuel feedstock. Carbon dioxide could be obtained from stack gases, separated from air or seawater, or recovered from a calcining kiln. The latter scheme is shown schematically in Figure 2-51. The calciner exhaust is cleaned and the carbon dioxide recovered. A portion of the CO_2 is passed through a reverse shift reactor where CO_2 and H_2 are converted to CO and water. Approximate performance and utilities requirements for the methanol synthesis plant were obtained from the Pullman Kellogg Company. (2-31)

2.4.3.3 Hydrogen Peroxide

Hydrogen peroxide manufacture is the third chemical process chosen for evaluation. Although not nearly as high a volume chemical as ammonia or methanol, its consumption is expected to grow as new markets are developed. Presently 70-75 percent of the 200 million pounds of hydrogen peroxide consumed annually is used for textile bleaching. However, the lack of harmful byproducts or chemical residue, the storage capability, and the ease of metering and feeding make hydrogen peroxide a strong candidate to replace other oxidizing agents in a variety of applications, such as municipal waste treatment.

Figure 2-50. Ammonia Synthesis Plant

Figure 2-51. Solar/Hydrogen/Methanol-Lime Complex

TABLE 2-39

MATERIAL BALANCE - AMMONIA SYNTHESIS PLANT

Stream No.	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	Total Aux. Power		
Option No.	Hydrogen 10 ⁶ SCFD	Flow Rate in Lbs. Per Hours										Ammonia TPD	KWe
1 (and 3,4,5)	12.74	2,818	13,053	15,871	79,390	1,587	77,803	77,803	63,519	14,284	15,871	190	9,006
2	8.47	1,873	8,675	10,549	52,767	1,055	51,712	51,712	42,219	9,494	10,534	127	7,442

The manufacturing process chosen was the autoxidation of hydroquinone⁽²⁻³²⁾. The process flowsheet is shown in Figure 2-52. An alkylated anthraquinone, usually 2-ethyl or 2-tertiary butyl anthraquinone, in a solvent is fed to the hydrogenator and reduced to the hydroquinone with hydrogen and a catalyst. After catalyst separation, the hydroquinone is oxidized with air or oxygen to regenerate quinone and form hydrogen peroxide. The product is a 35 percent solution of H_2O_2 in water. All vessels in contact with the H_2O_2 are high purity aluminum to prevent decomposition by trace metals.

2.4.3.4 Direct Iron Ore Reduction

The first step in iron production is the reduction of iron oxides, in the form of iron ore, pellets, mill scale, or dust, to basic iron. Most existing processes employ blast furnaces, utilizing coke as the reductant. However, an increasing number of new iron ore processing plants are employing direct reduction. In direct reduction processes the iron oxide is heated to below its melting point and reacted with a reducing gas, usually a mixture of CO and H_2 .

The use of a pure hydrogen reducing gas, without CO, has been studied by Bethlehem Steel Company⁽²⁻³³⁾. A pilot plant of the process, known as H-Iron, was operated for a short time, but presently the development effort is dormant. The process is shown schematically in Figure 2-53. Dry hydrogen is passed counter-current to 10-mesh hematite ore in a fluidized bed reactor yielding an iron power suitable for steel-alloy production in an electric furnace. The reduction reaction is endothermic and the heat is supplied by the sensible heat in the feed. The hydrogen is heated by the combustion of a portion of the hydrogen vented from the cooling tower.

2.4.3.5 Coal Liquefaction

Coal liquefaction, specifically the hydrogenation of coal to produce syncrude, was also identified as a potential candidate process. Present concepts for these processes use char and coal to react with water for the production of hydrogen. The hydrogen is used to increase the H/C ratio of the coal in the hydrogenation reactor. The carbon utilization efficiency (carbon in syncrude over carbon in coal) is only about 60 percent. Therefore, 1.7 times as much synthetic fuel could theoretically be produced from the same amount of coal if a solar/hydrogen plant were used for hydrogen production.

A meeting was held with the DOE Pittsburgh Energy Research Center to help quantify the aspects of a solar/hydrogen coal liquefaction plant. (2-34) Although potential coal savings were acknowledged, the impact of solar/hydrogen integration on process efficiency, coal utilization, char production and use, economics, etc. was not determined. There appears to be no accurate way to separate one major subsystem (i.e., the hydrogen generator) from the integrated liquefaction plant without impacting other variables. Preparation of a meaningful flowsheet requires the cooperation of the coal liquefaction plant designers to modify the process to accommodate the outside hydrogen source. Since this appeared outside of the scope of the present process studies, further work on a solar/hydrogen/coal liquefaction plant was deferred.

2.4.4 PROCESS FLOWSHEETS

Simplified process flowsheets were prepared for the various solar/hydrogen/chemical or fuel complexes. The ammonia plant was considered a base case and flowsheets were prepared for all five System Design Options (see Table 2-38). Flowsheets for the other four processes were prepared for Options 1 (steam turbines) and 3 (purchased power). For each option, flowsheets were prepared for both day (9 hours) and night (15 hours) operation.

2.4.4.1 Solar/Hydrogen/Ammonia Plant

- a) Option 1 - Electric Power Generation with High Pressure Steam Turbines and Thermal Energy Storage

The process flowsheets for Option 1 (Day and Night Operation) are shown in Figures 2-54 and 2-55. Total thermal energy input into the plant is 401 MW_t for nine hours per day, divided between the steam receiver (224 MW_t) and the acid receiver (177 MW_t). Steam turbine-generator efficiency is 34.7 percent when operated with high pressure steam direct from the solar receiver and 24.3 percent when operated with the lower pressure steam generated from the thermal storage system. The waste heat from the acid vaporization and decomposition system is entirely utilized in the electric power generation subsystem. Approximately one-third of the waste heat is used for feedwater heating and the remainder to charge the thermal energy storage system.

Figure 2-54. Solar/Hydrogen/Ammonia Plant Option 1 - Steam Turbines Daytime Operation

Figure 2-55. Solar/Hydrogen/Ammonia Plant Option 1 - Steam Turbines Night Operation

Since the solar thermal input is only available for nine hours per day, energy storage systems are required. Sensible heat oil/rock storage is used for thermal energy storage and results in a 30 percent degradation in steam turbine-generator performance during night operation. The acid receiver heat is stored as chemical energy in the form of liquefied sulfur dioxide. The acid vaporization and decomposition system is oversized in respect to the electrolyzer and sulfuric acid separation system to enable excess SO_2 generation during the day to charge the storage tanks. Based on nine hours of insolation, the decomposition system has 24/9 (267 percent) the capacity of the electrolyzer.

The ammonia synthesis plant operates twenty-four hours per day with a capacity of 190 tons per day of anhydrous ammonia. This is a small plant in comparison to new natural gas-fired ammonia plants with a capacity of 1000-1500 tons per day. Auxiliary power requirements for the ammonia plant are approximately 9,000 KW and are supplied from the solar/electric system. Total plant energy consumption is 64.8 MMBtu per short ton ammonia based on thermal energy absorbed in the receivers.

b) Option 2 - Electric Power Generation with Fuel Cells and Hydrogen/Oxygen Storage

Process flowsheets are shown in Figures 2-56 and 2-57. Two acid receivers of 175 MW_t each are used in order to produce enough hydrogen to feed both the fuel cells and the ammonia plant. Hydrogen plant operation and SO_2 storage is as in Option 1 (Steam Turbines). Electric power is produced by hydrogen/oxygen fuel cells fed with approximately 67 percent of the hydrogen produced by the electrolyzer. The electric power conversion efficiency of the fuel cells is assumed to be 61.5 percent (based on a cell voltage of 900 mV).

Waste heat from the acid vaporization and decomposition system is used to power a low pressure steam turbine cycle with a thermal efficiency of 15 percent. The low pressure steam turbine generates 45 percent of the daytime electrolyzer power requirements. Nighttime electrolyzer power is supplied solely by the fuel cells, which receive additional hydrogen from a storage system.

Figure 2-56. Solar/Hydrogen/Ammonia Plant Option 2 - Fuel Cells Daytime Operation

Figure 2-57. Solar/Hydrogen/Ammonia Plant Option 2 - Fuel Cells Night Operation

The ammonia plant capacity is 127 tons per day and auxiliary power requirements are approximately 7440 KW. Total plant energy consumption is 84.7 MM Btu per ton ammonia based on thermal energy absorbed.

c) Option 3 - Purchased Electric Power with no On-Site Power Generation

The process flowsheets for the purchased electric power option are shown in Figures 2-58 and 2-59. The acid receiver and SO_2 storage subsystems are identical to Option 1. No solar/electric plant is required. Acid waste heat is used to drive a low pressure steam turbine cycle which provides 45 percent of the daytime electrolyzer power. Purchased power requirements are approximately 20,100 KW during the day and 29,200 KW at night.

Ammonia production is the same as Option 1, 190 tons per day. Total plant energy consumption, based on thermal energy absorbed in the acid receiver and purchased electric power (3413 Btu/KW-Hr), is 39.7 MM Btu per ton of NH_3 . The significant decrease in plant energy consumption represents the deletion of a thermal energy to electric energy conversion step. If a 33 percent thermal efficiency is assumed for the off-site power energy consumption increases to 62.3 MM Btu per ton.

d) Option 4 - Day/Night ON/OFF Hydrogen Plant Operation with Electric Power Generation with Steam Turbines and H_2 Storage

This option is similar to Option 1 with the exception that the entire solar/hydrogen plant, including the electrolyzers, only operates for nine hours per day. In this case the electrolyzers and steam turbine-generators must also be oversized by 24/9 (267 percent) to produce sufficient hydrogen for twenty-four hour ammonia plant operation. Process flowsheets are shown in Figures 2-60 and 2-61.

Excess hydrogen produced during the day is stored chemically in combination with iron titanium hydride. Acid waste heat is used for feedwater heating and to charge a hot water storage system. The hot water (210°F) is used to release the hydrogen from the

Figure 2-58. Solar/Hydrogen/Ammonia Plant Option 3 - Purchase Electric Power Daytime Operation

Figure 2-59. Solar/Hydrogen/Ammonia Plant Option 3 - Purchase Electric Power Daytime Operation

Figure 2-60. Solar/Hydrogen/Ammonia Plant Option 4 - On/Off with H₂ Storage Daytime Operation

Figure 2-61. Solar/Hydrogen/Ammonia Plant Option 4 - On/Off with H₂ Storage Night Operation

hydride during night operation. Solar/electric thermal input is 136 MW_t . This is considerably less than Option 1 and represents the increased efficiency of hydrogen storage versus thermal storage and the lack of storage for ammonia plant night auxiliary power production. Night auxiliary power (9000 KW) is purchased from the grid.

Ammonia plant output is maintained at 190 TPD. Total plant energy consumption is 53.0 MM Btu per ton NH_3 .

e) Option 5 - Day/Night ON/OFF Hydrogen Plant Operation with Electric Power Generation with High-Temperature Helium Gas Turbines and H_2 Storage

As with Option 4, the helium gas turbine option is designed for nine-hour operation of the entire solar/hydrogen plant. Twenty-four hour operation of the electrolyzers, similar to Option 1, was not considered for the helium gas turbine cycle due to the lack of a viable high-temperature storage system. Process flowsheets are shown in Figures 2-62 and 2-63.

Overall plant design is similar to Option 4 except for the substitution of the helium closed-cycle Brayton system for the steam Rankine cycle. Helium is heated directly in the solar receiver and results in an electric power generation thermal efficiency of 47 percent. The acid waste heat drives low pressure steam turbines as well as charging the hot water storage system.

Ammonia production is the same as Options 1, 3, and 4, or 190 TPD. Total plant energy consumption is 49.6 MM Btu per ton NH_3 .

A summary of all five ammonia plant major characteristics is shown in Table 2-40.

TABLE 2-40

SOLAR/HYDROGEN/AMMONIA PLANT MAJOR CHARACTERISTICS

	<u>Option 1</u> (Steam Turbines)	<u>Option 2</u> (Fuel Cells)	<u>Option 3</u> (Purchased Power)	<u>Option 4</u> (On/Off)	<u>Option 5</u> (Gas Turbines)
Ammonia Production (tons/day)	190	127	190	190	190
Solar Input (Electric Power Generation) - MW_t	224	0	0	136	115
Solar Input (Acid Decom- position) - MW_t	177	350	177	177	177
Purchased Power Requirements					
• Day - MW_t	0	0	20.1	0	0
• Night - MW_t	0	0	29.2	9.0	9.0
Overall Energy Consumption (MM Btu/ton NH_3)	64.8	84.7	39.7	53.0	49.6

2.4.4.2 Solar/Hydrogen/Methanol Plant

- a) Option 1 - Electric Power Generation with High Pressure Steam Turbines and Thermal Energy Storage

The solar/hydrogen plant design for the methanol complex is similar to the design for the ammonia plant. Solar/hydrogen/methanol flow-sheets for Option 1 are shown in Figures 2-64 and 2-65. Except for reduced auxiliary power requirements, resulting in a 156 MW_t solar/electric receiver system, the operation and sizing is identical to Option 1, Ammonia.

The methanol plant receives hydrogen and electric power from the solar/hydrogen plant. Carbon dioxide from a calciner or similar source is recovered and cleaned and a portion shifted to CO as discussed previously. Methanol production, based on twenty-four hour operation, is 215 tons per day (65,000 gallons per day). As with the ammonia plant, this is a small capacity in comparison with modern 1000-1500 ton per day facilities. Auxiliary power requirements are 2,020 KW. Total plant energy consumption, based on thermal energy absorbed in the receiver, is 47.6 MM Btu per ton of methanol.

- b) Option 3 - Purchased Electric Power with No On-Site Power Generation

The Option 3 methanol Plant design is similar to the Option 3 ammonia plant except for the difference in auxiliary power requirements. Purchased power capacity is approximately 13,100 KW during the day and 22,200 KW during the night.

Methanol output is the same on Option 1 (215 tons per day). Total plant energy consumption is 32.5 MM Btu per ton based on the electric power entering the plant. The plant energy consumption increases to 47.0 mm Btu per ton when an off-site generation efficiency of 33 percent is considered.

Figure 2-65. Solar/Hydrogen/Methanol Plant
Option 1 - Steam Turbines
Night Operation

Figure 2-65. Solar/Hydrogen/Methanol Plant
Option 1 - Steam Turbines
Night Operation

2.4.4.3 Solar/Hydrogen/Hydrogen Peroxide Plant

- a) Option 1 - Electric Power Generation with High Pressure Steam Turbines and Thermal Energy Storage

The solar/hydrogen/hydrogen peroxide plant flowsheets are shown in Figures 2-66 and 2-67. The design is similar to Option 1 for the ammonia and methanol complexes. The solar/electric receiver is rated at 159 MW_t .

Hydrogen peroxide production is 489 tons per day of 100 percent H_2O_2 . The annual production of this plant would be 228 million pounds, which exceeds the total U.S. annual market of 200 million pounds. A typical new plant capacity is 70 million pounds per year. Total plant energy consumption is 21.1 MM Btu per ton of 100 percent H_2O_2 .

- b) Option 3 - Purchased Electric Power with No On-Site Power Generation

The Option 3 hydrogen peroxide plant is also similar to the ammonia and methanol plant designs. Purchased power requirements are approximately 13,400 KW during the day and 22,500 KW during the night.

Hydrogen peroxide production is maintained at 489 tons per day. Total plant energy consumption is 14.3 MM Btu per ton of 100 percent H_2O_2 based on electric power input and 20.8 MM Btu per ton when off-site energy conversion efficiency is considered.

2.4.4.4 Solar/Hydrogen/H-Iron Plant

- a) Option 1 - Electric Power Generation with High Pressure Steam Turbines and Thermal Energy Storage

The solar/hydrogen/H-Iron plant flowsheets are shown in Figures 2-68 and 2-69 and are similar to the other Option 1 designs. The solar/electric receiver absorbs reflected solar energy at the rate of 155 MW_t .

The H-Iron reduction plant has a capacity of producing 624 tons per day of iron powder. Annual production of 146,000 short tons compares with medium-sized direct reduction plants. Auxiliary power require-

Figure 2-66. Solar/Hydrogen/H₂O₂ Plant Option 1 - Steam Turbines Daytime Operation

Figure 2-67. Solar/Hydrogen/H₂O₂ Plant Option 1 - Steam Turbines Night Operation

Figure 2-68. Solar/Hydrogen/H-Iron Plant Option 1 - Steam Turbines Daytime Operation

Figure 2-69. Solar/Hydrogen/H-Iron Plant Option 1 - Steam Turbines Night Operation

ments are approximately 1,900 KW and total plant energy consumption is 16.3 MM Btu per ton of sponge iron.

b) Option 3 - Purchased Electric Power

The Option 3 H-Iron plant design is similar to the others and requires 13,000 KW of purchased power during the day and 22,100 KW at night.

Sponge iron production remains 624 tons per day. Total plant energy consumption is 11.2 MM Btu per ton and 16.2 MM Btu per ton based on electric power (3413 Btu/KW-Hr) and off-site thermal conversion, respectively.

A summary of the methanol, hydrogen peroxide, and H-Iron plant major characteristics is shown in Table 2-41.

2.4.5 SCOPING ECONOMICS

The economics of the various plant design concepts were analyzed using 1978 dollars. The methods of estimating used was similar to that employed in earlier studies.⁽²⁻³⁵⁾ The economic evaluation was based on the preliminary flow-sheets discussed above and was intended to represent "order of magnitude" estimates depicting relative cost differences between the various design options considered. The evaluation considered utility financing, with a 15 percent annual charge on depreciating investment. In general, DOE cost goals were used for the solar components (i.e., heliostats, receivers, thermal storage system). Heliostats, representing the largest single cost item, were estimated at \$72 per square meter of reflective surface (100 percent reflectivity basis). Sulfur Cycle plant equipment costs determined in an earlier EPRI study⁽²⁻³⁶⁾ were revised to a 1978 basis and adjusted for capacity differences. Ammonia and methanol plant costs were obtained from the Pullman Kellogg Company.⁽²⁻³⁷⁾ The other end-product processes (H_2O_2 and H-Iron) were estimated internally. A summary of the assumptions used in the economic analysis is given in Table 2-42.

TABLE 2-41

METHANOL, HYDROGEN PEROXIDE, AND H-IRON PLANT MAJOR CHARACTERISTICS

	Methanol		Hydrogen Peroxide		H-Iron	
	Option 1*	Option 3**	Option 1	Option 3	Option 1	Option 3
Production Rate (tons product/day)	215	215	489	489	624	624
Solar Input (Electric Power Generation) - MW_t	156	0	159	0	155	0
Solar Input (Acid Decomposition) - MW_t	177	177	177	177	177	177
Purchased Power Requirements						
• Day (MW_e)	0	13.1	0	13.4	0	13.0
• Night (MW_e)	0	22.2	0	22.5	0	22.1
Overall Energy Consumption (MM Btu/ton product)	47.6	32.5	21.1	14.3	16.3	11.2

*Option 1 - Electric Power Generation with Steam Turbines and Thermal Energy Storage

**Option 3 - Purchased Electric Power

TABLE 2-42

ECONOMIC ASSUMPTIONS

Parameter	Description
Analysis Method	Utility Financing
Cost Basis	1978 Dollars
Annual Charge Rate on Capital	15%
Contingencies and Spares	15%
Indirect Costs	10%
Interest During Construction	15%
Annual Operating and Maintenance Charges	1% of Capital (Solar/Hydrogen Plant) 5% of Capital (End-Product Process)
Oxygen Credit (two cases)	0 and \$25/ton
Solar Insolation Capacity Factor*	71%
Planned and Forced Outage Rate	10%
Net Plant Capacity Factor	64%
Purchased Power Cost	3¢/KW-HR

*Solar Insolation Capacity Factor = $\frac{\text{Annual Avg. Daily Direct Normal Solar Radiation}}{\text{Design Daily Direct Normal Solar Radiation}}$
(See Appendix A)

$$= \frac{6.7 \text{ KW-HR/m}^2\text{-day}}{1.045 \text{ KW/m}^2 \times 9 \text{ Hrs/day}} = 0.71$$

The capital cost estimate was based on preliminary sizing of the major plant equipment. Appropriate factors, based on experience with similar equipment types, were used to account for the costs of installation, piping, valves, instrumentation, structures, and miscellaneous equipment. Therefore, all capital costs were estimated on a "delivered and erected" basis. The overall plant was divided into the following major subsystems for accounting purposes:

Battery A - Electric Power Generation Subsystem

Battery B - Acid Decomposition System

Battery C - Hydrogen Production Plant

Battery D - End-Product Process

Battery E - Off-Sites

Battery A includes all components associated with electric power generation, including solar collectors (heliostats), receiver tower/steam generator, turbine-generator, thermal energy storage, and all associated equipment.

Battery B includes the receiver/decomposition reactor, associated solar collectors, subsystem control system, etc. Battery C contains the electrolyzers, process and separation components, storage tanks, and all other equipment associated with hydrogen production, with the exception of the decomposition reactor included in Battery B. Battery D includes the end-product production plant and storage and shipping facilities. Battery E is the off-sites including water systems, electric auxiliary power, land, site facilities, etc.

The capital cost summary for the five solar/hydrogen/ammonia plant options is given in Table 2-43. The total plant investment includes the direct costs plus contingencies, indirect costs, and interest during construction. Indirect costs and interest during construction were not estimated in detail, but were calculated as a percentage of the direct costs. Detailed construction schedules for each of the three main plants (solar, hydrogen, and end-product) were not worked out. Indirect costs are items of a general nature which apply to the overall project of building an operable plant, such as construction facilities and equipment, engineering services, environmental studies, etc.

TABLE 2-43
SOLAR/HYDROGEN/AMMONIA PLANT CAPITAL COST SUMMARY
(Millions of 1978 Dollars)

	System Design Option				
	1 (Steam Turbines)	2 (Fuel Cells)	3 (Purch. Power)	4 (ON/OFF)	5 (Gas Turbines)
Battery A - Electric Power Generation	64.5	19.7	4.6	44.5	35.8
Battery B - Acid Decomposition System	54.3	107.5	54.3	54.3	54.3
Battery C - Hydrogen Production Plant	19.8	37.3	19.8	49.6	49.6
Battery D - End-Product Process	16.9	13.3	16.9	16.9	16.9
Battery E - Off-Sites	5.8	5.5	4.2	5.7	5.7
Subtotal	161.3	183.3	99.8	171.0	162.3
Contingencies and Spares (15%)	24.2	27.5	15.0	25.7	24.3
Subtotal	185.5	210.8	114.8	196.7	186.6
Indirect Costs (10%)	18.6	21.1	11.5	19.7	18.7
Total Capital Costs	204.1	213.9	126.3	216.4	205.3
Interest During Construction (15%)	30.6	34.8	18.9	32.5	30.8
Total Plant Investment	234.7	266.7	145.2	248.9	236.1

TABLE 2-44
SOLAR/HYDROGEN/AMMONIA PRODUCTION COSTS
64% Capacity Factor
Utility Financing
1978 Cost Basis

Annual Costs (Millions of Dollars)	System Design Option				
	1 (Steam Turbines)	2 (Fuel Cells)	3 (Purch. Power)	4 (ON/OFF)	5 (Gas Turbines)
Depreciating Capital (15%)	35.2	40.0	21.8	37.3	35.4
Operation and Maintenance					
- Solar/H ₂ Plant (1%)	1.8	2.2	1.1	1.9	1.8
- Ammonia Plant (5%)	1.8	0.8	1.1	1.1	1.1
Oxygen Credit					
- at \$0/ton	0	0	0	0	0
- at \$25/ton	(1.8)	(1.0)	(1.8)	(1.8)	(1.8)
Purchased Electric Power	0	0	4.7	0.9	0.9
Total Annual Cost					
- without O ₂ credit	38.1	43.0	28.7	41.2	39.2
- with O ₂ credit	36.3	42.0	26.9	39.4	37.4
Plant Capacity (Tons/Day)	190	127	190	190	190
Annual Production Rate (10 ³ tons)	44.4	29.7	44.4	44.4	44.4
Ammonia "Gate Price" (\$/ton)					
- without oxygen credit	858	1448	646	928	883
- with oxygen credit	818	1414	606	887	842

Total plant investments for the solar/hydrogen/ammonia plant range from \$145.2 million for Option 3 (Purchased Electric Power) to \$266.7 million for Option 2 (Fuel Cells). Total plant investment for the base case, Option 1, is slightly less than that for the two ON/OFF cases, Option 4 and 5. In general, the thermal and SO_2 storage costs of Option 1 are offset by the hydrogen storage and increased equipment sizes of Options 4 and 5. Option 3 has the lowest capital investment due to the elimination of the solar/electric plant. Option 2 has the highest capital investment due to its lower efficiency, the doubling of the acid decomposition system, and the increase in electrolyzer capacity.

Ammonia production costs are shown in Table 2-44. Production costs are comprised of annual charges for depreciating capital, operation and maintenance (including catalyst replacement), and purchased electric power. "Gate prices" were calculated assuming zero and \$25 per ton credits for the by-product oxygen produced.

Assuming purchased power costs of 3 cents per kilowatt-hour, Option 3 (Purchased Electric Power) has the lowest production cost of \$606 per ton of anhydrous ammonia (with oxygen credit). Option 2, (Fuel Cells), with the highest total annual costs and the lowest annual production rate, results in a product cost of \$1414 per ton. A sensitivity check was run to determine the effect of purchased electric power cost on ammonia product costs. The breakeven point between Option 1 (base case with solar/electric power generation) and Option 3 (purchased electric power) was found to be 9 cents per kilowatt-hour. In effect, this represents the internal production cost of electric power and is consistent with recent estimates of solar thermal central receiver electric power production costs.⁽²⁻³⁸⁾

Similar estimates were made for the total capital investments for the solar/hydrogen/methanol, hydrogen peroxide, and H-Iron plants. Capital cost summaries are given in Tables 2-45 through 2-47. For each plant both Options 1 and 3 were estimated; in all cases Option 3 (Purchase Electric Power) had lower total capital investments. The methanol plant direct cost includes scrubbing and purification equipment for cleaning the carbon dioxide. The

TABLE 2-45
SOLAR/HYDROGEN/METHANOL PLANT CAPITAL COST SUMMARY
(Millions of 1978 Dollars)

	<u>System Design Option</u>	
	<u>1</u> (Steam Turbines)	<u>2</u> (Purch. Power)
Battery A - Electric Power Generation	46.6	4.6
Battery B - Acid Decomposition System	54.3	54.3
Battery C - Hydrogen Production Plant	19.8	19.8
Battery D - End-Product Process	12.1	12.1
Battery E - Off-Sites	5.4	4.3
Subtotal	138.2	95.1
Contingencies and Spares (15%)	20.7	14.3
Subtotal	158.9	109.4
Indirect Costs (10%)	15.9	10.9
Total Capital Costs	174.8	120.3
Interest During Construction (15%)	26.2	18.0
Total Plant Investment	201.0	138.3

TABLE 2-46
SOLAR/HYDROGEN/PEROXIDE PLANT CAPITAL COST SUMMARY
(Millions of 1978 Dollars)

	<u>System Design Option</u>	
	<u>1</u> (Steam Turbines)	<u>3</u> (Purch. Power)
Battery A - Electric Power Generation	48.6	4.6
Battery B - Acid Decomposition System	54.3	54.3
Battery C - Hydrogen Production Plant	19.8	19.8
Battery D - End-Product Process	89.3	89.3
Battery E - Off-Sites	5.5	4.2
Subtotal	217.5	172.2
Contingencies and Spares (15%)	32.6	25.8
Subtotal	250.1	198.0
Indirect Costs (10%)	25.0	19.8
Total Capital Costs	275.1	217.8
Interest During Construction (15%)	41.3	32.7
Total Plant Investment	316.4	250.5

TABLE 2-47
SOLAR/HYDROGEN/H-IRON PLANT CAPITAL COST SUMMARY
(Millions of 1978 Dollars)

	System Design Option	
	1 (Steam Turbines)	3 (Purch. Power)
Battery A - Electric Power Generation	48.1	4.6
Battery B - Acid Decomposition System	54.3	54.3
Battery C - Hydrogen Production Plant	19.8	19.8
Battery D - End-Product Process	5.3	5.3
Battery E - Off-Sites	5.6	4.3
Subtotal	133.1	88.3
Contingencies and Spares (15%)	20.0	13.2
Subtotal	153.1	101.5
Indirect Costs (10%)	15.3	10.2
Total Capital Costs	168.4	111.7
Interest During Construction (15%)	25.3	16.8
Total Plant Investment	193.7	128.5

TABLE 2-48
SOLAR/HYDROGEN/METHANOL PRODUCTION COSTS
64% Capacity Factor
Utility Financing
1978 Cost Basis

Annual Costs (Million of Dollars)	System Design Option	
	1 (Steam Turbines)	3 (Purch. Power)
Depreciating Capital ⁽¹⁾	30.1	20.7
Operation and Maintenance		
- Solar/H ₂ Plant (1%)	1.6	1.0
- Methanol Plant (5%)	0.8	0.8
Oxygen Credit		
- at \$0/ton	0	0
- at \$25/ton	(1.8)	(1.8)
Purchased Electric Power	0	0
Total Annual Cost		
- without O ₂ credit	32.5	26.0
- with O ₂ credit	30.7	24.2
Plant Capacity (Tons/Day)	215	215
Annual Production Rate (10 ³ Tons)	50.2	50.2
Methanol "Gate Price" (\$/Ton)		
- without oxygen credit	647	518
- with oxygen credit	612	482

(1) Annual Fixed Charge Rate = 0.15

hydrogen peroxide manufacturing process was estimated by item-by-item sizing and cost estimation; the uncertainties associated with these estimates and greater than for the other types of plants. More precise cost data could not be obtained due to the small number of existing hydrogen peroxide manufacturing plants and the competitive nature of the market. The H-Iron plant was estimated based on data published by Bethlehem Steel Company. (2-39, 2-40)

Methanol, hydrogen peroxide, and H-Iron production costs are shown in Tables 2-48 through 2-50. In each case the breakeven electric power cost is also 9 cents per kilowatt-hour. A sensitivity check was made on the effect of hydrogen peroxide manufacturing process direct cost on product costs. It was found that for manufacturing process direct costs of 50 percent, 100 percent, and 150 percent of the calculated value, product costs for Option 1 with oxygen credit were \$496, \$582, and \$667 per ton, respectively.

The method of cost estimation used permitted assignment of direct costs to the major system batteries as discussed previously. These battery designations were chosen to facilitate cost accounting and represent actual physical divisions of the plant. However, further analysis was performed to determine the proportion of costs on a functional, rather than physical, basis.

Figure 2-70 shows the relative costs for each plant, based on the Option 1 design, apportioned among costs related to solar energy collection, energy storage, hydrogen production, and end-product manufacture. Solar energy collection costs include the heliostats and related controls. The solar receiver costs are split between solar collection and hydrogen production, since a steam generator and acid decomposition reactor are required regardless of the heat source. Energy storage costs include both thermal and chemical storage. Hydrogen production costs include the electrolyzers and related process equipment, the electric power generation system, along with a percentage of the solar receiver costs. End-product manufacture costs include all of the Battery D equipment, including final product storage and shipping facilities.

TABLE 2-49

SOLAR/HYDROGEN PEROXIDE PRODUCTION COSTS

64% Capacity Factor
Utility Financing
1978 Cost Basis

Annual Costs (Millions of Dollars)	<u>System Design Option</u>	
	<u>1</u> (Steam Turbines)	<u>3</u> (Purch. Power)
Depreciating Capital ⁽¹⁾	47.5	37.6
Operation and Maintenance		
- Solar/H ₂ Plant (1%)	1.6	1.0
- H ₂ O ₂ Plant ⁽²⁾ (5%)	19.0	19.0
Oxygen Credit		
- at \$0/ton	0	0
- at \$25/ton	(1.8)	(1.8)
Purchased Electric Power	0	3.6
Total Annual Cost		
- without O ₂ credit	68.1	61.2
- with O ₂ credit	66.3	59.4
Plant Capacity (Tons/Day) - 100% Basis	489	489
Annual Production Rate (10 ³ Tons)	114	114
H ₂ O ₂ "Gate Price" (\$/Ton) - 100% Basis		
- without oxygen credit	597	537
- with oxygen credit	582	521

(1) Annual Fixed Charge Rate = 0.15

(2) Includes Makeup Chemicals

TABLE 2-50

SOLAR/HYDROGEN/H-IRON PRODUCTION COSTS

64% Capacity Factor
Utility Financing
1978 Cost Basis

Annual Costs (Millions of Dollars)	System Design Option	
	<u>1</u> (Steam Turbines)	<u>3</u> (Purch. Power)
Depreciating Capital ⁽¹⁾	29.1	19.3
Operation and Maintenance		
- Solar/H ₂ Plant (1%)	1.5	1.0
- H-Iron Plant (5%)	0.3	0.3
Oxygen Credit		
- at \$0/ton	0	0
- at \$25/ton	(1.8)	(1.8)
Purchased Electric Power	<u>0</u>	<u>3.5</u>
Total Annual Cost		
- without O ₂ credit	30.9	24.1
- with O ₂ credit	29.1	22.3
Plant Capacity (Tons/Day)	624	624
Annual Production Rate (10 Tons)	146	146
Sponge Iron "Gate Price" (\$/Ton)		
- without oxygen credit	212	165
- with oxygen credit	199	153

(1) Annual Fixed Charge Rate = 0.15

(2) Not including cost of iron oxide pellets

Figure 2-70. Functional Cost Breakdown for Option 1 (Steam Turbine) Designs

The solar energy collection costs represent approximately 50 percent of the total plant investment for the ammonia, methanol, and H-Iron plants. Energy storage is about 12 percent, hydrogen production 30 percent, and end-product manufacture 4 to 11 percent. The percentages are skewed for the hydrogen peroxide plant due to the very large H_2O_2 manufacturing plant costs, which exceed even the solar energy collection costs. The Sulfur Cycle hydrogen production plant costs represent a total plant investment of approximately \$5/SCFD, which is considerably higher than earlier estimates of approximately \$2/SCFD.⁽²⁻³⁶⁾ The higher unit cost is partly due to much smaller plant capacity and higher steam generator and acid decomposition reactor costs that result from integration with solar receivers. The earlier estimates had been made for a large nuclear-driven hydrogen plant whose capacity was approximately thirty times greater than the solar-driven plants. The primary factor, however, contributing to increased hydrogen production plant costs is the low capacity factor of the decomposition system and related compounds that only operate during periods of direct insolation.

2.4.6 CONCLUSIONS AND RECOMMENDATIONS

Five chemical or fuel processes (ammonia, methanol, hydrogen peroxide, H-Iron, and coal liquefaction) have been identified for integration with the solar/hydrogen plant. With the exception of coal liquefaction, process flowsheets have been prepared for each process and for several different design options. All identified plant options appear technically feasible and employ solar high-temperature technology being developed for solar thermal electric plants.

A major issue identified was the capacity matching of the solar/hydrogen subsystem with end-product process requirements. The ammonia and methanol solar plant capacities are equivalent to small, older existing fossil-fueled plants. New fossil-fuel ammonia and methanol plants are five or six times larger. The hydrogen peroxide solar plant capacity, on the other hand, is far larger than existing plants and would need to be scaled down by about a factor of three. The H-Iron plant capacity appears to be the best fit with existing plant capacities.

It represents an output equivalent to existing medium-sized direct reduction plants. Finally, coal liquefaction plant hydrogen requirements far exceed the solar/hydrogen plant capacity. Plans for large coal liquefaction plants call for twenty to thirty times the solar/hydrogen plant output.

It should be noted that some of the plant capacity discrepancies mentioned above could be resolved by adding additional solar "modules" to the hydrogen plant. This could be accomplished by using multiple solar central receivers and piping the steam and acid to a central production plant.

Comparison of the various system design options studied (Table 2-38) showed Option 3 (Purchased Electric Power) to be the most cost-effective. However, if solar electric generation is desired, Option 1 (Steam Turbines) appears to be the best choice. Option 2 (Fuel Cells) is the least cost-effective alternative and the least energy efficient.

As was expected, the product "gate prices" exceeded present production costs for all processes and all design options. For the most cost-effective cases studied, ammonia and methanol costs are about three times greater than current fossil-fuel production costs. H-Iron production costs for iron powder exceed fossil plant costs by a 2 to 1 margin. Hydrogen peroxide costs are estimated to be less than present selling prices, but further investigation is required due to the large-scale plant design and the uncertainties in hydrogen peroxide production plant costs. No cost estimates were made for coal liquefaction. At existing market prices for fossil fuels, higher production costs have also been shown for solar central receiver systems designed for stand alone electric power production. (2-38)

Since the solar collection and storage portions of the plants represent almost two-thirds of the total capital investment, this is the area where the greatest reduction in costs can be obtained. DOE's programs for advanced heliostat design, high-temperature solar receivers, and advanced storage systems are aimed at reducing these costs. In addition, continuing development on the Sulfur Cycle should permit reduction of the hydrogen production plant costs.

It would be premature at this point to make projections of breakeven fossil fuel prices or plant payback periods. The results reported herein in effect represent scoping studies aimed toward: (1) identifying potential candidate solar fuels and chemicals processes, and (2) determining first-cut approximations of technical performance and economics.

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3.0 ACID VAPORIZER DESIGN AND DEVELOPMENT

3.1 BACKGROUND

During 1980, the pressurized test unit (PTU) was defined conceptually and sized for a nominal 85 KW_t rate of hydrogen generation. This rating can permit the hybrid sulfur cycle to be coupled with a distributed solar collector of reasonable size. In 1981, design considerations of critical components were predicated on the conditions specified for the PTU configuration. The PTU process flow sheet is shown in Figure 2-26, with the flow rate and composition of each stream specified in Table 2-24.

The use of indirect coupling of the thermochemical system to the heat source was selected for the PTU configuration. A high temperature heat transport loop provides the thermal interface between the heat source and the sulfur cycle process as shown in Figure 3-1. Solar thermal energy is concentrated by a large parabolic dish, and helium is used as a heat transport medium to provide the heat requirements in the decomposition reactor and the second stage of acid vaporization (Vaporizer-2). The helium leaving Vaporizer-2 is returned to the solar receiver at the dish's focal point. Some of the enthalpy in the decomposed hot gases leaving the decomposition reactor on the acid side provides heat to a recuperator for preheating the acid vapor. This stream also provides heat to the first stage of acid vaporization, Vaporizer-1. At the time of the PTU definition, these four components, i.e., two stages of acid vaporization, recuperator, and acid decomposition reactor were judged to be "critical components." Accordingly, design and development activities during 1981 focused on these components. A detailed design of acid Vaporizer-2 was prepared and this section of the report focuses on that component.

3.1.1 SIZING OF THE ACID VAPORIZERS

Calculations to estimate the size of acid vaporizer-1 were performed with iterations to reduce its total length. These studies indicated that the

Figure 3-1. Solar Interface with Sulfur Cycle

Figure 3-2. Sulfuric Acid Vaporizer

configuration of Vaporizer-1 should be a countercurrent flow arrangement with the cooler acid on the tube side and the hot acid vapor on the shell side. The vaporizer consists of fifteen tubes arranged in a triangular pitch. A pre-vaporization section is used to heat the acid from 225°F to its initial boiling point (527°F). Approximately eleven feet of tube length is needed for the pre-vaporization section because the acid is in a low laminar flow region resulting in limited heat transfer. The acid leaving Vaporizer-1 is a two-phase flow at 730°F and the acid concentration in the liquid phase is approximately 89 w/o.

The two-phase acid leaving the acid Vaporizer-1 enters the tube side of Vaporizer-2 for complete vaporization, and leaves as a superheated acid vapor at 845°F. Some portion of the acid vapor has been decomposed at this temperature. The hot helium enters the shell side at 1375°F, flows countercurrent to the acid vapor and leaves at 1120°F. Vaporizer-2 consists of seven tubes, approximately 6 feet in length, arranged in a triangular pitch.

3.1.2 MATERIALS CONSIDERATION

In designing process equipment for containing hot sulfuric acid and sulfur oxides, a primary consideration for material selection must be corrosion resistance. In some cooler parts of the system, fluorocarbons (particularly Teflon, polytetrafluoroethane) are satisfactory, although the system pressure desired in the PTU requires that Teflon be structurally supported and, at temperatures above 400°F, that it be confined to prevent creep. Various nickel-base super-alloys have ranges of applicability limited on the low temperature side by resistance to the corrosive liquid phase and on the high temperature side by creep. Gold has excellent corrosion resistance to both the process liquid and its vapor, but its high cost and low strength rule out serious consideration of gold as a structural material. Ceramics are resistant to both corrosion and thermal degradation; if equipment can be designed to be compatible with the brittle characteristics of ceramics, these would be excellent structural materials.

Of all the ceramic materials tested for corrosion resistance to boiling sulfuric acid, silicon carbide is the best for almost every characteristic. There

are no generally accepted specifications (equivalent to ASTM or ASME) for silicon carbide properties and performance, and there are at present only two major suppliers of silicon carbide components in the United States. Each of the suppliers recommends a different grade of SiC for use in PTU heat exchangers, each has its own preferred fabrication procedures, and each has its own process limitations for size, wall thickness, joining techniques, etc. Until some further testing is done, it is not known which material is superior, or if they may be considered interchangeable. Therefore, as the proposed silicon carbide equipment designs were prepared, they were reviewed with both potential suppliers so that neither supplier would inadvertently be excluded from competition when PTU equipment is eventually procured.

The two grades of silicon carbide recommended are:

- sintered alpha phase silicon carbide
- reaction bonded silicon carbide

The essential difference is that the first is a single phase material while the second contains excess silicon as a second phase. The presence of elemental silicon limits the use of the reaction sintered material to service temperatures below 2550°F, but this is not a limitation for use in any PTU application. If a choice must be made between these materials, the selection criteria most likely will be surface finish, abrasion resistance, abrasiveness, and Weibull modulus, an indication of the statistical uniformity of the distribution of unavoidable flaws in the material.

3.2 DESIGN OF ACID VAPORIZER-2

Acid Vaporizer-2 is shown pictorially in Figure 3-2; a design study layout is shown in Figure 3-3. This apparatus is a counterflow shell-and-tube heat exchanger, with 514 lb/hr of helium entering the shell side at 1375°F and exiting at 1120°F. The process stream is 486 lb/hr of acid vapor entering at 730°F and exiting at 845°F. Both streams are pressurized to approximately 20 atmospheres so that the constant differential pressure on the tubes and tube sheets is very small and can be in either direction to control leakage and

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cross-mixing of the streams. The shell and heads must withstand this pressure continuously, and the tubes and tubesheets must survive it during accidental depressurization of either stream and during startup and shutdown transients.

Thermal stresses could be far more severe than pressure stresses. Considering only the normal operating temperature distribution, and neglecting the more harmful transient distributions which could occur during startup and shutdown, differential thermal expansion between the tubes, at a mean temperature of 760°F, and the shell, at a mean temperature of 1258°F, is 0.080 inch. (If the shell were brought up to service temperature with the tubes cold (70°F), a limiting case for startup, the differential expansion would be 0.191 inch.) The modulus of elasticity of SiC is very large (56.9×10^6 psi at 920°F); if the cross sectional area of the tubes is small compared with the shell, this thermal strain would predominantly cause axial tensile stress in the tubes. The minimum uniform stress at the operating conditions then would be 62,000 psi; this is obviously excessive, by comparison with the measured 4-point flexural strength of 65,000 psi of silicon carbide.

The design of the heat exchanger is based upon elimination of stress due to axial differential thermal expansion by permitting the tubes to slide through all-metal mechanical seals in the tube sheets. One such sliding connection on each tube would be sufficient, but this construction eliminates the attachment of the tube to the tube sheet and is therefore used at both ends of each tube. Instead of being attached to the tube sheets, the tubes are sealed and restrained by an unstressed perforated plate to limit motion. The success of this heat exchanger design is obviously dependent on the seals. The seals selected are Helicoflex seals, invented and developed in France by CEA (the French Atomic Energy Commission) for nuclear reactor service. The Helicoflex Company of Boonton, New Jersey, is the licensee in the United States. The seals chosen for this design, with the concurrence of the manufacturer, are standard catalog items. Each seal consists of a coil spring wound with initial tension and coiled into a torus. The spring is covered over most of its surface with a thin metal liner which has a circumferential gap. For this application, the spring will be made of Inconel X750 (chosen for creep resistance)

and the liner will be gold (chosen for corrosion resistance). The seals will be installed with the gaps facing the shell space so that the springs are bathed in helium rather than acid vapor. Sealing takes place when the torus is compressed, usually axially but in some cases radially, so that the cross section of the toroidal spring is elastically deformed. Pressure between two flanges (for axial deformation) or between a tube and tube-sheet cavity (for radial deformation) causes the liner to seal against the contacting surfaces. This sealing with proper dimensional control can be helium leak-tight. The proposed seal application, dimensions, and installation procedure are in accordance with the manufacturer's instructions, which have produced other satisfactory seals. In these, axial motion during installation certainly occurred, and some axial motion during thermal transients undoubtedly occurred, but the extent of such motion is not known. A test program to demonstrate the performance of these radial seals is planned and is discussed in Section 3.4.

In a conventional heat exchanger design, the tubes would be small diameter and closely spaced, in a small diameter shell. But fabrication limitations of both suppliers prompt the use of 1.0 inch O.D. and 0.62 inch I.D. tubes not more than 84 inches long; one supplier has made such tubes successfully in large quantities, and the other has produced this diameter and expects to demonstrate this length capability in the near future. Accordingly, the tube bundle will consist of seven tubes extending 72 inches between tube sheets with baffles spaced 12 inches apart. These baffles are necessary to produce cross-flow over the tubes, because of the very open bundle configuration resulting from the tube spacing being determined by the seal diameters. Because the baffles are not stressed and are in the helium stream, they can be made of stainless steel.

The seven heat exchanger tubes are arranged in a hexagonal pattern. The spacing of the tubes is 1.375 inch, determined not by the tube size or tube sheet ligament (as in a conventional tube bundle) but by the seal diameter. The shell enclosing the resulting tube bundle is 4.08 inches I.D.; the wall thickness is 0.75 inch. The nominal hoop stress is 800 psi tension, which is quite conservative. The adequacy of the shell design depends much more on its materials volume and stress concentration rather than this nominal hoop stress.

The shell is flanged at both ends with a helium nozzle close to each flange. The method of attaching the flanges and nozzle will probably be determined by the supplier; reaction sintered silicon carbide bodies can be brazed, using elemental silicon as the braze material, while sintered alpha silicon carbide bodies can be mated in the green condition and joined with no filler during the sintering process.

The partial tube bundle, consisting of one tube sheet, the seven tubes with seals, eleven baffles, and temporary support at the free ends of the tubes, is inserted into the shell, with large Helicoflex seal placed between the tube sheet and shell flange; the seal manufacturer considers this axially loaded seal (with a deflection limiting plate) to be entirely within the state-of-art. An identical seal is placed on the shell flange at the opposite end, and (after removal of the temporary tube support), the second tube sheet is installed on the bundle, with the tube seals in place and temporarily restrained.

The large bore of the heat exchanger tubes requires internal turbulence enhancers to assure adequate heat transfer at the low flow rate. Therefore, each tube is filled full length with loosely fitting blocks of square cross-section. The blocks are short compared with the tube length so that relative straightness of the tubes and the blocks is not a requirement. These blocks as well as the tube seals are retained by a perforated plate at each end; these plates are captured but not clamped between the tube sheets and the heads.

The heat exchanger is completed by installing at each end a hemispherical head with a central acid vapor nozzle. Each head is sealed to the tube sheet face with a Helicoflex seal having a gold liner. The shell flange, the tube sheet, the head flange, and the two Helicoflex seals are then clamped together. The drawing shows a split-ring wedge type closure (similar to the commercially available Marmon clamp), but other closures will be considered. The simplest closure would be multiple spring-loaded bolts extending through the head and shell flanges, the tube sheet, and the deflection-limiters of the seals. The basic requirements are to maintain sealing pressure on both seals during all

thermal transients, and to minimize bending moments in the silicon carbide components. Final design of the closure must be based on iteration of finite element stress analysis and thermal analysis. This is a costly process, but is straight-forward engineering; the absence of a final closure design does not compromise the feasibility of the design concept.

3.3 STRESS ANALYSIS

A preliminary component stress analysis of the acid vaporizer was performed to evaluate its structural adequacy. Finite element techniques were used to calculate stresses due to pressure, differential expansion, thermal loading and clamp arrangement. The tensile stress results were evaluated using tentative allowables developed for silicon carbide material. A preliminary reliability analysis was performed using the Weibull statistical analysis technique. The results of this evaluation indicated that, for the load conditions specified in Section 3.3.2, the vaporizer was found to be structurally adequate provided the following two critical areas are resolved.

- flange/clamp arrangement
- tube seal performance

The flange/clamp arrangement must be able to maintain a uniform clamping force and to accommodate differential thermal expansion. The tube seals must permit free axial motion during normal operation and insure leak tightness for helium application. Design modification and verification of these aspects need to be investigated during future efforts.

3.3.1 MODELING CONSIDERATIONS AND ASSUMPTIONS

The acid vaporizer shown in Figure 3-3 was analyzed using finite element techniques. A 3-D axisymmetric model of the shell, tube sheet, head, and clamp arrangement was used to evaluate steady state conditions, but thermal transient conditions were not included in this preliminary review. Due to the symmetrical nature of the ends of the vaporizer only one end and part of the shell structure are included in the model. A view of the model is shown in Figure 3-4.

Figure 3-4. Finite Element Model - Helium Acid Vaporizer

Figure 3-5. Temperature Distribution at Cold End (Acid Vapor Inlet)

The finite elements used in this model are the 8-node versions of WECAN's (Ref. 3-1) isoparametric solid element. STIF 58 of the WECAN element library is used for the thermal analysis and STIF 53 for the stress solutions. There are two elements through the thickness except at the clamp and tube sheet. This relatively coarse model provides a reasonable representation of the stresses developed in the flange and tube sheet regions since isoparametric elements are used. Effective material properties were used in modeling the six outer tubes and perforated tube sheet components. The remainder of the model was defined based on current material property values and geometric configuration.

The finite element model is based on the following assumptions:

- The segmented clamp acts as a solid ring producing axisymmetric loading at the flanges.
- The clamping pressure is large enough to preclude sliding between silicon carbide and Nitronic-60 clamp components.
- The outside surface of the vaporizer is wrapped with insulation to insure little or no temperature gradients through the wall.
- Start-up and cool-down transients occur over long periods of time and do not produce significant thermal stresses.
- Three-dimensional thermal effects are negligible.
- Localized stresses in the region of the inlet and outlet ports are not included in this preliminary evaluation.

3.3.2 LOAD CONDITIONS & STRESS RESULTS

The acid vaporizer is subjected to several types of loads during its service life. Those load conditions considered for this analysis are:

- 1) Pressure - acting on the inside surface of the head and shell and pressure differential across tubes.
- 2) Thermal Steady State Loads - temperature distributions at each end of the unit for steady state operation.

The individual load cases are discussed in more detail below. Thermal transients and mechanical piping loads were not included in this evaluation.

Both the acid and helium are pressurized to approximately 20 atmospheres to produce only a small differential pressure across the tube walls. The shell and heads must be capable of withstanding a continuous pressure as well as an accidental depressurization of either stream. The clamp interface pressure must be capable of maintaining contact pressure in the seal region without overloading silicon carbide members. Initial pressure results indicated the clamp arrangement produced relatively low stresses in clamp and vessel members.

Temperature distributions of each end of the vaporizer were determined based on a thermal equivalent WECAN-model. The cold end distribution was based on the acid vapor inlet of 730°F and the helium outlet of 1120°F. This distribution is shown in Figure 3-5. The hot end temperature distribution was based on an acid vapor outlet temperature of 845°F and a helium inlet temperature of 1375°F. This hot end temperature distribution is shown in Figure 3-6. These temperature distributions were used throughout this analysis.

The axial stress results for the first combined load case are shown in Figure 3-7. Clamp preload, internal pressure, and the cold end temperature distribution are applied simultaneously. It was found that the clamping pressures on the clamp/flange spacers were very nonuniform and that tension actually developed on the inside indicates separation. Additional clamping force did not improve the situation.

In order to study this problem the clamp was replaced by a uniform clamping pressure on shell and head flanges. The results of this case are shown in Figure 3-8 for the hot end temperature distribution and internal pressure. The results of this run indicated that uniform pressure was necessary to reduce stresses in both the silicon carbide members and the tube sheet spacers. These stresses can be reduced even more by using silicon carbide spacers instead of Nitronic 60. The results of this configuration are shown in Figure 3-9 with hot

Figure 3-6. Temperature Distribution at Hot End (Acid Vapor Outlet)

Figure 3-7. Helium-Acid Vaporizer - Axial Stress for Original Combined Load Case

Figure 3-8. Helium-Acid Vaporizer - Axial Stress with Uniform Clamp Pressure

Figure 3-9. Helium-Acid Vaporizer - Axial Stress with Uniform Clamp Pressure and SiC Spacer

end temperatures and uniform clamp pressure. These results confirmed the assumption that differential thermal stresses produced high stresses in this interface region. Based on these results it was recommended that the clamp design be revised to produce more uniform pressure distribution and that the Nitronic 60 spacers be replaced with silicon carbide spacers.

3.3.3 DESIGN PHILOSOPHY WITH SILICON CARBIDE

Silicon carbide is known to be a brittle material, and statistical evaluation of stress analysis results is widely accepted for such materials. The basic hypothesis for all statistical theories is that materials contain flaws, and that these flaws prevent the material from achieving its potential strength. The Weibull statistical approach was found to be appropriate for evaluation of tensile stress in silicon carbide in a recent program (Ref. 3-2). The Weibull method is documented in detail in Ref. 3-3.

Using silicon carbide material data in Ref. 3-2 and the methods of Ref. 3-3, the probability of failure for the acid vaporizer material was estimated. The estimate was developed in the form of probability of failure of a volume of material under uniform tensile stress as a function of that stress. This estimate is presented as Figure 3-10.

It is possible to determine the overall reliability of a structure with a complex stress distribution with the aid of Figure 3-10. The procedure can be described briefly as follows. First, the stress analysis must be performed. Next, the tensile stresses must be examined and the volume of material under the various stress levels determined. The probability of failure of each volume is determined from Figure 3-10. The probability of survival of each volume is one minus the probability of failure. Then the overall component probability of survival, the reliability, is the product of all of the individual probabilities of survival.

An overall probability of survival less than 0.99 is considered unacceptable although the actual reliability goal for the unit is not defined at this time.

Figure 3-10. Silicon Carbide Probability of Failure as a Function of Tensile Stress and Stressed Volume

Preliminary analysis indicates that the recommended design changes would produce a reliability somewhat greater than 0.99.

3.3.4 CONCLUSIONS AND RECOMMENDATIONS ON STRESS

A preliminary evaluation of the reliability results indicates that the current design will be structurally adequate provided the design concerns discussed in Section 3.3.2 are resolved. While these concerns are not developmental in nature, resolution will require time and effort. A basic requirement of the unit is free axial sliding of the tubes within the seals (plus sealing adequacy). Therefore, a successful seal test program is a fundamental requirement to the development of the unit.

The current finite element model is adequate for the preliminary design phase. A more detailed model of the shell/tube sheet/head region will be required in subsequent analyses. In addition, a post-processor will be developed to determine the probability of survival of the overall structure from taped stress results.

3.4 SEAL TEST RIG

As was stated above, but without adequate emphasis, "The success of this heat exchanger design is obviously dependent on the seals." Figure 3-11 is the design layout drawing of a test rig that can be used to demonstrate the performance of a single Helicoflex seal identical to those in the acid vaporizer in design, materials, installation, pressure loading, temperature, fluid environment, and axial displacement.

The Wiedemann testing machine which will be used in conjunction with the test rig is on-hand and available at Westinghouse Advanced Energy Systems Division. Its replacement, a mini-computer controlled testing machine is also on-hand; it can be made available for future long-term cyclic testing if this becomes desirable. All components of the test rig and the test articles are on order.

Figure 3-11B. Seal Test Rig Design

Figure 3-11C. Seal Test Rig Design

3.4.1 TEST RIG DESCRIPTION

The test rig consist of a stainless steel bed plate which supports an insulated and heated silicon carbide block that simulates the tube sheet of the heat exchanger. A central closed-end cavity in this block simulates a penetration of the tube sheet for a single tube. An annular recess at the open end of this cavity simulates the seat for the Helicoflex seal. A test article, a prototype Helicoflex seal consisting of an Inconel X-750 toroidal spring and an untreated gold liner, is installed in the recess. The mating test article, a short tube of sintered alpha silicon carbide or reaction sintered silicon carbide (test articles of both materials are on order) is inserted into the test seal. Each of these tubular test articles has the dimensions, contour, and surface finish specified for the ends of the heat exchanger tubes. The tube extends upwards through a sintered alpha silicon carbide block and through a stainless steel top plate which contains an internal elastomeric O-ring into a stainless steel block. This block, which also contains an internal elastomeric O-ring, is attached to the ram of the testing machine. A Helicoflex seal between the two silicon carbide blocks, a location which will be close to the test seal temperature, completes the isolation of the space on both sides of the test seal from the ambient environment (except for drilled channels in the stainless steel top plate and block that provide fluid and thermocouple access). In addition to the thermocouple readings, the test system will measure and record the ram position and load as the testing machine moves the tube end through the seal. The pressure of a test fluid on one side of the seal will be recorded, and the other side of the seal will be connected directly to a mass spectrometer (for tests involving helium leakage) or through a leak valve to a residual gas analyzer (for tests involving sulfur oxide leakage).

3.4.2 PLANNED TEST PROGRAM

A typical test is expected to follow this sequence:

- Install test articles and assemble test rig around them.
- Establish fluid environment (composition, pressure) on both sides of test seal.

- Measure static leak rate.
- Establish temperature at seal; measure leak rate during heat-up.
- At a very low speed (simulating thermal expansion during heat-up and cool-down), cycle the simulated tube end through the seal for a distance at least equivalent to the differential expansion corresponding to the test temperature. Repeat this cycling until the required force reaches some equilibrium value or until a trend is established. Monitor the leak rate during cycling.
- Establish new temperature level at seal and repeat mechanical cycling, or,
- Cool test rig, disassemble test rig and examine seal.

The experimental program is expected to follow this sequence:

- (a) Install seal with circumferential gap down. Install sintered alpha silicon carbide tube. Inject helium onto closed side of seal and evacuate other side to mass spectrometer leak detector. Slowly pressurize helium to 300 psig while monitoring leak rate. While holding helium pressure constant, raise temperature to 1375°F while monitoring leak rate. Cycle seal to equilibrium force through 0.20 inches. Cool, disassemble, and examine seal and tube.
- (b) Install new seal with circumferential gap up. Install new sintered alpha silicon carbide tube. Repeat the remainder of test (a).
- (c) Install new seal with circumferential gap down. Install reaction sintered silicon carbide tube. Repeat the remainder of test (a).
- (d) Install new seal with circumferential gap up. Install new reaction sintered silicon carbide tube. Repeat the remainder of test (a).

The purpose of these four tests is to determine if the direction of initial insertion of the tube into the seal is significant, and to determine if there

are differences in performance of sintered alpha and reaction sintered silicon carbide. No significant differences are anticipated.

(e) Install new seal and sintered alpha silicon carbide tube. Connect gap side of seal through leak valve to residual gas analyzer. Inject 65 w/o H_2SO_4 to closed side of seal and helium to gap side of seal. Pressurize both sides of seal to 300 psig. While monitoring for leakage of sulfur oxides through the seal, raise temperature to 1110°F (simulating acid vaporizer). Cycle seal 0.10 inches to five times the number of cycles to force equilibrium. Raise temperature to 1300°F (simulating recuperator hot exit). Cycle seal 0.11 inches to five times the number of cycles to force equilibrium. Hold at temperature for 100 hours. Repeat cycling. Raise temperature to 1570°F (simulating catalyst bed entrance). Cycle seal 0.11 inches to five times the number of cycles to force equilibrium. Hold at temperature for 100 hours. Repeat cycling. Cool, disassemble, and examine seal and tube.

(f) Install new seal and reaction sintered silicon carbide tube. Repeat remainder of test (e).

These two tests (e) and (f), are a demonstration of leaktightness (or leak rate) in acid vaporizer, recuperator hot exit, or catalyst bed entrance conditions. If a developing leak or increasing leak rate appears during cycling, it may indicate wear of the gold seal surface. A cobalt electroplated ductile gold coating* may reduce wear while still providing adequate corrosion resistance. Leakage following the high temperature holds may indicate creep of the gold liner into the gaps between turns of the toroidal spring. A double liner seal, with an Inconel X-750 liner adjacent to the spring and a gold liner outside this, may be necessary. Such seals are a catalog item of Helicoflex Company. If either of these design fixes is necessary, the up-graded test

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*by Vanguard Research Associates, Inc.

items will be obtained and tests (e) and (f) will be repeated before the test series continues.

- (g) Install new seal and sintered alpha silicon carbide tube. Inject mixed gases (7.4 w/o O_2 , 29.7 w/o SO_2 , 18.2 w/o SO_3 , 44.7 w/o H_2O) to closed side of seal and helium to gap side of seal. Pressurize both sides of seal to 300 psig. While monitoring for leakage of sulfur oxides through the seal, raise temperature to 1300°F (simulating recuperator hot entrance). Cycle seal 0.11 inches to five times the number of cycles to force equilibrium. Hold at temperature for 100 hours. Repeat cycling. Raise temperature to 1703°F (simulating catalyst bed exit). Cycle seal 0.11 inches to five times the number of cycles to force equilibrium. Hold at temperature for 100 hours. Repeat cycling. Raise temperature to 1790°F (simulating catalyst bed entrance). Cycle seal 0.11 inches to five times the number of cycles to force equilibrium. Hold at temperature for 100 hours. Repeat cycling. Cool, disassemble, and examine seal and tube.

Test (g) is a demonstration of leak tightness (or leak rate) at recuperator hot entrance and catalyst bed exit conditions. The catalyst bed entrance or exit conditions may be beyond the range of an Inconel X-750/gold Helicoflex seal; if this is found to be true, a new Waspaloy/platinum Helicoflex seal may be procured and tested. Waspaloy is a high-cobalt alloy superior in creep resistance to Inconel X-750; platinum has equivalent corrosion resistance and a higher melting temperature than gold. Such a seal is not a catalog item of the Helicoflex Company, but its fabrication does not require any extension of the technology necessary for the Inconel X-750/gold seal.

3.5 ACID VAPORIZER MATERIALS EVALUATIONS

3.5.1 OBJECTIVE AND BACKGROUND

The objective of this task was to experimentally evaluate the behavior of potential acid vaporizer structural materials under the expected operating conditions of the Sulfur Cycle. Due to the corrosiveness of sulfuric acid, even under ambient conditions, and because the Sulfur Cycle requires the

decomposition of sulfuric acid to take place between 361°C, 55 psia and 452°, 300 psia, the acid vaporizer has been identified as a critical component in the development of the Sulfur Cycle. These operating parameters present materials problems that are common to most thermochemical hydrogen production processes, but unique when compared to the commercial processing of sulfuric acid.

Production of sulfuric acid, either through the reconcentration of dilute waste acid or by means of an SO_2 absorption process, is generally carried out at or near atmospheric pressure at $\sim 300^\circ\text{C}$. There are several vacuum concentration processes operating at reduced pressures and temperatures, thereby lessening the severity of the environment and easing the materials problem.

Therefore, while there is an abundance of data and industrial experience with materials in these temperature and pressure regimes, little has been known about the behavior of materials when exposed to boiling sulfuric acid at elevated temperatures and pressures.

Gold, platinum and quartz are resistant to the corrosive attack of boiling concentrated sulfuric acid at high temperatures. However, gold and platinum, while suitable for small scale purposes such as the test vessels used in this task, are prohibitively expensive for use in large scale processes. Quartz, also utilized in the test vessels, 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 weight percent sulfuric acid at atmospheric pressure and have traditionally had wide industrial use in handling sulfuric acid. These alloys all contain 14.5 percent Si. In addition, Durichlor 51 and Superchlor contain 4.5 Cr while Duriron contains 0.5 percent Cr. However, use of these alloys is limited by the fact they are very hard and brittle, subject to thermal shock and have low tensile strength.

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

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 3-1 outlines the acid vaporizer materials test program. The first phase of the program consisted 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 were run at 361°C which corresponds to sulfuric acid vapor pressure of 3.7 atmospheres (55 psia). Additional screening tests were conducted at 452°C, corresponding to sulfuric acid vapor pressure of 20.0 atmospheres (300 psia).

Phase Two was intended to be a materials endurance test, lasting for 5000 hours. Materials tested in this phase were to be selected from the most promising materials identified in Phase One. However, due to unforeseen difficulties with both the equipment and the test vessels, Phase Two was not completed.

Complete discussions of the test results, test procedures and facilities, and the conclusions and recommendations based on the test results are presented in the following sections.

3.5.2 SUMMARY OF TEST RESULTS

In the course of this program, approximately three dozen materials were evaluated in 98 w/o sulfuric acid at 361°C, 55 psia. Materials were tested for up to 1000 hours or until they were so severely attacked that they could not be placed back into the test vessel. A list of all materials tested at 361°C, 55 psia is presented in Table 3-2. Based on weight change measurements, the materials which appeared to have the best corrosion resistance are polycrystal silicon, chemical vapor deposited (CVD) silicon carbide (SiC), and silicon nitride (Si_3N_4). The metallic materials which were most corrosion resistant were Duriron and Durichlor 51.

These six materials, along with several additional ceramics, some SiC bearing composites, and metallic silicon, were tested at 452°C, 300 psia for up to 1000

TABLE 3-1: 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	452	20.0 (300 psi)	5000 hrs total

TABLE 3-2: 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
 Durichlon 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
 Alonzied 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.

hours in boiling 98 w/o sulfuric acid. The weight change data indicated that CVD SiC, hot pressed Si_3N_4 , and metallic silicon had the best corrosion resistance. The list of materials tested at 452°C is presented in Table 3-3.

Section 3.5.4 of this report presents a detailed discussion of the test results.

3.5.3 EXPERIMENTAL PROCEDURE AND FACILITIES

The testing of materials in the presence of high temperature boiling sulfuric acid requires that the test vessel used to contain the samples and the boiling acid be inert to the acid environment.

The initial test vessels were made of stainless steel with a removable gold liner (Figure 3-12). The gold liner, compatible with high temperature sulfuric acid, was used to contain the acid and the test samples. The stainless steel vessel was employed to provide mechanical support to the gold liner. At 361°C, the vapor pressure of 98 w/o sulfuric is ~55 psia. Therefore, to prevent a large pressure differential across the gold liner, the stainless steel vessel was pressurized to ~55 psia. Thermocouples located between the gold liner and the outer pressure vessel were used for temperature measurement and control. This assembly was then placed into an upright tube furnace, as shown in Figure 3-13.

After the first two tests, the welds sealing the gold liner developed leaks, allowing the sulfuric acid vapors to escape. These leaks were thought to be a result of corrosion of impurities in the weld that preferentially segregated into the grain boundaries. Use of the gold liner and stainless steel outer pressure vessel was then discontinued and a new test vessel designed.

The remaining tests at 361°C were conducted using a Duriron test vessel. This material was selected based on its performance as a candidate material in the first series of screening tests. This vessel was constructed of a short length of Duriron pipe clamped to blank end flanges. Gaskets, made of 1.3 mm diameter gold wire O-rings were used to provide an adequate pressure seal. Samples were suspended from a gold sample holder using platinum wire. Three samples of each

TABLE 3-3: ACID VAPORIZER MATERIALS TESTS AT 452°C

99.7% Alumina
Aluminum silicate M-120
Hot pressed silicon nitride
Silicon (polycrystalline)
CVD silicon carbide
Duro-acid brick
Silicon carbide graphite (SCG) composite

Duriron
Durichlor 51
Chemically vapor reacted (CVR) + CVD SiC on graphite
CVR + CVD SiC on Carbon-Carbon
Infiltrated C-C with CVD SiC
Cer-Vit C-144 Lithium Aluminum Silicate (LAS)

Figure 3-12. Cross Sectional View of Cylindrical Pressure Vessel Apparatus for Testing of Acid Vaporizer Materials

Figure 3-13. Apparatus for Testing of Acid Vaporizer Materials

material were used in the tests: one in the liquid phase, one in the vapor phase, and one straddling the liquid-vapor interface. To prevent galvanic action between two dissimilar metals (including the sample holder material) the platinum wires were sheathed in quartz capillary tubing. The loaded sample holder was then placed into the Duriron test vessel, which was then half filled with concentrated (~98 w/o) sulfuric acid. The end flanges were clamped on and Belleville spring washers used to maintain compression on the gold O-ring during thermal exposure. A photograph of a loaded sample holder and the Duriron test vessel is presented in Figure 3-14. This particular test vessel was successfully used in all of 361°C, 55 psia acid vaporizer materials tests.

After completion of the 361°C screening tests, the materials that displayed the best corrosion resistance at 361°C, along with several newly identified materials, were evaluated at 452°C, 300 psia.

Original intentions were to use the Duriron test vessel for the 452°C, 300 psia screening tests. However, due to the higher temperature and pressure, it was extremely difficult to maintain a leak tight system. This resulted in several aborted tests, after each of which, upon inspection, contained little or no sulfuric acid inside the test vessel. These system malfunctions necessitated a third generation test vessel that was capable of withstanding 452°C sulfuric acid at 300 psia.

The 452°C screening tests were conducted using sealed quartz capsules. Each capsule contained two samples of each material, one in the liquid phase and one in the vapor phase. Figure 3-15 shows a quartz capsule in its various stages of preparation. The first step was to insert a quartz sleeve into a quartz tube. A small sample of the candidate material was then placed inside the quartz sleeve, resting on the bottom of the quartz tube. This is the liquid phase sample. A larger sample, for the vapor phase, was then inserted and allowed to rest on top of the quartz sleeve. The 98 w/o sulfuric acid was then added in sufficient quantity to totally cover the liquid phase sample, but not enough to contact the vapor phase sample. The loaded quartz tube was then immersed into liquid nitrogen to solidify the liquid sulfuric acid. The tube

Acid Vaporizer Materials Sample Holder, Showing Manner in which
Three Samples of Each Materials are Supported

Duriron Test Vessel
Figure 3-14.

Figure 3-15. Schematic of Quartz Sample Holders for Acid Vaporizer Tests at 452°C

Figure 3-16. Sealed Quartz Capsule

was then evacuated and sealed using standard glass blowing techniques. A photograph of a sealed quartz capsule is shown in Figure 3-16.

At 452°C, the vapor pressure of 98 w/o sulfuric acid is ~300 psia. This is the minimum pressure that can be generated inside the sealed quartz vessel. If there is a reaction between the sulfuric acid and the test samples, there is a possibility that the internal pressure will be higher. Therefore, to prevent the quartz capsules from exploding, they were placed in a secondary stainless steel containment vessel. The containment vessel was pressurized to ~300 psia using an inert gas. This reduced the pressure drop across the quartz wall to a minimum.

The containment vessel, loaded with several sealed quartz capsules, was then placed into a tube furnace. A schematic diagram of this test facility is shown in Figure 3-17.

Sample preparation was similar in all of the test facilities. Prior to loading into the test vessel, the samples were weighed and dimensioned, then cleaned using a degreaser, distilled water, and ethyl alcohol. Finally, the samples were dried with forced hot air and photographed.

After the materials were tested, visual observations were made and photographs taken. If possible, samples were weighed immediately upon removal. Due to the extent of corrosion of some of the materials, it was necessary to remove the corrosion products by boiling in dilute sulfuric acid. All samples were rinsed with distilled water and dried in a 100°C oven. The samples were then weighed and dimensioned and then, finally, sent for metallographic analysis. The results of the screening tests are presented in the following section of this report.

3.5.4 DISCUSSION OF TEST RESULTS

This section presents a detailed discussion of the Acid Vaporizer Materials Evaluation Tests. These screening tests were conducted at 361° and 452°C. Raw data and photographs of tested samples may be found in Appendix D.

Figure 3-17. Schematic of Acid Vaporizer Test Apparatus for Materials Evaluations at 452°C

Figure 3-18. Acid Vaporizer Materials Test Results at 452°C

3.5.4.1 361°C Test Results

Thirty-four materials were tested at 361°C in 98 w/o sulfuric acid for up to 1000 hours. Samples that did not survive 1000 hours were tested until they were so severely corroded that the sample could not be placed back into the test fixture. At 361°C the vapor pressure of sulfuric acid is ~55 psia.

A total of eleven samples survived 1000 hours exposure to the high temperature acid reaction bonded silicon nitride, hot pressed silicon nitride, acid proof brick, Macor machinable ceramic, metallic silicon. Durichlor 51, Duriron, CVD silicon carbide, Vitreous Carbon, Alumina, and Aluminum Silicate. The weight change data for these samples is given in Table 3-4. This data indicates that all of these materials, except for Macor, exhibited a high degree of corrosion resistance. The polycrystal silicon displayed excellent corrosion resistance, with virtually no observable change in weight. CVD silicon carbide also displayed excellent corrosion resistance in both liquid and vapor 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.

The acid proof brick displayed a constantly increasing weight loss, in the liquid phase, as a function of time.

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 3-4: 1000 HOUR 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	V	27.6	30.7	24.4	29.3
	I	25.4	8.08	24.6	25.2
	L	20.3	27.1	24.5	24.9
Silicon Nitride, Ceradyne Hot Pressed	V	-0.51	-0.55	-0.57	-0.6
	(No. I)	-	-	-	-
	L	-0.19	-0.21	-0.17	-0.2
Duro Acid-Proof Brick	V	0.50	0.30	.06	1.0
	I	-2.28	-1.51	-4.84	-7.3
	L	-4.30	-3.41	-7.84	-11.9
Macor Machinable Ceramic	V	-9.53	-16.3	-26.5	-35.8
	I	-23.1	-30.6	-53.9	-122. e,f
	L	-23.2	-40.9	-61.8	-74.9 e,f
Silicon, Polycrystal	V	0	0	0	0
	I	-0.02	-0.01	-0.02	-0.02
	L	0.02	0.02	0.02	0.02
Durichlor 51	V	-0.70	-1.08	-1.28	-1.81
	I	-0.23	-0.42	0.06	-1.16
	L	-0.13	-1.33	-0.18	-1.20
Duriron	V	-1.51	-4.88	-8.19	-10.9
	I	-0.55	-2.46	-4.23	-5.56
	L	-0.78	-3.20	-5.51	-7.40
Silicon Carbide, CVD	V	0.02	-0.03	-0.20	-0.09
	I	0.17	0.15	-0.11	-0.31
	L	0.01	0.28	-0.24	-0.57
Vitreous Carbon	V	-0.62	-1.10	-2.08	-3.25
	I	-0.77	-0.92	-4.04	-8.13
	L	-0.83	-2.68	-5.24	-10.0
Alumina	V	-19.7	-50.8	-93.8	-123.
	I	-2.47	-7.78	-28.5	-42.7
	L	-1.17	-7.01	-9.67	-13.3
Aluminum Silicate	V	-1.07	+1.25	.79	-4.39
	I	-1.20	+3.86	3.44	-4.60
	L	-2.57	+3.08	.58	-7.11

Durichlor 51, in these tests, out performed the Duriron and showed good corrosion resistance in both the liquid and the vapor phase. The Duriron proved to be susceptible to attack, particularly in the vapor phase.

Aluminum silicate also possessed good corrosion resistance whereas alumina was quite reactive in the vapor phase. Vitreous carbon had fair corrosion resistance in the vapor phase and at the liquid-vapor interface but was vulnerable to attack in the liquid phase.

The Macor displayed the poorest corrosion resistance of the eleven samples. Macor contains a dispersion of mica to impart its machining characteristics to the ceramic material. The reaction of the mica with the liquid phase was most likely responsible for the observed spalling and delamination.

Of the remaining samples, only three remained after 750 hours of testing, tungsten plate, Inconel 657, and tantalum. These samples were corroded so severely that there was not reason to extend the test to 1000 hours.

The balance of the tested samples were so vulnerable to the acid environment that they were severely corroded after 500 hours and, in some cases 250 hours of exposure.

Based on weight change data, the materials which appear to have the best corrosion resistance are polycrystal silicon, CVD silicon carbide, and silicon nitride. The most attractive metallic compounds are Durichlor 51 and Duriron.

3.5.4.2 452°C Test Results

This series of screening was conducted in two sets: Set one evaluated selected materials for up to 1000 hours, in 250 hour increments and set two evaluated a second set of samples for up to 500 hours. All tests were conducted at 452°C, corresponding to a sulfuric acid vapor pressure of 300 psia, using 98 w/o sulfuric acid. The samples tested were selected based on their performance in the 361°C tests or newly identified candidates. The test facility used in these tests, described in Section 3.5.3 utilized the sealed quartz capsule (see

Figures 3-15, 3-16, and 3-17) to contain the acid and test samples. Therefore, only two samples of each material, one in each of the vapor and liquid phase, were examined, whereas the 361°C test included a third sample, straddling the liquid-vapor interface. Table 3-5 presents the results of all the screening tests conducted at 452°C.

TEST SET ONE: 250 Hour Results

This test set evaluated the ceramic materials that survived the 361°C tests along with a newly identified candidate material, a silicon carbide graphite (SCG) composite. This sample consisted of a vapor deposited silicon carbide surface on a graphite substrate.

Upon completion of the 250 hour test, the capsule containing the SCG was discovered to be shattered. The vapor phase SCG sample showed slight attack, whereas the liquid phase sample was catastrophically attacked and fragmented into at least eight pieces. The other capsules were cracked but not totally fragmented as was the SCG containing capsule. It was theorized that the SCG capsule exploded and the shrapnel from this capsule cracked the others. As a result, the sulfuric acid contained in these capsules had completely vaporized. Only the capsule containing the alumina remained intact.

The explosion of the SCG capsule was thought to be a result of the hot concentrated sulfuric acid penetrating a defect in the SiC coating. The sulfuric acid would then have reacted with the graphite substrate according to the following reaction:

The gaseous products formed by this reaction would result in an increase in pressure within the quartz capsule, possibly causing it to explode.

A review of the temperatures and pressures of the test system indicated that the pressure inside the test vessel had decreased slightly approximately 18 hours into the test. This was compensated for by changing from a static

TABLE 3-5: ACID VAPORIZER MATERIALS SCREENING TEST RESULTS AT 452°C

TEST SET	SAMPLE	SAMPLE LOCATION	Δ WEIGHT/AREA, mg/cm ²			
			250 HOURS	500 HOURS	750 HOURS	1000 HOURS
1	99.7% Alumina	V	13.8	-106.0 ^c	9.13 ^c	-23.4 ^{cd}
		L	9.02	-68.8 ^c	-193.0 ^c	-14.6 ^{cd}
	Aluminum Silicate M-120	V	4.08 ^a	7.47	15.5	19.1
		L	5.84 ^a	6.95	6.90	3.86
	Polycrystal Silicon	V	0.09 ^a	0.43	1.12	-0.27
		L	0.15 ^a	0.0	0.16	1.04
	Hot Pressed Silicon Nitride	V	0.10 ^a	0.83	5.02	2.85
		L	0.15 ^a	-0.11	-2.14	0.09
	CVD Silicon Carbide	V	-0.03 ^a	0.23	1.89 ^c	1.91
		L	0.07 ^a	-0.37	-0.95 ^c	-0.49
	Duro Acid-Proof Brick	V	7.88 ^a	16.6	11.2	19.4
		L	9.44 ^a	6.94	2.75	0.61
	SCG Composite	V	4.55 ^a			
		L	-35.0 ^{ab}			
2	SCG Composite	V	-9.03 ^c	-5.64 ^c		
		L	-10.4 ^c	7.17 ^c		
	Cer-Vit C-144	V	-0.46	-1.36		
		L	0.18	0.76		
	Duriron	V	1.56 ^e	-0.13		
		L	0.21 ^e	0.03		
	Durichlor 51	V	7.53	-0.46 ^e		
		L	1.49	0.04 ^e		
	CVR + CVD SiC on Carbon-Carbon	V	-4.68 ^e	-21.9 ^e		
		L	-2.17 ^e	0.45 ^e		
	CVR + CVD SiC on Graphite	V	-5.82 ^e	-0.33 ^e		
		L	1.57 ^e	-0.47 ^e		
	Infiltrated Carbon-Carbon with CVD SiC	V	-3.43 ^e	-1.61 ^e		
		L	-3.65 ^e	-3.02 ^e		

TEST CONDITIONS: 98 w/o Sulfuric Acid at 452°C
20 Atmospheres (300 psia)

SAMPLE LOCATION: V - Exposed to Vapor Phase Only
L - Exposed to Liquid Phase Only

NOTES: Negative values indicate weight loss per unit area.

^a Quartz capsule holder cracked or broken, probably by 18 hours exposure; sulfuric acid completely vaporized.

^b Total weight of recovered sample pieces used in computation.

^c Quartz capsule holder broken during test.

^d Quartz capsule holder was intact at 126 hours exposure.

^e Quartz capsule holder cracked during test; sulfuric acid completely vaporized.

overpressure to a dynamic system. Prior to the test, the test vessel was leak checked at ambient temperature and 300 psia. It was not possible to leak check the vessel at elevated temperatures. At the completion of the 250 hour test the vessel was slowly cooled to ambient temperatures and again leak checked. Several small leaks were detected around the seal. Upon opening the vessel, there was a slight odor of SO_2 detected and evidence of corrosion along the inner rim of the vessel. These two observations support the theory that an internal pressure build-up caused the capsule to explode. Upon explosion the released acid vapor then attacked the test vessel, inducing the pressure leak. The results of the first 250 hours must be taken in context of the above mentioned malfunction.

SET ONE: 500 Hour Test Results

Due to its catastrophic failure in the first 250 hour increment, the SCG composite was not included in any of the remaining Set One tests. The test vessel was modified to include holder for each individual capsule, isolating them from one another.

After 500 hours of operation at 450°C the system was cooled to ambient temperature and inspected. All capsules were intact except for the alumina containing capsule. The capsule isolation holder was also fractured in the immediate of this sample. Both the liquid and vapor phase alumina samples were severely corroded. The polycrystal silicon, silicon nitride, and CVD silicon carbide displayed insignificant weight changes. The acid proof brick and aluminum silicate both experienced slight weight increases with the vapor phase sample of the acid proof brick gaining the most weight.

SET ONE: 750 Hour Test Results

Two capsules, one containing alumina and the other CVD silicon carbide, exploded during the 750 hour test period. Alumina displayed severe corrosion attack while the CVD silicon carbide had little visual change. The remaining materials displayed the same relative corrosion resistance as after the 500 hour test.

SET ONE: 1000 Hour Test Results

After testing for 1000 hours in 452°C, 98 w/o sulfuric acid, all of the capsules remained intact except for the alumina containing sample.

The corrosion mechanism thought to be occurring is:

This reaction produces $\text{Al}_2(\text{SO}_4)_3$ as a solid and steam. The production of steam may result in a pressure increase inside the capsule, causing it to explode.

A visual inspection of the samples revealed that some of the vapor phase samples experienced a more severe attack at areas where capillary action brought the liquid sulfuric acid in contact with the vapor phase samples. This attack appears, visually, to be more severe than that of the samples exposed to the liquid phase.

Figure 3-18 presents a plot of weight change as a function of time for all the materials, except alumina and SCG, tested at 452°C. This graph shows that three materials experienced minimal weight changes: polycrystal silicon, CVD silicon carbide, and hot pressed silicon nitride. Both the liquid and vapor phase samples of these materials displayed excellent corrosion resistance.

TEST SET TWO: 250 Hour Results

The materials which were evaluated in Test Set 2 included the only two metallic materials which survived the 361°C tests, Duriron and Durichlor 51. Other materials included the SCG composite, Cer-Vit C-144 (leached lithium aluminum silicate with crystalline phase of silica keatite plus mullite), and chemically vapor reacted (CVR) silicon carbide deposited on both graphite and carbon-carbon matrices.

After ~250 hours of testing the vessel was opened and only two of the seven capsules were intact, those containing the Cer-Vit samples and the Durichlor 51

samples. These two samples (along with the Duriron sample) displayed the most corrosion resistance based on the weight change data.

TEST SET TWO: 500 Hour Results

Only two capsules, containing Duriron and Cer-Vit samples, were intact at the end of the 500 hour test. The Durichlor 51 and CVR silicon carbide on carbon-carbon capsules were cracked and the remaining three totally destroyed. In the immediate areas of the shattered capsules the isolation holder was also broken, indicating a violent explosion of the capsules. The explosion of these capsules indicated that a gas producing reaction had occurred. The only reliable data in this test set indicated that Duriron samples, both in the liquid and vapor phases, possessed excellent corrosion resistance. The CVR silicon carbide on carbon-carbon vapor phase sample and the SCG liquid phase sample was totally fragmented.

3.5.4.3 Acid Vaporizer Materials Endurance Test

Based on the results of the 361°C and 452°C screening tests, CVD silicon carbide was selected for an endurance test at 450°C. This test was intended to evaluate the corrosion resistance of CVD silicon carbide as a function of time. Six capsules were installed into the test vessel, with a capsule to be removed every 1000 hours, starting at 1500 hours, up to the total test time of 6000 hours. The capsules were isolated from one another in case one or more of them fails catastrophically, the others would not be affected.

At the 1500 hour point, the test vessel was cooled to ambient temperature and pressure to remove the first set of samples. All of the capsules were discovered to be either broken or, at least, cracked. None of the capsules contained any liquid sulfuric acid.

The samples weighed before and after the test, showed weight increases from .1 to 1.5%, based on their original pre-test weight. Several of the samples had a white deposit that appeared to be sulfate and/or a hard, glassy-like substance. SEM and EDAX analysis found sulfur in extremely small quantities, not sufficient to account for a sulfate deposit. Most likely the sulfur was a

result of inadequate cleaning after the test. Additionally, the white deposit was not removed when immersed in a dilute sulfuric acid solution. The glassy-like deposit proved to be a silicon bearing compound. Other than the white deposit and the glassy like substance, the samples appeared to be virtually unaffected by their exposure to 452°C sulfuric. The total exposure time cannot be determined due to the failure of the capsules.

The problem with capsule explosion has been encountered in all the tests conducted using this particular test method. It was originally thought that by pressurizing the test vessel to ~315 psia, the pressure gradient across the quartz capsule would be minimized, and not likely to cause the capsule to explode (the vapor pressure of concentrated sulfuric acid at 452°C is ~300 psia). The overpressure in the last series of tests fluctuated between 315 and 395 psia. Thus, the possibility exists that either the pressure generated inside the capsule, the acid vapor pressure plus any pressure generated due to a chemical reaction between the acid and the samples, was sufficient to cause the capsule to explode or the overpressure fluctuated to such an extreme that the capsule imploded. Therefore, a series of tests were conducted to measure the pressure limitations of the quartz capsule.

The results of these tests showed that at 452° the capsule can withstand a pressure gradient of ~450 psi without exploding. In this test the capsule was pressurized, at 452°C, until it exploded. There was no overpressure maintained in the test vessel. When the vessel was pressurized, the sealed capsule (without sulfuric acid) was capable of withstanding a pressure gradient >1000 psi at 450°C. The capsule did not implode during this test. Finally, a sealed capsule, containing sulfuric acid only, was heated in the test vessel to 452°C and maintained there for 200 hours. The test vessel was not pressurized. After 200 hours the capsule was still intact. Based on these results, it was concluded that the capsule exploded rather than imploded and that a pressure of >750 psia was generated inside the quartz capsule. Assuming ideality, this calculates to 8.6×10^{-3} moles of gas generated either by means of a chemical reaction or by the vaporization of the sulfuric acid.

It was discovered that silicon carbide, under certain high temperatures and oxygen partial pressures, experiences either an active or passive oxidation^(3-5,3-6). In active oxidation, which occurs at low oxygen partial pressures, gaseous silicon monoxide (SiO) is formed which causes a continuous loss of material from the surface. Conversely, in passive oxidation, at high oxygen partial pressures, a thin protective layer of silica or silicate is initially formed on the surface which limits the rate of any further oxidation. Considering the acid vaporizer materials test environment, it appears that the SiC samples experienced passive oxidation. The probable passive oxidation reactions occurring are:

The situation is further complicated if secondary reactions are considered:

An analysis of the data for the 1500 hour test samples show that all but one of the samples had a weight increase. This weight gain may be attributed to the oxidation process in which heavier oxygen reacts with the SiC to form SiO₂ (Equation 3) and displaces a carbon.

If the secondary reaction (Equations 5 through 7) are assumed to occur, the increase in the total number of moles of gas could account for the high pressures generated within the quartz capsules.

A set of SiC samples were then preoxidized, in air, at 1000°C for 265 hours, before loading them into the quartz capsules. The 265 hours of preoxidation was the time required for the samples to achieve a constant weight. All of the preoxidized samples experienced a slight increase in weight.

The preoxidized samples were placed in the acid containing quartz capsules and sealed. The capsules were then loaded into the test vessel and maintained at 452°C for ~500 hours. To help prevent the capsules from exploding the test vessel overpressure was increased to ~750 psia.

Upon reaching 500 hours of thermal exposure the test vessel was opened. Of the six capsules in the vessel, one had cracked completely in half, one cracked, and had a ~1/8 inch diameter hole in it, one, although intact, has signs of stress cracks, and three had evidence of erosion of the quartz capsule. Photographs of these capsules are shown in Figures 3-19 and 3-20. The four capsules that remain intact appeared to show signs of corrosive attack on the quartz walls by the sulfuric acid. An examination of the test facility found that there was a slight temperature gradient between the bottom and top of the quartz capsule, with the bottom being slightly (~25°C) warmer. This could lead to a refluxing of the sulfuric acid, and, consequently, erosion of the quartz. Scheduling and funding limitations prevented any additional analysis of these particular test samples.

3.5.5 CONCLUSIONS AND RECOMMENDATIONS

Based on the results of the 361°C and 452°C tests, the materials that appear to have the best corrosion resistance to sulfuric acid, in both the liquid and vapor phase, are silicon, CVD silicon carbide, and silicon nitride. The most attractive metallic compounds were Durichlor 51 and Duriron. Silicon carbide, because of its desirable properties, such as good thermal shock resistance and thermal conductivity, coupled with its excellent corrosion resistance, was selected as the reference structural material for the acid vaporizer. Silicon, which is used as braze material for joining silicon carbide parts is also compatible with sulfuric acid at 452°C as shown by the test results.

Figure 3-19. Photograph of Quartz Capsules After 500 Hours at 452°C

Figure 3-20. Photograph of Quartz Capsules After 500 Hours at 452°C

The selection of silicon carbide as the reference acid vaporizer material does not resolve all of the material problem areas associated with the acid vaporizer. The oxidation of silicon carbide must be further explored and evaluated. Additionally, long term endurance tests, preferably in a dynamic mode, should be conducted to verify the screening test results. Attention should also be directed to transition joints, ceramic to metal, that may be required to integrate the acid vaporizer and other process system components.

3.6 REFERENCES

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4.0 REDUCTION REACTOR DESIGN AND ANALYSIS

4.1 BACKGROUND

As shown in Figure 3-1, the acid vapor leaving the vaporizer-2 enters the recuperator at 845°F and is further preheated to 980°F before entering the reduction reactor. Then the acid vapor goes through a preheat section of the reactor first to be further heated above 1500°F before entering the catalyst section. In the preheat section, all the sulfuric acid vapor is decomposed to sulfur trioxide and steam, and a small amount of sulfur trioxide is decomposed to sulfur dioxide and oxygen. In the catalyst section, most of the sulfur trioxide is decomposed to sulfur dioxide and oxygen so that the sulfur dioxide can be recycled to the electrolyzer. The helium that carries the thermal energy from the solar heat source provides all the heat requirements for the reduction reactor.

As a result of preliminary studies, the following thermal and performance design criteria for the preliminary design of the reduction reactor were adopted:

- The general concept will be a tube and shell configuration with packed catalyst to promote the decomposition of sulfur trioxide. The catalyst will be located on the shell-side of the reactor, with helium flow through the tubes.
- The preheat section of the reactor will be loaded with a packed bed of spheres or rings not containing catalyst, but intended to increase the rate of heat transfer.
- Cylindrical catalyst beads, consisting of iron oxide with alumina substrate, will be used.
- The minimum gas temperature in the catalyst bed will be maintained above 1380°F. It is more desirable to maintain the minimum temperature above 1450°F.
- The ratio of the shell-side equivalent diameter to catalyst diameter is to be in the range of 5 to 10.

- Acid vapor side (shell-side) pressure drop is to be less than 30 psi.
- Space velocity will be maintained less than 5000 hr⁻¹.
- The conversion of SO₃ to SO₂ will be in the range of 65 to 70%.
- The temperature of the helium entering the catalyst section should be kept below 1800°F.

4.2 DESCRIPTION OF REFERENCE CONFIGURATION

The reduction reactor is shown pictorially in Figure 4-1; a design study layout is shown in Figure 4-2. It is a shell-and-tube heat exchanger which the heat source, 514 lb/hr of helium, enters at 1790°F and exits at 1375°F, flowing through the tubes. The process gas stream, 486 lb/hr of mixed gases (mostly sulfur oxides), flows through the shell side. The shell side contains two pellet beds in series. The cooler bed consists of inert alumina spheres which are solely to increase the heat transfer from the tubes to the process gas stream. The function of this bed, which is about 10 feet long, is to heat the process gas stream to 1550°F, i.e., into the temperature range in which catalytic decomposition of SO₃ into SO₂ and O₂ proceeds rapidly. The hotter bed consists of alumina pellets coated with iron oxide; in this catalyst bed the SO₃ is rapidly decomposed at temperatures above 1450°F. This bed is approximately 5.5 feet long.

The design approach for this reactor is based on the realization that these vessels eventually must be in accordance with an appropriate design code (probably the ASME code for unfired pressure vessels) and that the earlier the design approaches the requirements of the code, the less difficult code-rating will be. The existing codes do not encompass the use of brittle materials such as silicon carbide as part of the system pressure boundary despite its strength and corrosion resistance. Recent corrosion testing has shown that Alonized Incoloy 800 has adequate corrosion resistance; it cannot be code-certified, however, for temperatures above 1500°F. Alonizing, however, is a surface treatment applicable to many similar alloys. On the assumption that it will serve equally well on Hastelloy-X, a material code-certified to 1700°F, this

Figure 4-1. Reduction Reactor

material has been tentatively selected for the entire pressure boundary of the reduction reactor. If this assumption is not confirmed by future tests, the design will be modified to incorporate an unstressed corrosion resistant liner of Alonized Incoloy 800 supported by a pressure-resistant shell of Hastelloy-X. The tubes are not part of the pressure boundary. Therefore, the pre-heater zone tubes will be Alonized Incoloy 800, because the temperature is below 1600°F and the internal and external pressures are approximately equal. The hot end of the catalyst bed tubes however are filled with helium at 1790°F. Even Hastelloy-X is seriously weakened at this temperature, so silicon carbide has been selected for these tubes and the hot tube sheet.

The selection of silicon carbide tubes for the reduction zone brings up the limitations of length and diameter which were encountered in the acid vaporizer. The same tube cross-section will be used (1.00 inch O.D. x 0.62 inch I.D.) and the length will be slightly less (72.0 inches). Twenty-one of these tubes will be mechanically sealed to a silicon carbide tube sheet at the hot end, with a tube spacing of 1.375 inches. The twenty-one tubes are arranged in a 5 x 5 square array, with the four corner tubes and tube sheet penetrations omitted. Helicoflex seals between the tube hot ends and the hot tube sheet are dimensionally identical to those at the tube cool ends in the intermediate tube sheet (and to those used in the acid vaporizer). At the hot ends, Waspalloy/platinum seals most likely will be necessary because of the higher temperature; this will be determined during the seal test program (Section 3.4, Seal Test Rig, Test (g)).

The tubes of the reduction zone and the preheating zone are continuous flow paths, joined by the penetrations through an intermediate tube sheet made of Incoloy 800. The silicon carbide hot tubes and the Incoloy 800 cool tubes are sealed to tube sheets by Helicoflex seals. The four corner locations of the 5 x 5 array are occupied between the intermediate tube sheet and the "cold" tube sheet by Hastelloy-X tie bars, threaded at both ends, which restrain and separate the two tube sheets so that the preheater zone is a pre-assembled tube bundle.

The reduction reactor is assembled by first building up the preheater tube bundle, consisting of the cold end tube sheet, 21 tubes, the intermediate tube sheet, and four tie bars. This assembly is inserted into the shell, and sealed to the shell flange with an axially compressed Helicoflex seal. The flanged cold end head is similarly sealed to the opposite face of the cold end tube sheet and the two flanges and the tube sheet are clamped together to close the seals. Working from the other end of the shell, the reactor tube bundle is assembled, one tube at a time into the intermediate tube sheet inside the shell, and the hot end tube sheet is fitted over the 21 projecting tube ends. A retainer plate for the tubes and seals is installed to be captured between the tube sheet and the hot end head. The flanges of the shell and hot head and the hot end tube sheet are clamped together to close the shell seals.

Further consideration must be given to the thermal design of the hot end head. To conform to existing code requirements, its metal temperature must be kept below 1700°F, even though it contains 1790°F helium. Some passive internal thermal insulation combined with radiative or convective cooling of the outer surface can be used to establish a thermal gradient through the insulation and metal membrane from the hot gas to ambient; the membrane position along this gradient will be chosen so that the metal temperature will be safely below 1700°F. If this passive solution results in unacceptably large thermal stresses, an alternative solution is active cooling of the head, using a hot unstressed liner to contain as an active heat sink a small flow of the cooled helium leaving the reduction reactor.

After the shell and tube bundles are assembled, the reactor is completed (probably after installation) by installing the two pellet beds. This is done by pouring the pellets into the two loading nozzles, one immediately below the cold end tube sheet for the preheater bed, and the other immediately below the intermediate tube sheet for the catalyst bed. These nozzles are capped during operation. The pellet beds can be removed for replacement through the normally capped drain nozzles, one immediately above the intermediate tube sheet for the preheater bed, and the other immediately above the hot end tube sheet for the catalyst bed.

4.3 THERMAL AND PERFORMANCE DESIGN CONSIDERATIONS

4.3.1 CHEMICAL THERMODYNAMICS

Decomposition of sulfur trioxide, $\text{SO}_3 \rightleftharpoons \text{SO}_2 + \frac{1}{2} \text{O}_2$, is a reversible chemical reaction that is highly temperature and pressure dependent. The decomposition reaction is an endothermic reaction and requires a heat input of 23.2 kcal/g-mole at 1600°F. The selected PTU configuration was based on a system pressure of 20 atmospheres and a SO_3 conversion of 67%. Figure 4-3 shows mole-percent of SO_3 decomposed at equilibrium at 1600°F versus feed acid concentration with pressure as a parameter. Figure 4-4 displays mole-percent of SO_3 decomposed at equilibrium at 20 atmospheres versus feed acid concentration with temperature as a parameter. Reference 4-2 was used to calculate the equilibrium compositions for both Figures 4-3 and 4-4.

The decomposition of sulfur trioxide proceeds at slow rates, even at high temperature. However, it is important to achieve the maximum possible conversion to sulfur dioxide and oxygen per pass through the decomposition reactor. If only a small conversion were obtained per pass, there would be a large amount of unreacted SO_3 carried through the remainder of the process. This would increase the capital and operating expenses while decreasing the overall process efficiency. Therefore, it is necessary to accelerate the decomposition rate of SO_3 to SO_2 and O_2 by catalyzing the reaction. It is recognized that the addition of a catalyst, according to the strict definition of the term, merely speeds up the attainment of equilibrium but does not change the point of equilibrium. That is, the maximum yield in the reaction cannot be changed by adding a catalyst. This consequence follows immediately from thermodynamic arguments, since the change in free energy which controls the equilibrium constant is dependent only on the initial and final states of the system and is independent of the path or mechanism of changing from one state to another. The amount of catalyst used in the reactor must be sufficient to accelerate the reaction so that near-equilibrium conversion is attainable at the desired gas flow rate (space velocity) in the reaction zone. Excess amounts of catalyst, however, will not speed up the reaction or increase conversion efficiencies. The amount of catalyst required is influenced by the flow conditions.

Figure 4-3. Mole Percent of SO_3 Decomposed at Equilibrium at 1600°F

Figure 4-4. Mole-Percent of SO_2 Decomposed at Equilibrium at 20 Atmospheres and Various Temperatures

Increasing the turbulence and mixing action will enhance the conversion rate. It is desirable, therefore, to have a pellet type catalyst to provide a reaction zone that has good mixing and maximum surface area for a given reactor volume.

During the past few years, Westinghouse has experimentally evaluated more than a dozen potential candidate catalysts, which were obtained from commercial vendors. These tests are described in Section 4.5.

Based on the experimental results, catalyst ALFA-4 was selected as a reference catalyst due to its satisfactory performance and low cost. The experimental results indicated that near-equilibrium conversions were obtained at temperatures above 1560°F. Below this temperature, the observed conversion deviated substantially from equilibrium values. Also, at temperatures below 1380°F sulfur was detected on the catalyst. Above 1380°F, there was no sulfur detected. It appeared that the H_2SO_4 feed was reacting with the substrate and/or the iron oxide catalyst. In either case, the catalyst was poisoned at lower temperatures thus degrading its performance. However, at temperatures greater than 1470°F, satisfactory conversions were obtained.

The results of the tests which were conducted at atmospheric pressure and 1650°F using 80 weight percent sulfuric acid are plotted in Figure 4-5. The space velocity (S.V.) is defined as

$$S.V. = \frac{\text{Reactant Volume Flow Rate}}{\text{Volume of the Catalyst Bed}}$$

As can be seen, the lower the space velocity the higher the SO_2 conversion, and the maximum conversion rate is obtained at a lower mass flow rate (G). At the same space velocity, the lower SO_3 conversion at a lower mass flow rate is attributed to the fact that the reaction is controlled by the rate of mass transfer. Due to the limits on the laboratory facilities, the tests could not be conducted at high mass flow rates that were comparable with the PTU operating conditions. Therefore, it is not certain that the maximum conversion has been reached for those cases tested under higher space velocity. For the PTU,

Figure 4-5. Percent SO_3 Conversion Versus Space Velocity and Mass Flow Rate

the space velocity is approximately 2300 hr^{-1} , but the mass flow rate (G) is close to 2.0 lb/sec-ft^2 , which is one to two orders of magnitude higher than tested mass flow rate. Thus, for the PTU the reaction is not mass limiting, instead it is rate limiting at isothermal conditions. Therefore, using the laboratory test data to predict the rate constant for the reactor of the PTU would tend to underestimate the rate constant.

By definition of space velocity and assuming an integral plug flow reactor.

$$S.V. = \frac{k V_{cata}}{F} = -\ln \left(\frac{X_e - X}{X_e} \right) \quad (4-1)$$

and the Arrhenius equation

$$k = K e^{(-E/RT)} \quad (4-2)$$

where k = rate constant, hr^{-1}

V_{cata} = the volume of the catalyst bed, ft^3

F = reactant volume flow rate, ft^3/hr

X_e = SO_3 equilibrium conversion at specified temperature and pressure

X = % SO_3 converted

K = Arrhenius constant, hr^{-1}

E = activation energy, Btu/lb-mole

R = gas constant = $1.986 \text{ Btu/lb-mole-}^\circ\text{R}$

T = reaction temperature, $^\circ\text{R}$

from Equation (4-1), $k = \frac{F}{V_{cata}} \left(-\ln \left(\frac{X_e - X}{X_e} \right) \right)$

combined with Equation (4-2),

$$k = \frac{F}{V_{cata}} \left(-\ln \left(\frac{X_e - X}{X_e} \right) \right) = K e^{(-E/RT)} \quad (4-3)$$

From the results of the tests conducted at 1472°F and 1652°F, knowing the actual and equilibrium SO₃ conversions, two rate constants (k) at two different temperatures can be calculated. Using the two rate constants at two specified temperatures, two equations can be obtained from Equation (4-3). Thus, the two unknowns, Arrhenius constant (K) and activation energy (E), can be determined. For designing the PTU reactor, E = 46924 cal/g-mole (84464 Btu/lb-mole) and K = $3.75 \times 10^{13} \text{ hr}^{-1}$ were employed.

4.3.2 HEAT TRANSFER RATE

As mentioned previously, decomposition of sulfur trioxide is an endothermic reaction and is highly sensitive to temperature. The heat flux will determine not only whether the reaction is heat transfer limiting or rate limiting but also the size of the reactor. Since the preheat section and the catalyst section are packed with spheres and catalyst pellets, respectively, calculations for heat transfer in packed beds were performed using Reference 4-4. With a few reactor configurations (tube arrangements) in mind, the overall heat transfer coefficient was calculated to be in the range of 27 to 33 Btu/hr-ft² - °F. The heat flux is in the range of 4,500 to 5,500 Btu/hr-ft². With this fairly low heat flux, the reactor needs a large heat transfer surface. However, to keep the size of the reactor compact, it is necessary to use a larger number of tubes with a smaller diameter to increase the heat transfer surface. Moreover, to avoid a radial temperature gradient in the catalyst bed, the tubes (hot helium in tube side) must be arranged fairly close together and still maintain a reasonable ratio of equivalent diameter to catalyst pellet diameter.

4.3.3 DESIGN OF CATALYST BED

The constraints of designing the catalyst bed are described as follows:

- The temperature of the helium entering the catalyst section would desirably be kept below 1800°F due to the consideration on the material of construction.
- The minimum gas temperature in the catalyst bed must be maintained above 1380°F to avoid sulfur deposition on the catalyst substrate. It is more desirable to maintain the minimum temperature above 1450°F.

- SO_3 conversion obtained in the catalyst bed is to be 67%.

For the heat flux range stated above, the rapid reaction is definitely controlled by the rate of heat transfer, thus a kinetic model would be unnecessary. The rate constant obtained from the laboratory tests would be rather sufficient to serve as a guideline; with the reference reactor tube arrangement stated previously, the appropriate design analysis is to determine the length of catalyst bed, and the temperature profiles for both acid and helium streams in the catalyst section. Using the rate constant and the heat transfer rate described previously, three differential equations can be written:

Heat balance on helium:

$$\frac{dT_1}{dL} = \frac{U_o A' (T_1 - T_2)}{\dot{m}_1 C_{p1}} \quad (4-4)$$

Heat balance on acid vapor:

$$\frac{dT_2}{dL} = \frac{U_o A' (T_1 - T_2)}{\dot{m}_2 C_{p2}} - \frac{\Delta H C_{Ao}}{\dot{m} C_{p2}} (K e^{-E/RT}) (x_e - x) \quad (4-5)$$

Plug - Flow Reactor:

$$\frac{dx}{dL} = \frac{A}{F} (K e^{-E/RT_2}) (x_e - x) \quad (4-6)$$

where T_1 is helium temperature, $^{\circ}\text{R}$
 T_2 is acid vapor temperature, $^{\circ}\text{R}$
 L is the length of catalysts bed, ft
 C_{p1} is the specific heat of helium, $\text{btu/lb-}^{\circ}\text{R}$
 $\dot{m}_1$ is helium flow rate, lbs/hr
 $\dot{m}_2$ is acid flow rate, lbs/hr

C_{p2} is the specific heat of acid vapor, Btu/lb-°R
 U_o is overall heat transfer coefficient, Btu/hr - ft²-°R
 A' is heat transfer surface area per unit length, ft²/ft
 A is the cross sectional area of the catalyst bed, ft²
 ΔH is the heat of decomposition of SO₃, Btu/lb - mole
 C_{A0} is the initial concentration of SO₃ in the gas stream entering the catalyst bed, lb - mole of SO₃/ft³ of gas
 K is Arrhenius constant, hr⁻¹
 E is activation energy, Btu/lb - mole
 R is gas constant in Btu/lb - mole - °R
 X_e is the fraction of SO₃ decomposed at equilibrium
 $(X_e = (0.1086 T_2 - 156.4)/100)$
 X is the actual fraction of SO₃ decomposed
 F is gas flow rate entering the catalyst bed, ft³/hr.

The simultaneous differential Equations (4-4), (4-5) and (4-6) can be solved with a computer digital method using Reference 4-5. The equilibrium and the actual SO₃ conversion and both the gas and helium temperature profiles are plotted in Figure 4-6 for the reference case. As the design goal is to obtain 67% SO₃ conversion, a catalyst bed length of 5.5 ft. is needed.

4.3.4 SENSITIVITY STUDIES ON THE CATALYST BED

As described previously, the reaction rate constant is based on the result of the laboratory tests which were conducted under different parameters than the projected operating conditions of the PTU. Moreover, the heat transfer rate is strictly based on theoretical calculations without confirmation from tests. Thus a scoping study to investigate the sensitivity of the size of the catalyst bed to the variations of the rate constant and the heat transfer rate is warranted.

Two inputs are required for the computer program (Reference 4-5). One is the temperature of the helium leaving the catalyst bed, and the other is the temperature of the gas entering the catalyst bed. Adjustments should be made on

Figure 4-6. Length of Catalyst Bed Versus Percent SO_3 Conversion and Temperatures (Reference Case)

TABLE 4-1

SUMMARY OF THE SENSITIVITY STUDIES

Cases	1 (R_{ref})	2	3	4	5	6	7
Catalyst Bed Length, ft.	5.42	4.08	7.67	3.50	6.33	6.17	4.42
Gaseous Stream Inlet Temp., $^{\circ}\text{F}$	1550	1500	1600	1600	1550	1550	1570
Gaseous Stream Outlet Temp., $^{\circ}\text{F}$	1620	1633	1611	1604	1637	1624	1619
Helium Inlet Temp., $^{\circ}\text{F}$	1791	1766	1819	1816	1798	1793	1804
Helium Outlet Temp., $^{\circ}\text{F}$	1600	1550	1650	1650	1600	1600	1620
Minimum Temp. in Catalyst Bed, $^{\circ}\text{F}$	1454	1456	1450	1418	1480	1485	1421
Arrhenius Constant, hr^{-1}	3.75×10^{13}	3.75×10^{13}	3.75×10^{13}	1.875×10^{13}	1.875×10^{13}	3.75×10^{13}	3.75×10^{13}
Overall Heat Transfer Coeff., $\text{Btu/hr-ft}^2\text{-}^{\circ}\text{R}$	32.4	64.8	16.2	32.4	32.4	32.4	32.4
Activation Energy/ Gas Constant (E/R), $^{\circ}\text{R}$	42530	42530	42530	42530	42530	63795	21265

the two input temperatures to meet the constraints mentioned previously. Seven cases were studied:

- Case 1: Case 1 is the reference case as described above.
- Case 2: Assuming the heat transfer rate between the helium and the gas is twice the rate of Case 1. In order to obtain 67% SO_3 conversion, it requires a catalyst bed of 4 ft. 1 in. in length.
- Case 3: Assuming the heat transfer rate between the helium and the gas is only one half of Case 1. A catalyst bed of 7 ft. 8 in. in length is required.
- Case 4: Assuming the rate constant is five times the rate of Case 1. A catalyst bed length of 3 ft. 6 in. is required. Case 4 may be an exaggerated case.
- Case 5: Assuming the rate constant is one half of Case 1. A catalyst bed length of 6 ft. 4 in. is required. As explained previously, the rate constant for Case 1 is more likely to be underestimated; therefore, Case 5 is not likely to occur.
- Case 6: Assuming the activation energy (E) is 50% higher than that of Case 1. A catalyst bed length of 6 ft. 2 in. is required. It is felt that the possibility of underestimating the activation energy for Case 1 is low; therefore, Case 6 is not likely to occur.
- Case 7: Assuming the activation energy is 50% lower than that of Case 1. A catalyst bed length of 4 ft. 5 in. is required.

The key parameters and the results of the studies are summarized in Table 4-1. For the seven cases studied above, the key parameters are all within the constraints required. The worst two cases are Cases 3 and 4. For Case 3, the reference configuration is 30% underestimated. For Case 4, only 65% of the capacity of the reference configuration is required.

4.3.5 DESIGN OF PREHEAT SECTION

The decomposition of H_2SO_4 into H_2O and SO_3 is a fairly fast reaction at the designed temperature range without catalyst. Therefore, the size of the preheating section is strictly based on the rate of heat transfer and the heat required for the reaction as well as for the preheat of the gas stream. For

the reference configuration, the length of the preheating section is approximately 9 ft.

The pressure drop of the reactor for the reference configuration is calculated to be approximately 2.0 psi for the tube side (helium) and 26 psi for the shell-side (acid). As can be seen from Figure 3-1, to overcome the shell-side pressure drop, only the pump, P-1, is required to pump the H_2SO_4 solution, therefore the power consumption is not significant.

4.3.6 TEMPERATURE DROPS ACROSS THE WALLS AND FILMS

For the purpose of stress analysis, the temperature drops across the walls and films were also calculated. They are as follows:

	Δt Across Inside Film	Δt Across Wall	Δt Across Outside Film
At the face where helium enters the catalyst bed	75°F	4°F	92°F
At the face where helium leaves the catalyst bed	22°F	1°F	27°F
At the face where helium leaves the preheat section	173°F	9°F	213°F

The face where the helium leaves the catalyst bed is also the face where the helium enters the preheat section. The temperature drops across the wall and films at that face are so low owing to the fact that there is only 50°F difference in temperature between the hotter and cooler streams.

For the shell side assuming 8 inch DYNA-FLEX insulation, the outside shell, the temperature drops across the wall and films are listed in the following:

	Δt Across Inside Film	Δt Across Wall	Δt Across Outside Film
At the face where helium enters the catalyst bed	11.5°F	0.7	1518
At the face where helium leaves the catalyst bed	11	0.6	1449
At the face where helium leaves the preheat section	7	0.4	887

As can be seen, the temperature drop across the shell wall is insignificant due to insulation, and most of the temperature drop is across the insulation.

4.4 STRUCTURAL DESIGN/ANALYSIS CONSIDERATIONS

Reviewing, the reduction reactor shown in Figure 4-1 and 4-2 is a shell-and-tube heat exchanger in which hot helium enters the inlet plenum and flows through the tubes to the helium exit plenum. The heads of the unit form the outer boundaries of the helium plena. Process gas flows lengthwise in the shell, through the catalyst around the tubes. The tubes and tube sheets maintain separation of the helium and process gas with the tubes providing the required heat transfer area. The shell holds the catalyst bed and the tubes and controls the flow of the process gas.

The heads and cylindrical shell form the outer pressure boundary of the reduction reactor. The head temperatures and pressures are determined by the helium loop conditions and the shell temperature and pressure is dependent on the process gas loop conditions. The tubing and tube sheet loadings are influenced by both fluids since they form the interface between the loops.

4.4.1 STRUCTURAL MODELS/ASSUMPTIONS

The analyses performed were preliminary in nature and many design details were not evaluated. Dead weight effects, bolt preload effects, and thermal stresses were assumed to be small and were not evaluated. In addition, transients and off-design conditions were not considered.

Pressure/Boundary

The reduction reactor shell stresses were calculated under internal pressure loading equal to process gas inlet pressure of 319 psia at a metal temperature of 1600°F, only 12°F below process gas outlet temperature. The shell will probably run cooler than this due to the convective heat loss at the outside surface.

The cold head was evaluated at helium exit pressure of 304 psia and temperature of 1375°F. The hot head was evaluated under helium inlet pressure of 307 psia, at 1600°F. It was assumed that a thermal liner can be provided inside of the head so that the metal temperature (with convection heat loss at the outer surface) can be maintained below the 1790°F helium inlet temperature.

Tubing/Tube Sheets

The tubing and tube sheet pressure differences are small under normal operation with flow in both fluid loops. Therefore, it was conservatively assumed that flow and pressure could be lost in either loop and the full pressure of the remaining loop could be applied across the loop/loop interface (tubing and tube sheets). It was also assumed that the tubing and tube sheet temperatures are at or near the fluid temperatures.

It was assumed that the tubes can slide axially in the tube sheet/tube seals due to axial differential thermal expansion between tubes and shell. If the seals were to function improperly, restraint of this motion would result in axial loading of the tubes.

Clamp Rings

Each clamp ring flange is assumed to be loaded in the axial direction by the mating head/shell flanges. The axial force applied is equal to the sum of the fluid pressure force on the seal over plus the force to compress the seal. The clamp flanges are bent away from each other by this loading. The clamp temperature is assumed to approach that of the adjacent components, about 1600°F maximum.

4.4.2 STRESS ANALYSIS SUMMARY

A tabulation of the calculated stresses in the shell, heads, tube sheets, clamps and tubing is provided in Table 4-2. These stresses are based on nominal dimensions, pressures and temperatures from the preliminary layout in Figure 4-2. For the metal components, primary membrane stresses and membrane plus bending stresses are listed. The maximum elastic stresses are listed for the silicon carbide tube sheet and tubes.

The membrane stresses are the average stresses across a section. Note the general low level of membrane stresses (1217 to 2923 psi). The membrane plus bending stresses are quite high in the various component flanges. It would appear from the numbers that more conventional bolted flanges should be used if possible.

The maximum peak stress in the silicon carbide tube sheet is 9831 psi at the ligament surface (in a very small volume of material). The maximum carbide tube stress is 666 psi.

4.4.3 STRUCTURAL DESIGN CRITERIA CONSIDERATIONS

Metal Components

The ASME Boiler and Pressure Vessel Code establishes formal safety rules for design, fabrication and inspection of pressure vessels. Therefore, the pressure boundary was evaluated using the applicable section, Section VIII, Division 1, of the 1980 code. The code does not provide rules for the design of internals such as the tubes which are important to the function of unit but not its safety. The metal internals were evaluated to ASME allowables for this study, although the unit could be code stamped even if alternate criteria were used.

ASME provides allowable stresses for various materials as functions of temperature. Only these materials are acceptable in a coded vessel and the materials can only be used at temperatures for which allowable stresses are provided. A number of materials were compared to determine which was the best for the

TABLE 4-2

DECOMPOSITION REACTOR STRESS SUMMARY

Component	Stress Combination	Stress psi	Temp °F
Shell cylinder flange	hoop stress → membrane	1217	1600°
	shear → membrane (equiv. tens.)	12062	<1600°
	shear + bending → mem. + bend.	33773	<1600°
Hot Head center flange hub	hoop stress → membrane	2923	1788°
	shear + bending → memb. + bend.	33773	<1788°
	tension + bending → memb. + bend.	208825	<1788°
Cold Head center flange hub	hoop stress → membrane	< 2923	1375°
	shear + bend. → memb. + bend.	< 33773	<1375°
	tens. + bend. → memb. + bend.	< 208825	<1375°
Cold Tube Sheet	surface averaged → membrane +	< 2809	1375°
	across ligament → bending		
Clamp flange ring	shear + bending → memb. + bend.	< 33733	<1600°
	bend. + tens. → memb. + bend.	42526	<1600°
Hot Tube Sheet	peak ligament → max @ surface elastic	9831	1788°
Hot End Tubes hoop + thermal	max elastic → pressure + thermal	666	1788°

TABLE 4-3

DECOMPOSITION REACTOR STRESS EVALUATION

Component	Stress Combination	Calculated		Allowable Stress - psi		
		Stress psi	Temp °F	Incoloy* 800 SB 409	Hast* G SB 582	Hast* X SB 435
Shell cylinder flange	hoop stress → membrane	1217	1600°	at 1500°F	at 1000°F	1700 ✓
	shear → membrane (equiv. tens.)	12062	<1600°	(800)	(19000)	1700
	shear + bending → mem. + bend.	33773	<1600°	(800)	(19000)	2550
Hot Head center flange hub	hoop stress → membrane	2923	1788°	at 1500°F	at 1000°F	at 1600°F
	shear + bending → memb. + bend.	33773	<1788°	(800)	(19000)	(1700)
	tension + bending → memb. + bend.	208825	<1788°	(1200)	(28500)	(2550)
Cold Head center flange hub	hoop stress → membrane	< 2923	1375°	1100	at 1000°F	4800 ✓
	shear + bend. → memb. + bend.	< 33773	<1375°	1650	(19000)	1700
	tens. + bend. → memb. + bend.	< 208825	<1375°	1650	(28500)	7200
Cold Tube Sheet	surface averaged → membrane + across ligament → bending	< 2809	1375°	1650	at 1000°F (28500)	7200 ✓
Clamp flange ring	shear + bending → memb. + bend.	< 33733	<1600°	Nitronic 60** (est. 50,000 @ 800°F)		
	bend. + tens. → memb. + bend.	42526	<1600°			
Hot Tube Sheet	peak ligament → max @ surface elastic	9831	1788°	Silicon Carbide*** ~10500 ✓		
Hot End Tubes hoop + thermal	max elastic → pressure + thermal	666	1788°	~10500 ✓		

* Based on ASME

** Estimated from hardened 301 SS

*** Silicon Carbide for Reliability of .99 in 1 in. 3

✓ indicates adequacy

unit. Incoloy 800 and Hastelloy G were examined because they appeared promising from a corrosion standpoint. Hastelloy X was considered because it is the best high temperature material in the code similar to Hastelloy G.

Table 4-3 compares the allowables for the above 3 materials with the stresses computed in Table 4-2. Note that Hastelloy G is not code rated above 1000°F and is not code acceptable for any component. Incoloy 800 is rated to only 1500°F and cannot be used except in the cold head and tube sheet unless a component cooling system is devised. Hastelloy X can be used everywhere except in the hot head. If this head temperature can be maintained at or below 1600°F by use of a thermal liner and convection cooling, Hastelloy X would be satisfactory. Note that all of the flanges must be modified as discussed above in Section 4.4.2.

Table 4-3 also shows the clamp flange and ring stresses although it is uncertain what the allowables are for Nitronic 60 material. It is likely that considerable flange redesign will be necessary, probably eliminating the clamp.

Silicon Carbide Components

The hot tube sheet and hot end tubes are made from silicon carbide rather than metal and, therefore, the ASME criteria is not applicable. It is necessary to use statistical methods to properly evaluate this material (see Section 3.3.3). A detailed statistical analysis was not performed, rather a tentative allowable stress for small volumes of material was selected from Figure 3-10. The 10,500 psi allowable listed in Table 4.3 represents a probability of failure of 0.01 (99% reliability) in a uniformly stressed tensile specimen of 1 cubic inch volume. The tube sheet is acceptable because the volume of material at 9831 psi is well below 1 cubic inch, and the tube is acceptable because the 666 psi stress is well below the 10,500 psi value for 99% reliability in 1 cubic inch.

4.4.4 CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations made during the stress analysis of the reduction reactor are listed below:

- 1) The basic concept of the decomposition reactor as shown in Figure 4.2 is satisfactory structurally, providing the tube seals permit free axial sliding of the tubes, but numerous modifications will be required before the design can meet ASME requirements.
- 2) Structurally, Hastelloy X is probably the best choice for head, shell, and tube sheet material. Incoloy 800 cannot be code certified for temperatures above 1500°F, and even at that temperature its allowable stress is about 26% of that of Hastelloy X.
- 3) If Hastelloy X cannot be coated to provide adequate corrosion protection, or if the coating process degrades the structural capability of the material, a thin coated liner can be provided for corrosion protection.
- 4) A thermal liner (ceramic or metal) is required inside of the hot head so that the structural metal temperature does not exceed 1650°F.
- 5) The flange clamp material, Nitronic 60, has a strength advantage over other choices only if it is cold worked. This specialty stainless steel will experience a significant strength loss with temperature and will become completely annealed at about 1300°F. If the clamp temperature exceeds about 700-800° (precluding insulation), a different material should be selected.
- 6) The flanges and flange hubs are undersized. Flange redesign will be required to meet ASME allowables.
- 7) The material combination at the hot flange joint produces differential thermal expansion problems at this hot, highly loaded joint. It would be better to trap the silicon carbide tube sheet between internal ledges in the shell and head and provide a conventional bolted flange between these metal components.

4.5 REDUCTION REACTOR CATALYST EVALUATIONS

4.5.1 BACKGROUND AND SUMMARY

Experimental evaluations of a number of potential catalysts for the reduction reactor were conducted under this contract. The results of these catalyst tests are reported herein.

The high temperature thermochemical portion of the cycle involves two steps, as shown in reactions (1) and (2).

Reaction (1) is the thermal decomposition of liquid sulfuric acid into its vapor products, steam and SO_3 . This step occurs in an acid vaporizer and only requires an input of thermal energy sufficient to vaporize the liquid acid.

Reaction (2), the endothermic reduction of sulfur trioxide, is carried out in a single pass, plug flow reactor. In order to effect heat economy, it is important to achieve the maximum possible conversion of SO_3 to SO_2 per pass through the reduction reactor. However, the purely thermal reduction of SO_3 to SO_2 proceeds at a very slow rate, even at high temperatures. Therefore, to achieve an acceptable reduction rate, it is necessary to catalyze the reaction.

The overall objectives of the test program was to identify attractive catalysts for the reduction of SO_3 . Since the reduction of SO_3 to SO_2 is not conducted commercially, there was an absence of published data and information regarding available catalysts. Thus, the overall scope of the catalyst evaluation task included the following efforts:

- identification and procurement of candidate catalysts,
- evaluation of all candidates via a series of screening tests.
- indepth testing of the most attractive candidate, and
- selection of the reference catalyst based on the results of the indepth testing.

It must be noted that the design and development of a custom catalyst was beyond the scope of the test program. All of the candidates that were tested are commercially available and were obtained after discussion with various catalyst manufacturers.

Acceptable catalysts had to fulfill two major criteria:

- sufficient catalytic activity to produce near equilibrium conversions, and

- the ability to maintain near equilibrium conversions over an extended period of time.

A listing of all the evaluated catalysts is presented in Table 4-4. On the basis of the screening tests, two quite attractive candidates were identified, ALFA-4 (iron oxide on an alumina substrate) and MB-3 (platinum on alumina). The remaining candidates were judged to be unacceptable because of poor catalytic activity, catalyst instability in the test environment, or (in reference to the precious metal candidates) activity less than that displayed by MB-3.

Catalysts ALFA-4 and MB-3 both produced conversions greater than 90% of equilibrium at temperatures above 850°C (1562°F). Additionally, both catalysts displayed the ability to maintain consistent performance levels for 1000 hours. Considering the relative economics of platinum and iron oxide, ALFA-4 was selected as the reference catalyst for the sulfur cycle.

The balance of this section includes a description of the evolution of the test procedures and facilities, a discussion on the screening tests and the indepth tests, and the results of a long term (5000 hour) endurance test on catalyst ALFA-4. Also evaluated are the results of a physical characterization of catalyst ALFA-4 after a 2800 hour exposure to the test environment.

4.5.2 EXPERIMENTAL TEST PROCEDURES

Although the operating parameters of the Sulfur Cycle require that the SO_3 reduction reaction occur in the presence of steam (as a result of the thermal decomposition of liquid sulfuric acid), the candidate catalysts were evaluated in any or all of three environments:

anhydrous	- 92% (by volume) Argon carrier gas 8% (by volume) SO_3
wet	- 63% (by volume) Argon carrier gas 26% (by volume) steam 11% (by volume) SO_3

TABLE 4-4: SO₃ REDUCTION CATALYSTS EVALUATED

CATALYST I.D.	COMPOSITION AND GEOMETRY
WX-2	V ₂ O ₅ , 6 x 6 mm Cylindrical Pellets
MB-2	1.0% Pt on 3.2 mm Al ₂ O ₃ Spheres, Intermediate Surface Area (>10, <100 m ² /G)
MB-3	1.0% on 3.2 mm Al ₂ O ₃ Spheres, Intermediate Surface Area
ENG-1	0.5% Pt on 3.2 mm Cylindrical Al ₂ O ₃ Pellets
ALFA-2	0.5% Pd on 3.2 mm Cylindrical Al ₂ O ₃ Pellets
ALFA-3	Cr ₂ O ₃ , 6 mm Cylindrical Pellets
ALFA-4	20% Fe ₂ O ₃ on 3.2 mm Al ₂ O ₃ Cylindrical Pellets
ALFA-5	98% MgO, 3.2 mm Cylindrical Pellets
KAT-1	Al ₂ O ₃ , 3.2 mm Pellets, Low Surface Area
CE-1	Fe ₂ O ₃ Powder, <10 Mesh
CE-2	Fe ₂ O ₃ Powder, >10, <20 Mesh

NOTE: The steam/SO₃ ratio represents an 80% (by weight) sulfuric acid feed. If the inert carrier gas is included the acid concentration is ~23%

Acid Decomposition - 80% (by weight) sulfuric acid

4.5.2.1 Anhydrous and Wet Test Procedures

All of the candidate catalysts experienced preliminary screening tests in the anhydrous environment. In these tests, Argon was used as carrier gas for the SO₃. These tests were conducted in test facility designed for use with an Argon-SO₃ feed. This type of system was simpler to operate than one rising steam-SO₃ and was believed to yield reaction kinetics substantially the same as the kinetics of a steam-SO₃ system.

The most attractive candidates in the anhydrous testing were then evaluated using the wet test environment. A schematic diagram of the test facility, used for both the anhydrous and wet tests, is presented in Figure 4-7 and a photo in Figure 4-8. The basic operation of the facility involves delivering a known gas flow over a specified volume of catalyst. Analysis of the product stream then provided the degree of conversion of SO₃ to SO₂. A detailed description on the operation of this test facility is provided in Appendix A.

By varying the gas flow rate, it was possible to evaluate a single catalyst bed volume over a range of space velocities. For the anhydrous and wet tests, space velocity was defined as:

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

The volumetric gas flow was calculated at the inlet to the reactor tube and the catalyst bed volume was simply the volume of the reaction tube occupied by the catalyst bed.

Figure 4-7. Schematic of Experimental Apparatus for Evaluating SO₃ Reduction Catalysts in Anhydrous and Wet Environments

Figure 4-8. Photograph of SO_2 Reduction Catalyst Screening Test Facility, Anhydrous and Wet Environments

Prior to a test series, the range of space-velocities to be tested was determined and then, using Equation 1, the total gas flows and catalyst bed volume calculated. The catalyst was loaded into a quartz reaction tube and the loaded reaction tube then centered in a split tube furnace. Physical limitations of the SO_3 delivery system restricted the space velocity range for a particular catalyst volume. Therefore, up to three separate catalyst beds were used to evaluate the catalyst over a space velocity range of 1000 to 50,000 hr^{-1} . Only catalysts that displayed significant activity at the lower space velocities were examined throughout this range.

During a test the Argon and SO_3 (and steam if a wet test) flow rates, furnace temperature and product stream flow were monitored and recorded. Tests were conducted over a temperature range of 650° to 900°C.

4.5.2.2 Acid Decomposition Test Procedures

As the catalyst evolution program matured it became evident that a more sophisticated means of evaluating the catalysts was needed. While the wet test facility provided a simulated acid environment a carrier gas was still used to entrain the SO_3 /steam fuel and carry it through the catalyst bed within a reasonable residence time. The effect of the carrier gas on the equilibrium conversion of SO_3 to SO_2 was a major area of concern. Thus, the need for a test facility that employed a liquid sulfuric acid feed became apparent. The H_2SO_4 Acid Decomposition Test Facility, shown in Figure 4-9 was then designed and constructed. By incorporating an acid metering pump and a quartz acid vaporizer, the need for a carrier gas was eliminated. A schematic diagram is presented in Figure 4-10 and detailed operating procedures in Appendix B. The use of this test facility provides the ability to evaluate catalysts under conditions approximating those of the Sulfur Cycle. The only significant difference between the test facility and the Sulfur Cycle is the operating pressure; the actual process is designed to operate at pressures up to 20 atmospheres whereas all testing was conducted at approximately one atmosphere.

A known flowrate of liquid sulfuric acid is delivered to the quartz acid vaporizer via a calibrated metering pump. The sulfuric acid is then thermally

Figure 4-9. Photograph of H₂SO₄ Decomposition Test Facility

Figure 4-10. Schematic of H_2SO_4 Decomposition Catalyst Test Facility

decomposed into its vapor products steam and SO_3 . The steam and SO_3 pass through the packed catalyst bed where the SO_3 is reduced to SO_2 and O_2 . Catalytic activity is determined by analyzing the product stream.

To evaluate the catalysts over a range of space velocities the liquid acid feed rate was adjusted accordingly. When using the liquid acid feed the relationship between the catalyst bed volume and the liquid acid feed rate was identified as the "liquid hourly space velocity" (LHSV)². LHSV is a commonly used term when the process feed is metered as a liquid at room temperature while the reaction mixture is a gas at the reaction temperature. LHSV is defined as:

$$\text{LHSV} = \frac{F_{\text{Ao}}}{V_r \epsilon} \quad (2)$$

where F_{Ao} = liquid acid feed rate

V_r = reactor volume

ϵ = void fraction of catalyst bed

To compensate for the irregularities in pellet size, the denominator of Equation 2 was defined as

$$V_r \epsilon = V_r = \frac{W}{\rho} \quad (3)$$

W = catalyst weight

ρ = full density of catalyst

Equation 2 then becomes:

$$\text{LHSV} = \frac{F_{\text{Ao}}}{V_r \frac{W}{\rho}} \quad (4)$$

By loading a prescribed mass of catalyst into the reaction tube and measuring the length of the catalyst bed, the required feed rate to produce a consistent LHSV between respective catalyst loadings was determined. This provided a

reliable and accurate relative basis of comparison for the catalysts tested using liquid sulfuric and acid.

As in the anhydrous and wet tests, catalysts were evaluated between 650° and 900°C. The following section of this report presents a brief discussion of the reaction kinetics, the procedures used to calculate the extent of SO_3 conversion to SO_2 , and the equilibrium conversion.

4.5.2.3 Reaction Kinetics

The reduction of pure SO_3 can be written as:

The conversion, X , in a plug flow reactor is given by

$$X_A = \frac{F_{A0} - F_A}{F_{A0}} \quad (6)$$

where F_{A0} - molar flowrate of species A at the reactor inlet

F_A - molar flowrate of species A at the reactor outlet

The conversion of SO_3 to SO_2 can then be calculated by

$$X_{\text{SO}_3} = \frac{F_{\text{SO}_{3A}} - F_{\text{SO}_3}}{F_{\text{SO}_{3A}}} \quad (7)$$

from the stoichiometry of Equation 5, the quantity $(F_{\text{SO}_{3A}} - F_{\text{SO}_3})$ equals the molar flow rate of SO_2 (F_{SO_2}) produced. Thus, the conversion of SO_3 becomes

$$X_{\text{SO}_3} = \frac{F_{\text{SO}_2}}{F_{\text{SO}_{3A}}} \quad (8)$$

If ideality is assumed for both SO_2 and SO_3 , the molar flowrates can be equated to the volumetric flowrate (Q) of each respective gas. The conversion of SO_3 is then calculated in terms of easily measured parameters as shown:

$$x_{\text{SO}_3} = \frac{Q_{\text{SO}_2}}{Q_{\text{SO}_3}} \quad (9)$$

This equation proves extremely useful when calculating the conversion in the anhydrous and wet tests. In both of these tests, SO_3 flowrate (Q_{SO_3}) is metered with a calibrated rotameter. The SO_2 flowrate of the product stream is determined using a DuPont Model 411 Photometric SO_2 Analyzer and a bubble flowmeter. The SO_2 analyzer measures the percentage of SO_2 in the product stream and the bubble flowmeter measures the total volumetric flowrate of the product stream. The product of these two terms yields the volumetric flowrate of SO_2 (Q_{SO_2}). By know Q_{SO_3} and Q_{SO_2} , the conversion can be calculated using Equation 9.

In the wet tests and acid decomposition tests, the conversion can be calculated by relating the concentration of the unreacted sulfuric acid with the concentration of the feed acid. In these test modes the reaction occurring can be written

where the SO_3 on the right side of the equation represents the unreacted SO_3 . The product stream in these tests passed through a water cooled condenser to collect the steam and unreacted SO_3 in the form of dilute sulfuric acid.

The conversion calculation procedure simply involves titrating the feed acid and the collected unreacted condensate. The conversion is then calculated by:

$$x_{\text{SO}_3} = \frac{C_i - C_f}{C_i} \quad (11)$$

where C_i = initial concentration of feed acid
 C_f = concentration of unreacted acid

When evaluating the catalysts in the acid decomposition test facility it is possible to determine the conversion in a more accurate manner. This procedure involves measuring the specific gravity and temperature of the feed acid and the unreacted acid. A correlation between the difference in specific gravity (compensated for solution temperature) of the feed and unreacted acid was developed and used to determine the conversion.

To determine the efficiency of each catalyst, the measured conversion was normalized with the equilibrium conversion. Equilibrium conversion represent the maximum possible conversion of SO_3 to SO_2 that can occur under the thermodynamic restrictions imposed by the test parameters. Using NASA computer code TRAN 72⁽³⁾ the equilibrium conversions as a function of temperature, pressure, and acid concentration were calculated. Table 4-5 presents the equilibrium conversion at various temperatures and acid concentrations at one atmosphere pressure. Equilibrium conversions at elevated pressures were not included as all testing was conducted at approximately one atmosphere. Equilibrium conversion will decrease as the pressure increases by a factor of $(P_{\text{Total}})^{-1/2}$.⁽⁴⁾ The effect of higher pressures on catalyst efficiency was assumed to be equal for all the catalysts. Since the equilibrium conversion is a function of acid concentration, it was necessary to normalize the measured conversion with the equilibrium conversion so that the efficiencies of the catalyst under the various test environments could be compared.

4.5.3 TEST RESULTS

4.5.3.1 Screening Test Results

In this section, the results of the screening tests conducted on each catalyst are presented. Each catalyst is discussed separately, with detailed test data contained in Appendix C.

TABLE 4-5: EQUILIBRIUM CONVERSIONS AT VARIOUS TEMPERATURES AND
H₂SO₄ FEED CONCENTRATIONS AT ONE ATMOSPHERE

TEMP. °C	H ₂ SO ₄ CONCENTRATION		
	92% Ar 8% SO ₃	63% Ar 26% Steam, 11% SO ₃	80% H ₂ SO ₄
650	63.0	59.5	48.5
700	71.5	68.9	60.0
750	79.5	77.5	69.0
800	86.5	84.5	78.0
850	91.5	90.5	85.0
900	94.5	93.1	90.5

Catalyst ALFA-4

Catalyst ALFA-4, 20% (by weight) Fe_2O_3 on a 3.2 mm cylindrical alumina substrate, was selected as the reference catalyst for the Sulfur Cycle based in part on the tests discussed in this section. ALFA-4 was evaluated in three environments; anhydrous, wet, and decomposed acid, over a broad spectrum of test parameters.

In the anhydrous environment ALFA-4 was evaluated at space velocities of 1000, 5000, 10,000, 20,000 and 25,000 hr^{-1} . These results are presented in Figure 4-11. The maximum conversion, at a space velocity of 1000 hr^{-1} at 900°C, was ~57.2%. When compared to the equilibrium conversion, this represents an efficiency of 61%.

Under the wet test conditions, the maximum conversion of 48.3% was achieved at 1000 hr^{-1} and 900°C. This is an efficiency of ~53%. The wet test results are shown in Figure 4-12.

In both series of tests, the conversion increased as the space velocity decreased. This follows the basic design equation for a plug flow reactor:

$$\frac{F}{V} = \frac{dx}{r} \quad (12)$$

where F = inlet feed rate

V = reactor volume

r = reactor rate

X = conversion

and $F/V = (\text{SV})^{-1}$

While these results were not encouraging, a literature review revealed that iron oxide had demonstrated the ability to achieve conversion efficiencies in excess of 90% at temperatures above 800° when tested in a sulfuric acid environment⁽⁴⁾.

Figure 4-11. Anhydrous Test Results - Catalyst ALFA-4

Figure 4-12. Wet Test Results - Catalyst ALFA-4

Catalyst ALFA-4 was then evaluated using liquid sulfuric acid as the process stream. The first series of tests (Series 100) were conducted on a constant volume of catalyst over a range of feed rates and temperatures. Figure 4-13 presents these results.

The maximum conversion was ~89% at 900°C and an LHSV of 37.1 hr⁻¹. When compared to the thermodynamic equilibrium at 900°C, the conversion represents an efficiency of ~98%. From the data shown in Figure 4-13, efficiencies greater than 90% were achieved at temperatures above 850°C. Below this temperature, the performance curve diverged from the equilibrium curve. This behavior indicated that while the reactor was rate limited at high temperatures, an additional rate controlling mechanism was present at the lower temperatures. Possible rate-controlling mechanisms include mass transfer limitations, lower reaction rates, or catalyst poisoning.

The potential of catalyst poisoning was an area of major concern. To determine if the catalyst was being poisoned by the feed stream, a series of tests were conducted between 700 and 900°C in 50°C increments. Several catalyst particles were removed after each test and analyzed using EDAX and SEM techniques. Sulfur was detected only on the samples removed after the 700° and 750°C tests, see Figure 4-14. The possible reactions involving the process stream and the catalyst and/or substrate are:

The reaction that was thermodynamically favored was not determined since either of these reactions leads to catalyst failure at temperatures below 750°C.

Additional testing determined that the sulfation reaction is reversible. Initially, the tests were conducted at 900°C, then at successively lower temperatures to a minimum of 700°C. Catalyst pellets were removed and analyzed at each 50° interval. Fresh catalyst pellets were installed to replace those

Figure 4-13. Catalyst ALFA-4 Series 100 Test Results

CURSOR: 6.400KEV =348

A. Catalyst ALFA-4 as-received.

CURSOR: 7.050KEV =535

B. Catalyst ALFA-4 after testing at 700°C.

CURSOR: 1.400KEV =587

C. Catalyst ALFA-4 after testing at 900°C.

Figure 4-14. EDAX Analysis of ALFA-4

removed in order maintain a constant catalyst bed volume. Tests were then repeated in the opposite direction, starting at 700°C and continuing up to a maximum of 900°C. For each sequence the conversions were approximately equal and the pellet analysis identical, sulfur was only detected on the 700° and 750°C samples.

Subsequent testing in Series 100 was conducted at various acid feed rates. After numerous testing, the parameters of the first test were repeated. The catalyst, exposed to the vaporized sulfuric acid environment for more than 175 hours and thermally cycled numerous times, maintained its original activity as the initial conversion of ~88% was reproduced. A summary of the test results of Series 100 is presented in Figure 4-15.

Further studies of catalyst performance were carried out on a second volume of catalyst ALPA-4. This series of tests, Series 200, were conducted in a bed volume approximately double that used in Series 100. The acid feed rate was adjusted accordingly to maintain LHSV's consistent with those tested in Series 100. To expedite the testing process, Series 200 tests were conducted at 700, 750, and 900°C. By combining the Series 100 and 200 test results, a detailed assessment on the kinetics of the reaction is possible (although schedular and funding limitations did not permit a full kinetic evaluation).

The results of the Series 200 tests are shown in Figure 4-16 and 4-17. In Figure 4-16 the effect of the acid feed rate on conversion (at constant temperature) is shown. Figure 4-17 reveals that the basic design equation is obeyed; increasing conversion with decreasing space velocity. These tests results are comparable with the results of the Series 100 tests, as shown in Figure 4-18. Pellet analysis was also identical. Catalyst activity in Series 200, maintained for the entire test period ~375 hours, produced ~98% of the equilibrium conversion at 900°C.

Subsequent testing of catalyst ALFA-4 was carried out exclusively at 900°C. In this series of tests, Series 300, the LHSV was varied by an order of magnitude. These tests, with the results given in Figure 4-19 produced a maximum

Figure 4-15. Catalyst ALFA-4 Series 100 Test Result Summary

Figure 4-16. Catalyst ALFA-4 Series 200 Test Results

Figure 4-17. Catalyst ALFA-4 Series 200 Test Results

- SERIES 100, LHSV = 36 hr^{-1} vs. SERIES 200 LHSV = 30 hr^{-1}
- Δ SERIES 100, LHSV = 667 hr^{-1} vs. SERIES 200 LHSV = 60 hr^{-1}
- SERIES 100, LHSV = 668 hr^{-1} vs. SERIES 200 LHSV = 72 hr^{-1}

Figure 4-18. Comparison of ALFA-4 Test Results

Figure 4-19. Catalyst ALFA-4 Series 300 Test Results

conversion of 88% (98% of equilibrium) at the lowest LHSV (28 hr^{-1}) and a minimum conversion, 26%, at the highest LHSV (288 hr^{-1}). Figure 4-20 shows the correlation of the Series 100, 200, and 300 tests at 900°C . At the highest LHSV's the conversion asymptotically approaches a minimum. This decline can be attributed to a number of rate controlling mechanisms including mass transfer of the reactant stream to the active catalyst sites or heat transfer to the catalyst bed.

It was beyond the scope of the program to determine actual reaction mechanisms. However, if the reactor was limited by heat transfer to the catalyst bed the activity of the catalyst could not be fully evaluated.

The reduction of SO_3 is an endothermic reaction, requiring $\sim 23.5 \text{ kcal/g-mol}$. Therefore, the thermal energy supplied to the catalyst bed had to exceed this value. If the heat input equalled the heat of reaction, a temperature gradient within the catalyst bed would be observed.

To determine if sufficient thermal energy was being supplied to the catalyst, a thermocouple was installed at the center of the catalyst bed. The temperature at the center of the catalyst bed was compared to the surface temperature of the reaction tube. A significant temperature difference between these two thermocouples would indicate that the thermal energy being supplied to the catalyst bed was insufficient and did not satisfy the energy requirements of the reaction.

Baseline performance was determined by installing a thermocouple immediately upstream of the catalyst bed. This internal thermocouple was located at the center of the reaction tube. An external thermocouple was fastened to the outside of the reaction tube along the same radial path as the internal thermocouple. To prevent localized heating from the furnace, the external thermocouple and the entire reaction tube was loosely sheathed with stainless steel foil. The internal thermocouple was sheathed in quartz capillary tubes with only the thermocouple junction (Pt - Pt 1% Rh) exposed to the acid stream. The amount

Figure 4-20. Summary of Catalyst ALFA-4 900°C Tests

of Pt exposed to the process stream was insignificant when related to the catalyst mass and, therefore, did not influence the reaction.

At the start of the test the temperature difference between the internal and external thermocouples was $\sim 2^{\circ}\text{C}$, at this point the internal thermocouple was not in the catalyst bed and was measuring the process stream temperature prior to its reduction. While the acid was being delivered (and thus the endothermic reduction of SO_3 occurring), the thermocouple was slowly drawn downstream with the internal thermocouple being pulled through the catalyst bed. The external and internal temperatures were continually monitored. There was no observable change in the temperature difference between the two thermocouples. Finally, the internal thermocouple was located immediately downstream of the catalyst bed. Here the temperature difference was constant at $\sim 2^{\circ}\text{C}$. These tests were repeated at successively higher flow rates with identical results. Therefore, it can be concluded that at high LHSV's the reaction was not limited by heat transfer but by a mass transfer associated restriction.

The results of these screening tests indicate that catalyst ALFA-4 possesses sufficient activity to accelerate the reduction rate of SO_3 to near equilibrium levels at temperatures above $\sim 850^{\circ}\text{C}$.

Additionally, the catalyst has shown that it is stable above this temperature. As a result, catalyst ALFA-4 was selected for evaluation in an endurance test, the results of which are discussed in a Section 4.5.3.2 of the report.

Catalyst MB-3

Catalyst MB-3, 1% Pt on a 3.2 mm diameter spherical alumina substrate, proved to be the most attractive of the precious metal catalysts. Tests were conducted in both anhydrous and wet environments over a space velocity range of 1000 to $50,000\text{ hr}^{-1}$.

Three separate catalyst volumes were tested, one for each of the following space velocity ranges; 1000 and 5000 hr^{-1} ; 10,000 and $20,000\text{ hr}^{-1}$; and, 30,000,

40,000 and 50,000 hr^{-1} . Each catalyst volume was evaluated under both anhydrous and wet test conditions.

The anhydrous test results are shown in Figure 4-21. A space velocity of 500 hr^{-1} at $\sim 890^\circ\text{C}$ produced the most efficient conversion, 77.5% of equilibrium (representing 72.9% conversion of SO_3 to SO_2). A close examination of the data shows that for each respective catalyst volume, the most efficient results were obtained at the maximum temperature and space velocity. The increase in efficiency with temperature was expected, however, the higher efficiency at high space velocities was contrary to the predicted behavior (as expressed by Equation 12).

Similar behavior was observed during the wet tests, as shown in Figure 4-22. In these tests the maximum conversion efficiency, $\sim 84\%$ was obtained at $\sim 900^\circ\text{C}$ and at the highest space velocity, 50,000 hr^{-1} . To expedite the testing, tests were not conducted at 10,000 and 20,000 hr^{-1} . A plausible explanation for this behavior involves a brief discussion on the kinetics of the reaction.

A mass balance over a differential volume element of the reactor gives

$$-F \frac{dx}{dv} = r \quad (15)$$

where F = volumetric flow rate

x = fraction of SO_3 converted to SO_2

r = rate of reaction

Assuming that the reaction is first order with respect to SO_3 concentration, the rate of reaction can be expressed as:

$$r = k [\text{SO}_3] \quad (16)$$

where k = overall reaction rate constant

$[\text{SO}_3]$ = concentration of SO_3

706875-1A

Figure 4-21. Anhydrous Test Results for Catalyst MB-3

706875-2A

Figure 4-22. Wet Test Results for Catalyst MB-3

The concentration of SO_3 can be rewritten as

$$[\text{SO}_3] = (1-X) [\text{SO}_3]_0 \quad (17)$$

where $[\text{SO}_3]_0$ = initial concentration of SO_3 .

Substituting this into Equation 16 yields

$$-F \frac{dx}{dV} = k (1-X) [\text{SO}_3]_0 \quad (18)$$

$$- \frac{dx}{(1-X)} = k [\text{SO}_3]_0 \frac{dV}{F} \quad (19)$$

At a constant flowrate, integration between $1-X_0$ and X_L , where L = reactor length gives

$$- \int_{1-X_0}^{1-X_L} \frac{dx}{(1-X)} = k \frac{[\text{SO}_3]_0}{F} \int_0^V dX \quad (20)$$

Thus:

$$\ln \frac{(1-X_0)}{(1-X_L)} = k [\text{SO}_3]_0 \frac{V}{F} \quad (21)$$

Finally

$$\frac{(1-X_0)}{(1-X_L)} = \text{Exp } k [\text{SO}_3]_0 / SV \quad (22)$$

therefore, the fraction of SO_3 exiting the reactor is given by

$$(1-X_L) = (1-X_0) \exp -(k [SO_3]_0/SV) \quad (23)$$

for a solid-catalyzed reaction, the vessel reaction rate, k , may be controlled by any of the following:

k_g = gas film resistance

k_{pR} = pore diffusion resistance for reactant

k_s = surface phenomena resistance (adsorption, desorption, reaction)

k_{pD} = pore diffusion resistance for products

k_H = heat flow resistance

Assuming that these resistances occur in series and combining k_g , k_{pR} , and k_{pD} as a single mass transfer resistance k_m , the overall reaction rate constant becomes:

$$k = \frac{1}{1/k_m + 1/k_s + 1/k_H} \quad (24)$$

Test results using a thermocouple located with the catalyst (as described in Section 4.5.4) included that there is a sufficient supply of heat transfer to the catalyst bed, thus k_H can be neglected:

$$k = \frac{1}{1/k_m + 1/k_s} \quad (25)$$

To determine which of these resistances is rate controlling involves an indepth analysis and significant testing both of which are beyond the scope of this program. However, from the reported data it appears that the controlling resistance is k_m . An increase in the flowrate would increase the turbulence, the process stream. This in turn would increase the mass transfer of SO_3 from the process stream through the laminar boundary surrounding each catalyst particle. This results in an increased concentration of SO_3 present on the catalyst surface, and available for reduction to SO_2 . Simply stated, the SO_3 cannot be reduced to SO_2 if it is not able to reach the catalyst surface.

While these tests produced conversion efficiencies of $\sim 80\%$, catalyst MB-3 appeared to be very attractive. The conversion efficiency can be substantially increased by either increasing the gas flowrate relative to the catalyst volume or decreasing the catalyst particle size. Either of those two remedies are thought to be effective in achieving higher conversion of SO_3 to SO_2 .

Catalyst MB-2

Catalyst MB-2 is also 1% Pt on alumina. It is geometrically similar to MB-3 except that MB-2 has a slightly lower surface area than MB-3. Anhydrous tests were conducted at 1000 and 5000 hr^{-1} . Wet tests, using the same catalyst volume, were at 1000 and 5000 hr^{-1} .

The anhydrous tests produced a conversion of $\sim 60\%$ at 900°C, $\text{SV} = 1000 \text{ hr}^{-1}$, representing an efficiency of $\sim 63\%$ at $\text{SV} = 5000 \text{ hr}^{-1}$, the maximum conversion was 60.5%, obtained at 800°C for an efficiency of $\sim 70\%$. The 5000 hr^{-1} tests at 850° and 900°C were not reliable due to the displacement of several catalyst particles. Comparing the results at 800°C the higher space velocity produced a higher efficiency, 70% versus the 61% obtained at 1000 hr^{-1} .

At equal temperatures and space velocities, the wet tests produced higher conversion efficiencies than the dry tests. The maximum conversion, 81.4% (an efficiency of $\sim 87\%$), occurred at 900°C, $\text{SV} = 5000 \text{ hr}^{-1}$. A comparison between the wet and anhydrous tests is best made at 800°C and a space velocity of 5000 hr^{-1} . Under these conditions the wet test efficiency was $\sim 76\%$ and the anhydrous $\sim 70\%$.

Disregarding the anhydrous results at 850° and 900° at $\text{SV} = 5000 \text{ hr}^{-1}$, the higher efficiency was found at the higher space velocities. The explanation for this behavior is analagous to that of MB-3.

Tests were attempted at 10,000 hr^{-1} but were unsuccessful because the test facility could not handle the high flowrates required to reach 10,000 hr^{-1} .

Catalyst ENG-1

In addition to the evaluation of MB-2 and MB-3 (both 1% Pt) a third platinum catalyst was evaluated. Catalyst ENG-1, 0.5% Pt on a cylindrical alumina substrate as tested under both anhydrous and wet environments. The maximum anhydrous conversion, at 900°C, was 63%. Under a wet environment the maximum conversion was ~58%. A comparison of the test results shows that the anhydrous environment produced a higher efficiency than the wet environment 67% versus 63%.

Due to the relatively poor performance (when compared to MB-2 or MB-3) testing on ENG-1 was halted at this point.

Catalysts CE-1 and CE-2

These two catalysts, both Fe_2O_3 , were briefly examined under both anhydrous and wet environment. Catalyst CE-1 is <10 mesh while CE-2 is 10-20 mesh. Neither of these catalysts produced attractive conversions, the maximum efficiency, ~60%, was obtained under anhydrous conditions at 1000 hr^{-1} and 900°C for catalyst CE-1. There was no significant difference between catalyst CE-1 and CE-2.

Tests were halted for two reasons, the poor catalytic activity, and the high pressure drop across the catalyst bed due to the geometry of the catalyst. The abbreviated tests, however, did indicate that in this test series the reduction reaction was rate controlled and not controlled by the mass transfer of SO_3 to the catalyst's surface. This is supported by the fact that the higher conversions were obtained at the lower space velocity.

Catalyst ALFA-2

Screening tests on Catalyst ALFA-2, 0.5% Pd on a 3.2mm alumina circular cylinders, were conducted under both anhydrous and wet environments at space velocities of 1000 and 5000 hr^{-1} . Maximum conversions, all obtained at 900°C, were 57.8 and 64.2 percent for the 1000 and 5000 hr^{-1} anhydrous tests and 64.0 and 68.0% at wet space velocities of 1000 and 5000 hr^{-1} . These conversions translate to efficiencies of 61 and 68% for the anhydrous tests and 69 and 73% for

the wet tests. As with the previously tested precious metal candidates, the reaction appeared to be controlled by the diffusion of SO_3 onto the catalyst surface as the conversion efficiency increased with increasing space velocity.

A brief examination using liquid sulfuric acid was also conducted. At an LHSV of 7.8 hr^{-1} the maximum efficiency of 95% was reached at 900°C . This represents a conversion of $\sim 86\%$. The results of this test are shown in Figure 4-23. The conversion efficiency decreased with decreasing temperature although efficiencies of $\sim 90\%$ were obtained at temperatures as low as 800°C . A substantial decline in conversion was experienced between 650 and 700°C .

EDAX and SEM analysis of catalyst particles, removed after testing at each temperature, revealed the presence of sulfur on the catalyst's surface. The source of the sulfur was thought to be a result of the alumina substrate reacting with the process stream.

Catalyst ALFA-3

Catalyst ALFA-3, $15\% \text{Cr}_2\text{O}_3$ on 6mm alumina cylinders, was evaluated under anhydrous, wet, and decomposed sulfuric acid environments. In the anhydrous environment, a conversion of $\sim 76\%$ was obtained at 900°C and $\text{SV} = 5000 \text{ hr}^{-1}$. This represents an efficiency of $\sim 80\%$. However, during the wet test series, the maximum conversion efficiency dropped to $\sim 56\%$ at 900°C , $\text{SV} = 5000 \text{ hr}^{-1}$.

Inspection of the reaction tube revealed that catalyst had volatilized and was transported downstream of the reactor zone where it was deposited on the walls of the condenser.

Similar behavior was observed when testing with liquid sulfuric acid. An initial conversion of $\sim 90\%$ (99% efficiency) was reached at 900°C , $\text{LHSV} = 5.8 \text{ hr}^{-1}$. After ~ 18 hours of testing a significant decline in the conversion was observed. EDAX analysis of the deposit on the condenser walls indicated chromium. Due to the thermal instability of the chromium, catalyst ALFA-3 was eliminated as a candidate for the Sulfur Cycle catalyst.

Figure 4-23. Catalyst ALFA-2 Decomposition Test Results

Catalyst ALFA-5

Catalyst ALFA-5, 3.2 mm cylindrical pellets of MgO, proved to be an unacceptable candidate. Tests at 900°C and LHSV = 4.5 hr⁻¹ produced a conversion of ~12%. This represents an efficiency of ~13%. In an anhydrous environment, at 900°C and SV = 5000 hr⁻¹, the efficiency was 35%. Wet tests under similar parameters produced an efficiency of ~8%. Due to its poor performance, testing of ALFA-5 was terminated.

Catalyst KAT-1

KAT-1, 3.2 mm Al₂O₃ spheres, is representative of the substrate used in many of the previously tested catalysts. This candidate was tested for two reasons:

- to measure the extent, if any, of its catalytic activity, and
- to determine if the Al₂O₃ and sulfuric acid react under process conditions.

All tests were conducted using a liquid sulfuric acid feed. As expected, KAT-1, did not possess significant catalytic activity, producing a maximum efficiency of ~48% at 900°C, LHSV = 13.4 hr⁻¹.

To determine if the alumina substrate reacted with the sulfuric acid, several catalyst pellets were removed from the catalyst bed after each test. These pellets were analyzed for sulfur using EDAX and SZM techniques. If the aluminum reacts with the sulfuric acid (as shown in Equation 26) there exists the possibility of catalyst poisoning and, in turn, reduced conversion or shorter catalyst life.

Tests were initiated at 700°C and continued, in 50° increments, to 900°C. Sulfur was detected only on samples removed after the 700° and 750°C tests. At tests alone 800°C, there was no evidence of sulfur. The test series was then repeated in the reverse order, starting at 900°C and continuing to 700°C. Analytical results were identical to the first test series from these tests it was

verified that Al_2O_3 doesn't possess sufficient catalytic activity to be considered a catalyst but it is an acceptable catalyst substrate at temperatures above 800°C .

Catalyst WX-2

This catalyst, V_2O_5 , was selected for evaluation based on its reputation as the standard catalyst in the sulfuric acid industry. It is commercially used to oxidize SO_2 to SO_3 at $\sim 500^\circ\text{C}$. Earlier tests were conducted at Westinghouse Research and Development Center in an anhydrous environment⁽⁵⁾. Tests conducted in this program were in a wet environment using simulated sulfuric acid. After two tests at 650°C it became apparent that the catalyst was not thermally stable. Deposits of vanadium (verified by EDAX) were observed collecting at the cooling condenser. This behavior is similar to that observed for Catalyst ALFA-3. Testing was suspended at this time.

Non-Catalyzed

Due to the absence of data on the purely thermal reduction (with no catalyst present) of SO_3 , several tests were conducted. In these tests only the construction materials, quartz and teflon, were in contact with the sulfuric acid feed stream. Extremely low acid feed rates (~ 1 cc/min) were used to provide the maximum residence inside the reaction tube. At 900°C the observed conversion was $\sim 10\%$ for an efficiency of $\sim 1\%$. These tests supported the need for an acceptable catalyst.

4.5.3.2 Endurance Test Results

The catalyst selected for use in the sulfur cycle must not only possess sufficient catalytic activity to accelerate the reduction of SO_3 to an acceptable level, it must also be able to maintain this performance for an extended period of time. To measure catalytic activity as a function of time, two endurance test facilities were constructed. One test facility used a simulated sulfuric acid feed and the most recent employed liquid sulfuric acid as the process feed.

The results obtained using the most recent test facility are discussed first, as this facility is more representative of the sulfur cycle's operating conditions. A brief discussion of the results of two endurance tests using simulated sulfuric acid follow.

H₂SO₄ Endurance Test Results - Catalyst ALFA-4

The operation of this test facility is similar to that discussed in Appendix A for the H₂SO₄ Decomposition Screening Test Facility, shown in Figure 4-8. Additional controllers, temperature monitors, etc. were installed in the endurance test facility to permit unattended operation overnight and through weekends.

Catalyst ALFA-4 (20% Fe₂O₃ or Al₂O₃) was selected for the endurance test based on the results of the screening tests conducted using 80% H₂SO₄. The results of the 5000 hour endurance test was presented in Figure 4-24. Test conditions were 900°C at an LHSV = 8 hr⁻¹ using 80% (by weight) sulfuric acid.

For the first ~1300 hours the average measured conversion was ~87%. This represents an efficiency of ~96%, which correlates quite well with the previously reported data obtained from the short term (less than 400 hours) screening tests.

After ~1300 hours of test time (t = 1300 hours) a feed pump malfunction caused the acid flow to be interrupted for more than 24 hours (the malfunction occurred on a weekend) before being detected. During repairs the catalyst was kept at temperature under an argon atmosphere. When the test was restarted the conversion decreased slightly to an average of ~83% (92% of equilibrium). This performance continued until ~1650 hours when a furnace heating element failed.

While the element was being replaced, the catalyst bed was visually inspected. There was evidence of a small quantity of iron oxide on the quartz wool packing on the downstream side of the catalyst bed. This small amount of iron oxide was apparently physically transported by the process stream. Under normal handling procedures the iron oxide is easily removed from the substrate, therefore

Figure 4-24. Photograph of Catalyst Bed After 3700 Hours of Testing

this was not considered a problem. Additionally, the amount of iron oxide displaced was insignificant when compared to the total catalyst bed and it was deposited immediately downstream of the catalyst bed where the reduction of SO_3 was still thermodynamically favored. If it were transported sufficiently far downstream to a much cooler location (where the temperature is less than $\sim 650^\circ\text{C}$) the kinetics then favor the reverse reaction, the oxidation of SO_2 to SO_3 .

After the heating element was replaced, the test was resumed with the catalyst performance increasing to $\sim 86\%$ conversion. This was maintained for ~ 200 hours ($t = 2000$ hours) when an extended weekend necessitated a brief suspension of the test. This interruption was necessary because the capacities of the feed and condensate reservoirs were unable to contain volumes required for the long weekend.

After restarting the test, the conversion averaged $\sim 83\%$ for the next 550 hours. At $t = 2550$ hours, the conversion suddenly dropped to $\sim 80\%$. Inspection of the system revealed a second furnace heating element was failing. During the shutdown, the catalyst bed was again visually inspected and it was discovered that the amount of iron oxide deposited on the quartz wool had increased. However, it still remained in the hot zone of the furnace where the forward reaction was favored.

At this time, three catalyst pellets (less than 1% of the total catalyst bed) were removed and analyzed for sulfur. The EDAX results indicated that there was no sulfur present on the catalyst or substrate. Three fresh pellets were installed to replace those removed for analyses.

After restarting, the first measured conversion was $\sim 86\%$. This performance continued for ~ 100 hours when it began to steadily decrease ($t = 2700$ hours).

The decline in conversion continued for more than 750 hours when it began to stabilize at $\sim 65\%$ (72% of equilibrium). After producing constant conversions

for more than 250 hours ($t \sim 3700$ hours) the test was temporarily halted and the catalyst bed and reaction tube examined.

Upon inspection, a significant amount of iron oxide was noticed on the downstream side of the catalyst bed. This can be seen in Figure 4-25. The iron oxide was physically transported as far as ~ 4 inches from the end of the catalyst bed. The catalyst bed itself changed from a rust color to predominately white, indicating the iron oxide had been removed from the substrate. While the bulk of the transported iron oxide had deposited immediately downstream of the catalyst bed where the forward reaction was favored, there was detectable amounts of iron oxide in regions where the temperature shifted the kinetics towards the reverse reaction.

The catalyst bed was removed from the reaction tube and the tube cleaned of all traces of iron oxide. Fresh downstream packing was installed and the catalyst bed reloaded. In addition, five catalyst pellets were removed and sent for analysis. Fresh pellets replaced those removed for analysis.

The first conversion measured after restarting the endurance test was $\sim 69\%$. This slowly increased to $\sim 86\%$ at $t = 3920$ hours. At this point, the conversion began to decline until it stabilized at $\sim 77\%$ (85% of equilibrium). This performance was maintained for approximately 1000 hours ($t = 5000$ hours).

The significant decrease in conversion beginning at $t \sim 2800$ hours and lasting until $t \sim 3700$ hours was suspected to be a result of the transported iron oxide. It was thought that the amount of catalyst remaining in the hot zone was insufficient to reduce the amount of SO_3 being delivered. Even though the bulk of the displaced iron oxide remained in a thermodynamically favorable region, the temperature and, thus, the equilibrium conversion was somewhat lower.

If this was the case, mass transfer restrictions could possibly become the rate controlling step in reducing the SO_3 . If there was insufficient catalyst on the surface, the SO_3 must then diffuse into the pores of the pellet, react, then diffuse outward. A reduction in conversion would be the result.

Figure 4-25. Photograph of Catalyst Bed After 3700 Hours of Testing

To eliminate the mass transfer restrictions, the acid feed was reduced to .5 cc/min. This would provide a longer residence time in the catalyst bed.

When the feed rate was reduced to .5 cc/min the conversion increased to ~83% (92% of equilibrium).

The reduced flow tests were conducted intermittently between $t = 3100$ and $t = 3300$ hours. When the acid feed rate was increased to the original 1.00 cc/min, the conversion dropped to ~65%. Each time the flow was reduced to .5 cc/min, the conversion increased to ~83%. These tests were conducted prior to the reloading of the catalyst bed in the cleaned reaction tube.

After the tube was cleaned and the catalyst reloaded, the conversion increased to ~85% then slowly declined and stabilized at 77%. The increase to 85% can be attributed to the fresh catalyst pellets replacing those removed for analysis. The decline indicates the erosion of the iron oxide from the catalyst bed.

A comparison of the steady performance levels between $t = 3300$ to 3800 and $t = 4100$ to 4800 hours shows an increase of ~12% (65% conversion versus 77%). This difference can be explained by removal of trace amounts of iron oxide from the cooler regions of the reaction tube. The quantity of iron oxide present in the regions where the reverse reaction was favored was so small that only a small percentage of the SO_2 was oxidized back to SO_3 .

A review of the entire endurance test reveals that catalyst ALFA-4 possessed sufficient activity to achieve more than 90% of equilibrium for ~2800 hours. Throughout the entire test the catalyst experienced a gradual, but steady decline in performance due to the physical erosion of the iron oxide. Nevertheless, ALFA-4 was able to achieve more than 85% of equilibrium for more than 4800 hours. This test indicates that a more physically stable iron oxide catalyst could produce near equilibrium conversion for at least 4800 hours.

In the following section of this report, the details of the analysis of the pellets removed at $t = 2700$ and $t = 3800$ hours are discussed. These results support the theory of physical and not chemical erosion of the iron oxide.

Simulated Acid Endurance Tests

In the early stages of this program, two endurance tests were conducted using the wet test environment. The composition of the feed stream (in percent by volume) was 63% Ar, 26% steam, and 11% SO_2 . The steam/ SO_3 ratio represents an 80% H_2SO_4 concentration. If Ar is regarded as a diluent, the acid concentration drops to $\sim 23\%$ by weight. Operation of this system is analogous to that of the Wet Test Facility, described in Appendix A.

Two catalysts, ALFA-4 and MB-3, were evaluated in this test facility. These candidates were selected on the basis of their respective screening tests; MB-3 was the most attractive precious metal candidate while ALFA-4 was the most attractive "non-precious" metal. Both catalysts were evaluated under identical conditions: 871°C and $\text{SV} = 10,000 \text{ hr}^{-1}$ for a period of 1000 hours.

Catalyst MB-3

The simulated acid endurance test results, conducted at 871°C , $\text{SV} = 10,000 \text{ hr}^{-1}$, for Catalyst MB-3 are presented in Figure 4-26. The initial conversion of 65% gradually increased to 74% after ~ 65 hours of testing. The 74% conversion, representing more than 80% of the thermodynamic equilibrium conversion, was maintained for the balance of the 1000 hour test. This performance level correlates with the previously discussed screening test results. EDAX analysis of catalyst particle removal after the 1000 hour test failed to identify the presence of sulfur.

Catalyst ALFA-4

Catalyst ALFA-4 also experienced a 1000 hour endurance test using the simulated acid feed. Test parameters were similar to those of MB-3; 871°C , $\text{SV} = 10,000 \text{ hr}^{-1}$. These results are given in Figure 4-27. The average conversion was $\sim 53\%$, representing an efficiency of $\sim 58\%$. There was no evidence of significant

Figure 4-26. Wet Endurance Test Results - Catalyst MB-3

SV = 10,000 HR⁻¹
TEMP = 871°C
FEED = 80 w/o H₂SO₄ (SIMULATED)

Figure 4-27. Wet Endurance Test Results for Catalyst ALFA-4

degradation in catalytic activity as a function of time. Conversions obtained in the endurance test were approximately equal to those observed in the screening tests. Additionally, EDAX analysis verified that the catalyst did not react with the process stream.

4.5.4 CATALYST CHARACTERIZATION

Selected catalysts were physically and chemically characterized to determine if the process stream had any adverse effects on the structure of the catalyst. Three catalysts MB-2, MB-3, and ENG-1 were characterized before and after screening tests. Catalyst ALFA-4 was examined before and midway through the 5000 hour endurance test.

Analysis techniques employed included Auger Electron Spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA), hydrogen chemisorption (CHEMI), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), and nitrogen physisorption (BET). A brief summary describing these techniques is given in Appendix D.

A summary of the characterization efforts is presented in Table 4-6. BET and CHEMI results reveal that prior to evaluation, Catalyst MB-3 had a greater total surface area than Catalyst MB-2 (both are 1% Pt on 3.2 mm alumina spheres), but a substantially lower metal depression on the surface. The "percent metal dispersion" is, in effect, the percent of the total surface area that can be assigned to the catalyst (not the substrate). The active catalyst surface area is essentially the product of the total surface area times the percent metal dispersion. Thus, it would appear that Catalyst MB-2 should possess more catalytic activity than MB-3. ENG-1 cannot be related to MB-2 or MB-3 because of its different geometry and lower Pt content.

When exposed to the anhydrous environment, Catalyst MB-2 experiences little or no physical change in surface area. Catalyst MB-3 undergoes a slight decline in total surface area and a significant decrease in active catalyst surface area.

TABLE 4-6: RESULTS OF CATALYST CHARACTERIZATION ANALYSIS

Catalyst	BET (m ² /g)	% Metal Dispersion	TEM Average Particle Size	Atomic Concentrations					
				AES	ESCA				
MB-2 (fresh)	61.2	7.1	90°A	12% Pt	9% Pt	48% O	42% Al	-S	-Si
MB-2 (wet)	36.3	0.14	400	4	3	48	34	1% S, 1% SO ₄	12%
MB-2 (dry)	63.3	5.7	300	20	5.6	47	43	4.3% S	.4
MB-3 (fresh)	79.3	1.4	90	6	6.6	47	42	1.1% S	1.6
MB-3 (dry)	62.9	5.7	250	3	2.3	48	46	.6% S	2.0
ENG-1 (fresh)	87.7	43	120	--	--	--	--	--	--
ENG-1 (wet)	39.2	4.8	300	--	--	--	--	--	--

NOTE: The discrepancy between AES and ESCA results for Pt is due to the fact that AES samples only a portion of the surface while the ESCA is averaged over the entire surface. ESCA may be more reliable.

The addition of steam resulted in pronounced effects on Catalyst MB-2 and ENG-1. Both catalysts had a decrease of ~40% in total surface. MB-2 had a decline of ~90 in active surface and ENG-1 ~95% in the same. Both catalysts show a large increase in average particle size, possibly indicating that the metal agglomerates into larger particles. This is supported by the observations made using TEM. MB-2 and ENG-1 both revealed considerable particle movement when exposed to the electron beam. Catalyst MB-3 was free from any observable particle movement.

On MB-2 and ENG-1, two types of particle movement were observed: the migration of particles to combine with other particles to form a single, larger particle and the appearance of melting and spreading on the substrate. Both of these result in a decrease in total surface and active catalyst surface area. This phenomena may explain the reason MB-3 displayed higher conversions than MB-2, even though prior to testing, MB-2 has a higher active catalyst surface area.

Results obtained using XRD shows that the substrate of MB-2, MB-3 and ENG-1 is primarily gamma alumina, a high surface area phase.

After exposure to the wet test environment, both Catalysts MB-2 and ENG-1 experienced a phase transformation to alpha and theta alumina, both lower surface area phases. Catalyst MB-2 and MB-3, when exposed to only an anhydrous environment, did not undergo a phase transformation.

Initially, it appears that the addition of steam to the environment causes a phase transformation from high to low surface area phases. However, it must be noted that the catalysts experiencing a wet test were exposed to high temperatures longer than those tested only in an anhydrous environment. Thus, the phase transformation may be time dependent. Maximum temperatures for all catalysts was 900°C. The phase transformation not only reduces the total surface of the catalyst, it may also envelope active catalyst sets, further reducing the amount of catalyst available for the reaction.

AES and ESCA were employed to determine the surface composition of catalyst MB-2 and MB-3 before and after testing. Untested MB-2 and MB-3 were very similar, with ~9 atomic percent Pt, mostly on the surface. No significant impurities were present.

Anhydrous tests had little or no effect on the surface composition of either catalyst. The most significant change was observed in the Pt content after the wet tests conducted on MB-2. The Pt content decrease to ~3 atomic percent and was considered to be a result of sintering and diffusion of Pt into the substrate. An insignificant increase in sulfur was also detected. The substantial level of SiO_2 on MB-2 of the wet test is attributed to a reaction between the quartz reaction tube and the process stream. The Al and O observed are the components of the substrate.

Catalyst ALFA-4 experienced a different sort of physical analysis. Samples of ALFA-4 were taken before testing and at two points in the H_2SO_4 decomposition endurance test.

The first sample was taken after approximately 2700 hours of testing. This sample was only analyzed for sulfur deposition. It was determined that there was no sulfur present either on the catalyst or the substrate.

The second sample was removed after 3800 hours of testing and experienced a more thorough examination. Analysis, performed on both untested and tested samples, included SEM, EDS, and ESCA.

Using these techniques, and comparing the untested and tested results, it was possible to determine what effects the endurance test had on the catalyst.

Figure 4-28 presents an optical micrograph comparing two surfaces of a tested (Sample A) and untested (Sample B) catalyst pellet. The untested pellet was rust in color indicating it was coated with iron oxide. There was a small amount of iron oxide removed due to handling, but the substrate (alumina) was not visible. The tested sample had no sign of iron oxide as it was white with

Figure 4-28. Optical Micrograph of Catalyst ALFA-4

no traces of the rust color. Samples C and D represent the inner surface of the tested and untested pellets, respectively. This surface was exposed by cleaving the pellet with a sharp razor blade. The internal structure of the samples was similar; three different regions can be seen: a center region (1), a middle region (2), and an outer region (3).

In the untested sample's inner surface, the iron oxide concentration was highest (as determined by color) in region 2, then region 1, and region 3, respectively. The difference in concentration between regions 1 and 2 was very slight, whereas a distinct color difference was obvious in region 3.

The tested sample reveals a similar concentration profile; highest in region 2, followed by 1, and region 3 exhibiting virtually no iron oxide. Region 3, the outermost region, extends inward for approximately 20% of the pellet's radius. This would be the region where most of the reaction occurs. The absence of iron oxide here explains the decline in conversion.

From these optical micrographs, it cannot be determined if the iron oxide was physically or chemically removed. If the iron oxide had chemically reacted with the process stream, one of the following reactions were possible:

In either case, the product, an iron sulfate, would not have been rust colored. If the product was white, it could not have been optically detected. There was no evidence of any other color to suggest that there was a sulfate formation.

These samples were then examined using energy dispersive spectrometry (EDS). The untested sample (top surface) showed only iron and aluminum (only elements with an atomic number greater than eleven can be identified). The tested

sample (top surface) revealed aluminum, iron, silicon, and possibly (less than .5%) sulfur. The peak indicating sulfur was extremely small, and, therefore, it was extremely difficult to determine if it was a sulfur peak.

While a qualitative analysis was not possible, a semi-quantitative comparison between similar samples can be made. It appears that the top surface of the tested sample had much less iron than the top surface of the untested sample.

EDS examination of the respective inner surfaces revealed a distinct difference in iron and aluminum concentrations as a function of distance from the center of the pellet.

An elemental dot map, generated by EDS, provides a visual representation of the concentration of the element being mapped. The density of the dots is directly related to the elemental concentration. Figure 4-29 presents the iron and aluminum distribution in the inner surface of the untested sample. Figure 4-30 is a similar description of the inner surface of the tested sample.

The untested sample had a relatively uniform aluminum dispersion throughout the pellet. There may be a slightly lower aluminum concentration in Region 3, but it was difficult to ascertain. However, there was a distinct iron concentration gradient. The iron concentration was greatest in Region 2, slightly lower in Region 1, and significantly lower in the outer Region 3.

The iron and aluminum concentration gradients of the tested sample, Figure 4-30, were similar. Note that a chip was accidentally removed from the lower corner of this sample. The aluminum concentration was greatest in Regions 1 and 2 and slightly less, but more noticeable than the untested sample, in Region 3. The iron concentration profile shows a substantial depletion of iron in the outer Region 3. Regions 1 and 2 were relatively uniform with, perhaps, a slightly lower concentration in Region 1.

ALUMINUM

IRON

Figure 4-29. Elemental Dot Maps, Catalyst ALFA-4, Untested

ALUMINUM

IRON

Figure 4-30. Elemental Dot Maps, Catalyst ALFA-4, Tested 3700 Hours

Taking into consideration the limits of the EDS analysis, there appeared to be an approximate three to five-fold decrease in iron concentration in Region 3 of the tested pellet as compared to Region 3 of the untested pellet.

Comparing the interior sections (Regions 1 and 2) of the two samples indicated relatively equal iron concentration. This implies that the iron depletion in Region 3 of the tested sample was not a result of thermally induced diffusion into the pellet, but a physical removal away from the surface.

EDS elemental maps of silicon and sulfur did not locate either of these two elements. The silicon was most likely a result of the quartz reaction tube. The absence of sulfur indicates that the iron oxide did not chemically react with the process stream.

To further verify the surface composition of the two samples electron spectroscopy for chemical analysis (ESCA) was used. Figures 4-31 through 4-36 present the data obtained using the ESCA technique. The difference between the two samples was quite evident in Figure 4-31. By ratioing the peak heights of the iron (~ 60 eV) and aluminum (~ 130 eV) peaks, an indication of surface iron can be obtained. The iron in the tested catalyst has been depleted in comparison to the aluminum. Additional evidence of iron depletion was obtained by ratioing the oxygen auger peak (~ 749 eV) and iron peak (~ 715 eV).

The absence of sulfur in these results further indicate that the process stream and the iron oxide catalyst did not react.

4.5.6 CONCLUSIONS AND RECOMMENDATIONS

Based on the results of the screening and endurance tests and coupled with the established criteria the reference catalyst must fulfill, the most attractive candidate catalyst is ALFA-4 (20% Fe_2O_3 in Al_2O_3). Catalyst ALFA-4 displayed sufficient activity to achieve near equilibrium conversions and the ability to maintain satisfactory conversions for an extended period of time.

Figure 4-31. ESCA Results of Test and Untested Catalyst ALFA-4

Figure 4-32. ESCA Results of Tested and Untested Catalyst ALFA-4

Figure 4-33. ESCA Results of Tested and Untested Catalyst ALFA-4

Figure 4-34. ESCA Results of Tested and Untested Catalyst ALFA-4

Figure 4-35. ESCA Results of Tested and Untested Catalyst ALFA-4

Figure 4-36. ESCA Results of Tested and Untested Catalyst ALFA-4

Although the mechanical stability of this particular catalyst must be improved, the use of iron oxide has proven to be successful in accelerating the reduction rate of SO_3 . Even under the penalty of mechanical transport of the Fe_2O_3 to less thermodynamically favorable location, ALFA-4 maintained a conversion of 85% of thermodynamic equilibrium for more than 4800 hours of continuous testing.

Analysis of samples of ALFA-4 exposed to the sulfuric acid environment verify its chemical stability at temperatures above 850°C . After ~2800 hours exposure, sulfur was not detected on catalyst samples. Also verified was the satisfactory behavior of the alumina substrate in the vaporized sulfuric acid environment above 800°C . Test revealed that the Al_2O_3 is not reactive with the process stream under these conditions.

Future efforts should include a task to locate and/or develop a more mechanically stable iron oxide catalyst. This may simply involve treatment of ALFA-4 to more adequately bind the iron oxide to the substrate. A second possibility is the elimination of the substrate and having a pure iron oxide catalyst. Also recommended is an in-depth kinetic analysis of the reference to provide the necessary data for designing the Sulfur Cycle reduction reactor. Additionally, a compatibility test using the proposed materials of construction for the reduction reactor and the catalyst is highly recommended.

4.6 REDUCTION REACTOR MATERIALS EVALUATIONS

4.6.1 INTRODUCTION

The objective of this task was to screen potential structural materials for compatibility with anticipated reduction reactor process stream conditions in the temperature range 482 to 871°C. In the sulfur cycle hydrogen production process, intermediate heat exchangers are utilized to recover sensible heat from the process stream exiting the reduction reactor at 871°C to preheat the process stream prior to entrance into the reduction reactor. This assessment of materials compatibility with various process stream compositions throughout the temperature range of interest was considered critical to the development of the hydrogen production process. Because the temperatures and pressures involved departed significantly from standard sulfuric acid manufacturing practice, a dearth of information existed concerning the compatibility of structural materials with sulfuric acid under the expected system operating conditions. Thus, the purpose of this task was to evaluate materials including metallic alloys and ceramics recommended by vendors that supply the acid manufacturing industry with corrosion resistant materials. The development of alloys for this application was beyond the scope of this task. The test plan for achieving the program objective is given below.

REDUCTION REACTOR MATERIALS TEST PROGRAM

<u>TEST TYPE</u>	<u>TEST ENVIRONMENT</u>	<u>TEST TEMPERATURE</u> (°C)	<u>TEST DURATION</u> (Hours)
Materials Screening	Inlet Conditions H ₂ O and SO ₃	482 and 871 650 and 871	100 hr increments 1000 hr Total
	Outlet Conditions H ₂ O, SO ₂ , O ₂ SO ₃	650 and 871	100 hr increments 1000 hr Total
Endurance	Inlet Conditions H ₂ O and SO ₃	871	2000 Hr. Increments 6000 Hr. Total

The test program consisted of two parts, a screening phase in which a large number and variety of potential structural material samples were exposed to the

anticipated process stream conditions at several temperatures for times up to 1000 hours in one hundred hour increments. The second part of the test program involved an endurance test, in which selected materials that performed well in the screening phase were exposed to the process stream conditions for up to 6000 hours. The endurance test was carried out to verify the screening test results and to extend the compatibility behavior characterization to longer times.

4.6.2 EXPERIMENTAL PROCEDURES

The materials test beds utilized quartz structural materials for operations at or near atmospheric pressure. A quartz sample holder capable of holding six specimens 19 mm x 19 mm x 1.6 mm was fitted inside a 40 mm quartz combustion tube and was heated to the exposure temperature. The process stream for the inlet conditions was a once-through type, permitting either anhydrous SO_3 or SO_3 with superheated steam to be introduced past the materials samples in proportion to the expected reduction reactor inlet process stream composition. The SO_3 Reduction Reactor Materials Test Facility for inlet conditions is shown in Figure 4-37. A schematic diagram of the experimental inlet conditions test apparatus is presented in Figure 4-38.

A second materials test bed, simulating reduction reactor outlet conditions, was similar to the reduction reactor inlet conditions test apparatus except for the addition to SO_2 and O_2 to simulate the outlet gas streams whose constituents include SO_3 , SO_2 , O_2 , and steam. Although the initial inlet conditions test utilized Ar as a carrier gas, no carrier gas was used in the outlet conditions tests. The SO_3 Reduction Reactor Materials Test Facility for outlet conditions is shown in Figure 4-39. A schematic of the outlet conditions test apparatus is given in Figure 4-40.

During the experimental program, the test beds were modified, flash evaporators were incorporated into both the inlet and outlet test facilities so that a sulfuric acid feed could be used in place of the individual anhydrous SO_3 and steam feed which were previously used to simulate the sulfuric acid feed. An 80 w/o sulfuric acid feed was used in the inlet conditions tests; a 48.5 w/o

Figure 4-37. Reduction Reactor Materials Test Facility - Inlet Conditions

Figure 4-38. Schematic of Experimental Apparatus for Evaluating Materials Under Reduction Reactor Inlet Conditions

Figure 4-39. Reduction Reactor Materials Test Facility - Outlet Conditions

Figure 4-40. Schematic of Experimental Apparatus for Evaluating Materials Under Reduction Reactor Outlet Conditions

sulfuric acid feed was used for the outlet conditions tests, corresponding to the SO_3 - steam ratio of the expected reduction reactor outlet stream in addition to the SO_2 and O_2 . The modified reduction reactor materials test facilities for inlet and outlet conditions are shown in Figures 4-41 and 4-42, respectively. Schematics of the modified inlet and outlet facilities are presented in Figures 4-43 and 4-44, respectively.

Samples were loaded into the quartz combustion tube and heated to the test temperature for the incremental time period. Upon attainment of the incremental exposure time, flow of the process stream was stopped and argon flow was initiated and continued until samples attained ambient temperature. The samples were removed for visual inspection, photographing, weighing and thickness measurements, after which they were returned to the test apparatus for the next exposure increment.

4.6.2.1 Discussion of Screening Test Results

A total of 109 test specimens were exposed to reduction reactor "inlet" and "outlet" condition for 1000 hours in the materials screening test program. The materials that were evaluated are listed in Table 4-7 along with their compositions. Included in the materials evaluated were 18 alloys, 4 elements, and 11 ceramics. Some of the alloys were coated with aluminum by a packcementation process commercially known as "Alonizing".

A summary of the screening test that were carried out is given in Table 4-8. Listed are the number of test sets conducted at a given temperature, under "inlet" and "outlet" conditions, and the source of the environmental test condition-simulated or actual sulfuric acid decomposition products. A more detailed listing of test materials and test environment is given in Table F-1 of Appendix F.

The following nomenclature was used to identify the various test runs according to test parameters as follows:

Figure 4-41. Modified Reduction Reactor Materials Test Facility Incorporating a Flash Evaporator - Inlet Conditions

Figure 4-42. Modified Reduction Reactor Materials Test Facility Incorporating a Flash Evaporator - Outlet Conditions

Figure 4-43. Schematic of Modified Reduction Materials Test Facility Incorporating a Flash Evaporator - Inlet Conditions

Figure 4-44. Schematic of Modified Reduction Reactor Materials Test Facility Incorporating a Flash Evaporator - Outlet Conditions

TABLE 4-7. REDUCTION REACTOR SCREENING TEST MATERIALS

<u>ALLOY DESIGNATION</u>	<u>COMPOSITION</u>
Hastelloy C276	Ni-16Cr-16Mo-6Fe-4W-2.5Co
Hastelloy G*	Ni-22Cr-19Fe-6Mo-2Co-2Nb-2Cu-1Mn-1W
Hastelloy B2	Ni-28Mo-2Co-1Cr
Incoloy 800*	Fe-32Ni-21Cr-0.4Al
Incoloy 825*	Fe-46Ni-22Cr-3Mo
IN 793*	Fe-32Ni-21Cr-1.8Al
SS-310	Fe-26Cr-20Ni-2Mn
SS316*	Fe-18Cr-12Ni-2Mo-2Mn
SS-18-18-2	Fe-18Cr-18Ni-2Si-1Cr
SS-444*	Fe-18Cr-2Mo-1Mn-1Ni-1Si
Carpenter 20Cb3	Fe-35Ni-20Cr-3.5Cu-3Mo-1Nb-1Si
Duriron	Fe-14.5Si-0.5Cr-0.5Mo-1.5Mn
Durchlor 51	Fe-14.5Si-4.5Cr-0.5Mo-0.7Mn
Carbon Steel 1018*	Fe-0.6Mn-0.2Si-0.18C
Inconel 625*	Ni-22Cr-9Mo-4Fe-3Nb
Inconel 617	Ni-22Cr-13Co-9Mo-1.5Fe-1Al
Inconel 671*	Ni-48Cr-0.4Ti
Inconel 657	Ni-48Cr-1.6Nb-1Fe
Tantalum	Ta
Tungsten	W
Zirconium	Zn

*Samples were also tested in alonized condition.

TABLE 4-7 (Continued)

<u>ALLOY DESIGNATION</u>	<u>COMPOSITION</u>
<u>CERAMICS</u>	
Macor	Al_2O_3 + Mica
Acid Proof Brick	
Silicon	Si
Silicon Carbide	SiC
Silicon Nitride	Si_3N_4
Alumina	Al_2O_3
Vitrous Carbon	C
Sialon, 80, 81 and 88	Si_3N_4 -AlN- Al_2O_3 - SiO_2
Titanium Diboride	TiB_2
Aluminum Silicate	Al_2O_3 - SiO_2

TABLE 4-8. SUMMARY OF SCREENING TEST

TEST CONDITIONS	TEST ENVIRONMENT	NUMBER OF TEST SERIES COMPLETED			
		482°C	650°C	871°C	TOTALS
Inlet Conditions $H_2O + SO_3$	Simulated (H)	6	0	3	9
	Decomposed (D)	0	0	3	3
	H_2SO_4				
Outlet Conditions H_2O, SO_3, SO_2 & O_2	Simulated (H)	0	3	1	4
	Decomposed (D)	0	0	4	3
	H_2SO_4				
	TOTALS	6	3	10	19

- RR - test simulated dynamic reduction reactor conditions
- 482 - the number immediately after RR indicates the test
- 650 - temperature in degrees centigrade
- 871 - temperature in degrees centigrade
- H - Test conducted using anhydrous SO_3 and steam to simulate decomposed sulfuric acid
- D - Test conducted using actual decomposed sulfuric acid as the feed
- I - Reduction reactor "Inlet" process stream composition
- O - Reduction reactor "Outlet" process stream stream composition
- 1, 2, 3, etc. - The final number identifies the test run in a particular test series.

Cumulative weight change data and macrographs of specimens "before" and "after" exposure are reported in Appendix F. The weight change data are summarized graphically in this section in Figures 4-45 through 4-59.

Ideally, materials which display parabolic weight gain behavior are the most desirable candidate reduction reactor. Parabolic weight gain behavior can be characterized by the following equation:

$$W^2 = Bt$$

where W is weight gain for a given time, B is a constant and t is the exposure time. Such behavior is indicative of the formation of a particular surface oxide film through which metal and oxygen ions must diffuse to carry out the corrosion process. Linear or erratic weight change data with time is indicative of nonprotective oxidation at the surface or actual spalling of the reaction products from the sample surface. Erratic or linear behavior is undesirable for the reduction reactors application. It is recognized that parabolic weight gain behavior can change to linear or erratic type after an incubation period. The thousand hour time was selected to uncover such behavior in the initial screening runs with longer term endurance testing scheduled to provide behavior verification for selected materials which performed well in the screening phase.

FURNACE TEMPERATURE 482°C
 ANHYDROUS SO₂ 12 CC/MIN
 ARGON 128 CC/MIN

Figure 4-45. Corrosion Behavior of Reduction Reactor Materials Samples in Anhydrous Environment RR482AI-1

Figure 4-46. Reduction Reactor Materials Weight Change Data Inlet Conditions
 - 482°C RR482HI1

Figure 4-47. Reduction Reactor Screening Test Results in Steam Environment
Inlet Conditions - Run RR482HI2

Figure 4-48. Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR482HI3

Figure 4-49. Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR482HI4

Figure 4-50. Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR482HI5.

Figure 4-51. Reduction Reactor Screening Test Results in Steam Environment - Outlet Conditions - Run RR650H01

Figure 4-52. Reduction Reactor Screening Test Results in Steam Environment - Outlet Conditions - Run RR650H02

Figure 4-53. Reduction Reactor Materials Screening Test Results - Outlet Conditions - Run RR650H03

Figure 4-54. Reduction Reactor Screening Test Results in Steam Environment
 Inlet Conditions - Run RR871HI1

Figure 4-55. Reduction Reactor Screening Test Results in Steam Environment - Inlet Conditions - Run RR871HI2

Figure 4-56. Reduction Reactor Materials Screening Test Results - Inlet Conditions - Run RR871HI3

Figure 4-57. Reduction Reactor Materials Screening Test Results - Outlet Conditions - Run RR871H01

Figure 4-58. Reduction Reactor Materials Screening Test Results in Acid Decomposition System - Inlet Conditions - Run RR871DI1, 2,

705548-18

Figure 4-59. Reduction Reactor Materials Screening Test Results in Acid Decomposition System - Outlet Conditions - Run RR871D01, 2, 3

As shown in Table 4-8, six test series were conducted at 482°C under simulated reduction reactor inlet conditions. Three series were conducted at 650°C involving simulated reduction reactor inlet conditions. The remainder and bulk of the testing program was carried out at 871°C and included both simulated and actual decomposed sulfuric acid test environments. The following is a brief description of each test series with a comparison of 871°C results discussion and selection of materials for endurance testing.

4.6.2.2 Series 482 and 650

Weight change data for test samples exposed to inlet conditions at 482°C are given in Figures 4-45 through 4-50, Run RR482AI-1 and Runs RR 482HI-1 through 5. Run RR482AI-1 was conducted using anhydrous SO_3 without intentional addition of steam to process stream. The run was used to checkout the system and was restricted to 500 hours in duration. The data are given in Figure 4-45. In the following test series which included steam to simulate the process stream macor, carbon steel, tantalum, Hastelloy B and zirconium exhibited excess reaction with the test environment displaying either significant weight gain, loss or a combination gain and loss. The 18-18-2, Hastelloy C276, Inconel 625 also displayed some evidence of spalling. The remainder of the materials tested in this series exhibited stable behavior with weight gains of less than 2 mg/cm^2 .

Weight change data for the series conducted at 650°C under "outlet" conditions are shown in Figures 4-51, 4-52, and 4-53. The 17 materials tested at 650°C were also included in the test series at 482°C previously discussed. A number of materials which performed well at 482°C also performed well at the higher temperature as well. They include elemental silicon, silicon carbide, silicon nitride, alumina, aluminum silicate, Inconel 625, Alonized Inconel 625, Hastelloy G, Sialon 88 and Hastelloy C276. The metallic alloys exhibited higher weight gains at the higher temperature as would be expected. The ceramic materials exhibited little change in weight change behavior except for Sialon 80 and 81, both which lost weight. A number of metallic materials such as Duriron, Durchlor 51, 310 stainless steel and Inconel 657 exhibited

significantly higher weight gains or gross spalling behavior compared to their behavior at 482°C.

4.6.2.3 Series 871

While initially included in the program plan, materials compatibility testing with the process stream at 482 and 650°C was restricted to those test series discussed above in order to concentrate the available resources on the critical 871°C process environment. The test data for materials exposed to "inlet" and "outlet" process stream conditions produced by simulation and actual acid decomposition are presented in Figures 4-54 through 4-59. Test runs RR871HI-1, -2, -3 and RR871HO-1 shown in Figures 4-54 through 4-57 were conducted using simulated process stream while test runs RR871D-1, 2, 3 and RR871DO-1, 2, 3 were conducted using decomposed acid as the process stream.

In Figure 4-54, the results of RR871HI-1 are plotted Inconel 657 and Inconel 625 exhibited erratic behavior indicative of spalling silicon, silicon carbide, and silicon nitride displayed modest weight increases over the exposure period. Alonized Inconel 625 after an initial weight loss displayed relatively little changes. The initial weight loss was most probably due to loss of an aluminum-alumina crust which is a product of the Alonizing process. If the crust is not mechanically removed by wire brushing prior to thermal exposure it usually spalls off after the first thermal cycle.

In run RR871HI-2 shown in Figure 4-55, Duriron and Durchlor exhibit behavior indicative of gross reaction and spalling. The ceramic materials, alumina, acid proof brick, and alumina silicate showed little effect of the thermal exposure. The minor erratic behavior of aluminum silicate and the acid proof brick material was most likely due to their porous nature and the difficulty in removing condensate from the samples. The Hastelloy G alloy exhibited classic behavior with an initial modest weight gain and relatively little change after 200 hours exposure.

In runs RR871HI-3 Figure 4-56 and RR871HO-1 Figure 4-57, samples of Inconel 671 and Incoloy 800 in the "as received" and Alonized condition were tested in

"inlet" and "outlet" environments. Under "inlet" conditions, the non-alonized samples of Inconel 671 and Incoloy 800, displayed breakaway behavior after 20 hours of exposure. After a small weight gain, each alloy displayed an abrupt weight increase followed by a significant weight loss after subsequent incremental exposures. The Alonized samples of each alloy were relatively stable throughout the exposure to "inlet" conditions. The same alloys under "outlet" conditions, Figure 4-57, behaved in a slightly different manner. The non-Alonized versions each gain weight and displayed more or less classical behavior with a tendency to lose weight after 400 hours of exposure. The Alonized sample of Inconel 671 gained more weight under the "outlet" conditions compared to exposure under "inlet" conditions. The Alonized sample of Incoloy 300, initially lost weight then gained weight in an erratic manner. This behavior was attributed to the loss of the outer scale which was not removed after the Alonizing process.

Results of the final six screening tests are presented in Figures 4-58 and 4-59. In Figure 4-58, data are plotted for runs RR872DI-1, 2, and 3 which were exposed to "inlet" conditions produced by the thermal decomposition of sulfuric acid. In this series of test runs, sulfuric acid at a concentration of 80 percent by weight was introduced into the flash evaporator at the rate of 0.5cc per minute. This rate produced a process stream test environment which was six times greater than "inlet" conditions produced by the use of anhydrous SO_3 and steam.

In Figure 4-59, data are plotted for runs RR871DO-1, 2, and 3 which were exposed to "outlet" conditions produced by the thermal decomposition of sulfuric acid at a concentration of 48.5 weight percent. The "outlet" composition was achieved by augmenting the process stream with oxygen and sulfur dioxide additions prior to entry into the combustion tube. This combination of decomposed sulfuric acid with oxygen and sulfur dioxide additions represented the composition of the process stream after passing through the reduction reactor. In both of these series, the same alloys were evaluated. They included Inconel 793, Incoloy 800, Incoloy 825, Inconel 625, Hastelloy G, SS316, SS444, SS-18-18-2, Hastelloy C276, Inconel 617, and Carpenter 20Cb3. The Alonized

versions of each of the above listed alloys were also included with the exception of the SS18-18-2 alloy. This alloy was only run under "inlet" condition and replaced in the "outlet" series by Inconel 671. Alonized plain carbon steel 1018 was included in both the "inlet" and "outlet" test series to complete the series.

The test results recorded in Figure 4-58, show weight losses or erratic weight change data for all non-Alonized sample except SS444. This alloy exhibited relatively stable behavior after an initial weight gain during the first 400 hours. All the Alonized samples exhibited weight gains with the exception of Alonized Inconel 671 which lost weight after the initial 200 hour exposure. Alonized Inconel 625, IN793, Incoloy 300, Hastelloy G and Incoloy 825 exhibited the least weight gain and most stable behavior over the 1000 hours of exposure.

The test results shown in Figure 4-59, give similar results compared to the "inlet" test conditions. All non-Alonized alloys exhibited weight losses over the test period with the exception of alloy SS444 which displayed a weight gain. All the Alonized alloys with the exception of alloy Inconel 671 displayed weight gains. The best performing alloys were Alonized IN793, Hastelloy G, Incoloy 800, Incoloy 825, and Inconel 625. Again Alonized alloy Inconel 671 exhibited significant losses after the first incremental exposure. Both Alonized SS316 and Carbon Steel 1018 displayed positive weight change behavior with values much higher than other Alonized alloys.

4.6.3 ANALYSIS OF TEST RESULTS

In Table 4-9, materials are ranked according to maximum absolute weight change data after exposure to inlet and outlet conditions for 1000 hours at 871°C. Materials are grouped according to classification: metallic alloys, Alonized alloys and ceramics, materials exposed to simulated process streams and actual decomposed H_2SO_4 . The decomposed acid test environment was considered to be more severe because a higher process stream flow rate was used. In cases where a given material was exposed to both environments, the material was ranked according to the data taken from the sample exposed to decomposed acid. The decomposed acid environment more closely approximated actual expected process

TABLE 4-9: RANKING OF REDUCTION REACTOR MATERIALS BY ABSOLUTE WEIGHT CHANGE DATA AFTER 1000 HOUR EXPOSURE TO INLET AND OUTLET CONDITIONS AT 871°C

INLET CONDITIONS				OUTLET CONDITIONS			
RANK	MATERIAL	WT CHANGE (mg/cm ²)	TEST COND.	RANK	MATERIAL	WT CHANGE (mg/cm ²)	TEST COND.
<u>ALLOYS</u>				<u>ALLOYS</u>			
1	Inconel 671	0.80	A-1	1	Incoloy 800	0.57	B-2
2	Inconel 625	1.01	A-1			2.20	A-2
3	Inconel 617	1.30	B-1	2	IN 793	1.20	B-2
4	SS 444	2.16	B-1	3	Carpenter 20Cb3	1.59	B-2
5	Carpenter 20Cb3	2.27	B-1	4	Incoloy 825	2.04	B-2
6	Durichlor 51	2.56	A-1	5	Hastelloy G	3.24	B-2
7	IN 793	2.96	B-1	6	Inconel 625	3.72	B-2
8	Inconel 657	3.66	A-1	7	Inconel 617	3.89	B-2
9	Hastelloy G	6.28	B-1	8	SS 444	4.49	B-2
		0.89	A-1	9	Inconel 671	9.68	B-2
10	Incoloy 825	6.66	B-1			5.80	A-2
11	Incoloy 800	7.75	B-1				
		4.13	A-1				
12	SS-18-18-2	37.8	B-1				
13	Duriron	40.0	A-1				
14	Hastelloy C276	62.5	B-1				
15	SS 316	63.4	B-1				
<u>ALONIZED MATERIALS</u>				<u>ALONIZED MATERIALS</u>			
1	Incoloy 825	0.70	B-1	1	Hastelloy G	0.70	A-2
2	Hastelloy G	0.71	A-1	2	Incoloy 800	0.73	B-2
3	Incoloy 800	0.73	B-1			1.00	A-2
		1.15	A-1	3	IN 793	0.85	B-2
4	Inconel 625	0.77	B-1	4	Incoloy 825	0.91	B-2
		0.32	A-1	5	Inconel 625	1.23	B-2
5	IN 793	0.88	B-1	6	Inconel 671	3.29	B-2
6	SS 316	3.50	B-1			3.00	A-2
7	Inconel 671	3.50	B-1	7	SS 444	3.72	B-2
		1.20	A-1	8	CS 1018	4.89	B-2
8	CS 1018	4.56	B-1	9	SS 316	5.95	B-2
<u>CERAMICS</u>							
1	Silicon Carbide	0.09	A-1				
2	Alumina	0.14	A-1				
3	Silicon Nitride	0.24	A-1				
4	Silicon	0.32	A-1				
5	Aluminum Silicate	0.44	A-1				
6	Acid Proof Brick	0.77	A-1				

A-1 - Inlet simulated process stream SO₃ - 25 SCC/min, steam - 58 SSS/min, Argon - 78 SCC/min

A-2 - Outlet simulated process stream SO₃ - 25 SCC/min, SO₂ - 47 SCC/min, O₂ - 23 SCC/min, steam - 169 SCC/min

B-1 - Inlet decomposed acid - 0.5 cc/min liquid 80 w/o feed to acid vaporizer

B-2 - Outlet decomposed acid - 1.0 cc/min liquid 48.5 w/o feed to acid vaporizer, SO₂ - 276 SCC/min, O₂ - 138 SCC/min

conditions for a full size system. After exposure to the process stream, samples were sectioned and examined metallographically to determine the degree of interaction of the surface with the environment. Since weight change data can be misleading, inspection of the cross section of selected test samples was carried out to determine the degree of subsurface reactivity with the test environment. To quantify the degree of reactivity, surface recession was determined by subtracting the final sample thickness from the initial thickness divided by two to determine the average change per side. The final thickness was determined by measuring the distance between the surface oxide scale and the substrate on each side of the test specimen. This interface is illustrated in Figure 4-60. A second factor considered was the degree of penetration of subsurface oxidation also illustrated in Figure 4-60. The amount of surface recession along with the amount of oxide penetration provided a means for quantitatively measuring the degree of reactivity of each material to the process stream under the given test conditions. In Tables 4-10 and 4-11, the test materials are ranked according to the degree of surface attack under inlet and outlet conditions, respectively. Only the metallic alloys and ceramic materials were evaluated. The Alonized-metallic alloys were not readily subject to this type of analysis and were treated separately. In order to arrive at a materials selection, the alloys were listed according to their surface attack and weight change ranking. Materials which exhibited gross weight changes or surface attack were not included. The alloys which provided the best combination of weight change and surface attack were SS 444 and Carpenter 20Cb3.

The Alonized materials due to the nature of the surface as seen in Figure 4-61 could not be assessed with regard to surface attack. Variability of the coating thickness from sample to sample prevented assessment of the surface attack parameter. However, initial and final outside thickness as well as Alonized layer thickness measurements were made after exposure is shown in Figure 4-62. Some alternation of the outside layer of the aluminide coating appears to have taken place; however, the layer adjacent to the metallic substrate appears to be intact. Of primary concern with respect to Alonized materials was the possibility of sulfide formation commonly associated with the "hot corrosion" phenomena. SEM and EDAX inspection failed to indicate the presence of nickel or

50X

SCALE

PENETRATION

400X

Figure 4-60. Hastelloy G Exposed 1,000 Hour at 871°C - Outlet Conditions

TABLE 4-10: RANKING OF SELECTED REDUCTION REACTOR MATERIALS BY SURFACE ATTACK AFTER EXPOSURE TO INLET CONDITIONS FOR 1000 HOURS AT 871°C

RANK	MATERIALS	INITIAL SAMPLE THICKNESS T_0 (Mils)	FINAL SAMPLE THICKNESS T_F (Mils)	SURFACE RECESSION $\frac{T_0 - T_F}{2}$ (Mils)	SCALE THICKNESS (Mils)	PENETRATION (Mils)	PENETRATION + SURFACE RECESSION (Mils)	TEST CONDITION
<u>ALLOYS</u>								
1	SS 444	39.0	36.2	1.4	2.4	0.0	1.4	B
2	Inconel 657	52.2	46.7	2.8	2.7	2.5	5.3	A
3	Inconel 671	125.0	124.2	0.4	1.3	5.3(P)	5.4	A
4	Inconel 625	64.1	58.3	2.9	1.1	3.4	6.3	A
5	Carpenter 20Cb3	62.0	58.8	1.6	2.7	5.7	7.3	B
6	Incoloy 825	63.8	57.8	3.0	1.6	5.8	8.8	B
7	Hastelloy G	63.4	60.1	1.7	2.9	7.5(P)	9.2	B
	Hastelloy G	62.9	57.5	2.7	2.4	7.2	9.9	A
8	In 793	97.0	85.3	5.9	1.2	4.2	10.1	B
9	Incoloy 800	115.0	114.0	0.5	1.2	5.2	5.7	B
	Incoloy 800	121.7	121.5	0.1	1.4	18.0(P)	18.1	A
10	Duriron	50.4	-	-	-	-	50.4	A
<u>CERAMICS</u>								
1	Silicon	57.2	57.0	0.1	0.00	0.0	0.1	A
2	Alumina	48.9	48.7	0.1	0.00	0.0	0.1	A
3	Silicon Nitride	55.4	55.0	0.2	0.10	0.0	0.2	A
4	Silicon Carbide	55.6	55.0	0.3	0.20	0.0	0.3	A
5	Aluminum Silicate	74.5	73.8	0.35	0.20	0.0	0.35	A
6	Duro Acid Brick	55.7	45.6	5.0	0.0	0.0	5.0	A

A - Simulated Process Stream - SO_3 - 25 SCC/min, Steam - 58 SCC/min, and Argon - 78 SCC/min.

B - Decomposed Acid - 0.5 cc/min Liquid - 80 w/o H_2SO_4 feed to flask evaporator.

P - Localized Pitting

(1 mil = 25.4 μm)

TABLE 4-11: RANKING OF SELECTED REDUCTION REACTOR MATERIALS BY SURFACE ATTACK AFTER EXPOSURE TO OUTLET CONDITIONS FOR 1000 HOURS AT 871°C

RANK	MATERIALS	INITIAL SAMPLE THICKNESS T_o (Mils)	FINAL SAMPLE THICKNESS T_F (Mils)	SURFACE RECESSION $\frac{T_o - T_F}{2}$ (Mils)	SCALE THICKNESS (Mils)	PENETRATION (Mils)	PENETRATION + SURFACE RECESSION (Mils)	TEST CONDITIONS
1	SS 444	39.7	38.5	0.6	4.1	1.8	2.4	B
2	Carpenter 20Cb3	62.8	62.0	0.4	0.0	3.0	3.4	B
3	Inconel 625	64.4	64.0	0.2	1.3	4.0	4.2	B
4	Incoloy 800	120.5	116.8	1.9	0.9	2.5	4.4	B
		121.7	113.0	4.0	0.2	3.8	7.8	A
5	Inconel 671	126.2	123.7	1.3	2.6	3.6	4.9	A
6	Incoloy 825	63.9	62.1	0.9	1.0	5.0	5.9	B
7	Hastelloy G	63.1	57.8	2.7	2.6	3.5	6.2	B
8	Inconel 617	63.4	61.1	1.2	0.2	5.0	6.2	B
9	In 793	99.5	86.0	6.8	0.4	0.8	7.6	B

A - Simulated Process Stream - SO_3 - 25 SCC/min, SO_2 - 47 SCC/min, O_2 - 23 SCC/min, Steam 169 SCC/min.

B - Decomposed Acid - 1.0 cc/min Liquid - 48.5 w/o H_2SO_4 feed to acid vaporizer, SO_2 - 276 SCC/min, O_2 - 138 SCC/min.
(1 mil = 25.4 μm)

Figure 4-61. Alonized Incoloy 800 as Received

UNETCHED

30X

UNETCHED

400X

Figure 4-62. Alonized Incoloy 800 Exposed 1,000 Hour at 871°C Outlet Conditions

chrome sulfides in the specimens that were inspected. Alkali metals such as sodium and potassium are a necessary ingredient for "hot corrosion". These elements are not expected to be present in the process stream.

In Table 4-12, a qualitative assessment of the Alonized materials was conducted. The overall thickness of the samples before and after exposure to the test environment is given along with the change per side. The final thickness of the Alonized layer is also given. Generally, Alonized layers of as-received materials ranged from 127 μ m (0.005 inch) to 229 μ m (0.009 inch) for highly alloyed materials-superalloys. Alonized layers for plain carbon steel (CS 1018) range from 254 μ m (0.010 inch) to 380 μ m (0.015 inch).

From the weight change data in Table 4-9 and the results of the metallographic inspection reported in Tables 4-10, 4-11, and 4-12, a number of general observations can be made:

- Silicon and high silicon containing ceramics appear to have the best corrosion resistance irrespective of the test environment.
A number of commercially available tubing alloys such as SS444, Carpenter 20Cb3, Inconel 625, appear to possess superior corrosion resistance of the materials tested on this program.
- Alonizing, a surface aluminizing process, has demonstrated that substrates to which it has been applied exhibit improved corrosion resistance over untreated substrates of the same composition.
- Based on weight gain data and metallographic inspection, Alonized Incoloy 800 and Hastelloy G exhibited excellent resistance to attack by the process stream.
- Neither the "Inlet" or "Outlet" test conditions appear to be a more significantly corrosive environment. Of the nine materials tested in each, the difference in weight change and surface recession-penetration data fall within a reasonable experimental scatter band.
- Comparison of weight change and recession-penetration data of materials tested in both the simulated and decomposed acid environments, indicates no significant effect of the test environment on test results.

TABLE 4-12: QUALITATIVE EVALUATION OF ALONIZED MATERIALS AFTER 1000 HOUR EXPOSURE TO INLET AND OUTLET REDUCTION REACTOR ENVIRONMENTAL CONDITIONS AT 871°C

SUBSTRATE MATERIAL	INITIAL THICKNESS (Mils)	FINAL THICKNESS (Mils)	THICKNESS CHANGE PER SIDE (Mils)	ALONIZED LAYER THICKNESS (Mils)	TEST CONDITION	COMMENTS
INLET CONDITIONS						
Inconel 625	66.5	66.6	+ 0.05	9.7	A-1	
Inconel 625	67.4	68.6	+ 0.6	3.6	B-1	
Incoloy 800	127.2	127.6	+ 0.2	7.2	A-1	
Incoloy 800	124.4	124.2	- 0.1	6.0	B-1	
In 793	62.0	61.2	- 0.4	4.6	B-1	
Incoloy 825	66.2	66.0	- 0.1	7.0	B-1	
Inconel 671	132.4	133.0	+ 0.3	7.9	A-1	
Hastelloy G	65.3	66.0	+ 0.35	4.8	B-1	
SS 316	77.0	75.8	- 0.6	19.6	B-1	
CS 1018	84.0	86.2	+ 1.1	26.8	B-1	
OUTLET CONDITIONS						
Inconel 625	68.6	67.8	- 0.04	4.0	A-2	
Incoloy 800	126.6	127.4	+ 0.4	6.2	A-2	
Incoloy 800	123.7	125.0	+ 0.7	4.5	B-2	
Inconel 671	131.4	133.0	+ 0.9	6.2	A-2	
Incoloy 825	66.5	68.0	+ 0.8	5.0	B-2	
Hastelloy G	65.7	66.0	+ 0.15	3.8	B-2	
In 793	56.0	56.4	+ 0.2	4.5	B-2	
SS 316	81.9	71.0	- 5.5	8.0	B-2	12.0 penetration
SS 444	49.7	49.0	- 0.3	6.4	B-2	15.0 penetration
CS 1018	82.2	78.0	- 2.1	16.0	B-2	

A-1 - Inlet simulated process stream - SO₃ - 25 SCC/min, steam - 58 SCC/min, Argon - 78 SCC/min.

A-2 - Outlet simulated process stream - SO₃ - 25 SCC/min, SO₂ - 47 SCC/min, O₂ - 23 SCC/min, Steam - 169 SCC/min.

B-1 - Inlet decomposed acid - 0.5 cc/min liquid - 80 w/o H₂SO₄ feed to acid vaporizer.

B-2 - Outlet decomposed acid - 1.0 cc/min liquid - 48.5 w/o - H₂SO₄ feed to acid vaporizer, SO₂ - 276 SCC/min, O₂ - 138 SCC/min.

(1 mil = 25.4 μm)

4.6.4 SCREENING TEST CONCLUSIONS

Upon completion of the screening tests and based on weight change and metallographic data, a number of materials can be identified as possessing promising compatibility with the sulfuric acid decomposition process stream. The Alonizing process also gives indications of providing protection for substrate materials under the described test conditions. A screening test program of necessity must be cursory in nature, because a large number of materials must be tested and evaluated in enough detail in order to assess their relative potential as structural materials. This objective was accomplished for the reduction reactor materials. Two alloys, SS 444 (Fe-18Cr-2Mo-1Mn-1Ni-1Si) and Carpenter 20Cb3 (Fe-34Ni-20Cr-3.5Cu-3Mo-1Nb-1Si) were selected for further investigation along with two Alonized substrate materials, Hastelloy G (Ni-22Cr-19Fe-6Mo-2Co-2Nb-2Cu-1Mn-1W) and Incoloy 800 (Fe-22Cr-1Mn).

4.6.5 ENDURANCE TEST

In this phase of the materials test program, the four materials selected as a result of the screening test program were exposed for 6000 hours to reduction reactor "inlet" conditions to determine long term compatibility. The materials selected for this evaluation were Type 444 stainless steel, Carpenter 20 Cb 3, Alonized Incoloy 800 and Alonized Hastelloy G. The tests were conducted in the facility shown in Figure 4-41 and shown schematically in Figure 4-43. The test rig utilized a flash evaporator to convert 80 wt percent sulfuric acid to the vapor state prior to entry into the quartz combustion tube which held the samples that were heated to 871°C.

In this test series, three samples of each alloy were utilized to characterized compatibility behavior. The test program plan consisted of a 6000 hour run with interruptions after 2000 and 4000 hours to remove samples. Due to the time constraint and the limitation on the number of samples which could be accommodated in the specimen holder at one time, a schedule was developed to enable the 12 samples (3 each for 4 materials) to be exposed in the test rig in the time available. The schedule is shown in Table 4-13. Upon removal of 4 samples after 2000 hours, four samples, one of each material was to be included for the remaining 4000 hours of the test period. Prior to starting the test,

TABLE 4-13. TEST SCHEDULE OF REDUCTION REACTOR MATERIALS ENDURANCE TEST

MATERIAL	TIME IN (hours)	TIME OUT (hours)	TIME TESTED (hours)
Type 444-SS-1	0	2000	2000
Type 444-SS-2	0	4000	4000
Type 444-SS-3	0	6000	6000
Alonized Incoloy 800-1	0	2000	2000
Alonized Incoloy 800-2	0	6000	6000
Alonized Incoloy 800-3	2000	6000	4000
Alonized Hastelloy G-1	0	2000	2000
Alonized Hastelloy G-2	0	6000	6000
Alonized Hastelloy G-3	2000	6000	4000
Carpenter 20 Cb-3	0	6000	6000
Carpenter 20 Cb-3	2000	6000	4000
Carpenter 20 Cb-3	2000	4000	2000

each sample was characterized as to dimension, visual appearance, and weight. Upon removal from the test environment, the samples were weighed, photographed, wire brushed and reweighed, and sectioned for metallographic examination.

4.6.5.1 Discussion of Test Results

The test program was implemented with the first group of eight samples in place as indicated in Table 4-13. A flow of 0.6 cc of 80 weight percent sulfuric acid to the flash evaporate was used to establish the process stream over the test samples. Details of the experimental operating procedure are discussed in detail in Section 4.6.2. The test program was carried out as planned with interruption at 2000 and the 4000 hour intervals with completion of the program after 6000 hours. At the 2000 hour interruption the samples were removed from the combustion tube and visually examined. It was determined that all of the SS444 alloy samples had undergone significant reaction with the test environment. On the basis of the visual observation, all three SS444 were removed from the sample holder and further exposure of that material was discontinued. The samples were stored in a desiccator along with the Alonized Hastelloy G and Incoloy 800 samples scheduled for removal at that time. In order to utilize the additional available sample slots in the sample holder, a silicon carbide sample and additional Alonized Incoloy 800 sample were added to the test program. The remainder of the test program was completed as scheduled. The resulting weight change data are reported in Table 4-14. All samples were weighed "as removed" from the test facility. The samples were lightly brushed to remove loosely adherent scale and then reweighed. The Alonized samples, Incoloy 800 and Hastelloy G each exhibited "as removed" weight gains which diminished with exposure times. The sample weights after wire brushing were erratic. For example, the two Alonized Incoloy 800 samples exposed for 4000 hours exhibited divergent results, one sample had a weight gain while the other lost weight. The Carpenter 20 Cb 3 alloy samples exhibited large weight losses after 2000 and 4000 hours with a slight gain after 6000 hours for the "as removed" condition. The sample which was exposed for 6000 hours was severely oxidized on the up stream end of the sample as noted in the micrograph in Figure 4-73. All three samples of SS444 alloy that were removed after 2000 hours exposure exhibited gross weight gains. The silicon carbide sample which was

TABLE 4-14. ENDURANCE TEST WEIGHT CHANGE DATA

MATERIAL	EXPOSURE TIME (hours)	INITIAL AREA (cm ²)	INITIAL WEIGHT (g)	FINAL WEIGHT (g)	Δ WT (mg)	Δ WT/A (mg/cm ²)	BRUSHED* WEIGHT (g)	Δ WT (g)	Δ WT/A (mg/cm ²)
ALONIZED INCOLOY 800	2000	6.20	5.6986	5.7068	8.2	1.3	5.7039	5.3	0.9
	4000	5.68	2.4937	2.5247	31.0	5.6	2.4944	0.7	0.12
	4000	5.61	2.1193	2.1646	45.3	8.1	2.1184	-0.9	-0.16
	6000	6.49	5.3806	5.3880	7.4	1.1	5.3680	-12.6	-1.9
CARPENTER 20 Cb-3	2000	6.35	3.1446	3.0985	-46.1	-7.3	3.0836	-60.9	-9.6
	4000	6.36	3.1427	3.0869	-55.8	-8.8	3.0598	-82.9	-13.0
	6000	6.79	3.3676	3.3721	4.5	0.7	3.3542	-13.4	-2.0
ALONIZED HASTELLOY G	2000	5.84	3.0358	3.0392	6.1	1.3	3.0306	-5.2	-0.9
	4000	4.45	2.1367	2.1428	3.5	0.6	2.1364	-0.3	-0.07
	6000	5.84	3.2380	3.2392	1.2	0.2	3.2205	-17.5	-3.0
TYPE 444 STAINLESS STEEL	2000	5.78	1.9337	2.3972	463.	80.	2.3940	460.3	79.6
	2000	5.73	1.9431	2.4628	520.	91.	2.4517	508.6	88.7
	2000	5.81	1.9431	2.3958	465.	80.	2.2155	272.4	46.8
SiC	2000	7.4	0.7657	0.7657	0	0	0.7649	-0.8	0.11
*Sample wired brushed to remove loose surface scale.									

included in the final 2000 hour segment of the test, displayed essentially no change in weight and with a slight loss after wire brushing. From the weight change data presented in Table 4-14 and from visual observation of the samples after exposure and during handling, it is apparent that the weight change data can only be used as a trend indicator and cannot be used as an absolute indication of material compatibility with the process stream. Two competing processes are responsible for this observed behavior. The oxidation at the surface initially forms a scale which becomes nonadherent with time and spalls off. Ideally, a dense tenaciously adherent scale which protects the substrate from the process stream is preferred. This type behavior is a strong function of the alloys substrate composition.

In order to further evaluate compatibility with the process stream, the samples were sectioned and examined metallographically to determine the degree of sub-surface interaction. The results of the metallographic examination are shown in Figures 4-63 to 4-80.

The visual appearance of the alonized Incoloy 800 samples "as received" and "as removed" after 2000, 4000, and 6000 hours exposure is shown in Figure 4-63. The 2000 hour sample had been sectioned prior to the photograph of the samples. In Figure 4-64, a cross section illustrates the Alonize coating on the sample surface. The coating has two distinct zones which is typical. Each zone is characterized by the degree of aluminum present in the intermetallic compound that makes up the aluminide coating. The concentration of aluminum is greater in the outer layer and diminishes with movement toward the substrate. In Figure 4-65 a full size cross section of the 2000 hour Alonized Incoloy 800 sample is shown in Part A. Portions of the coating at higher magnification are shown in Parts B and C. At this stage of exposure, the aluminide coating appears intact with some indication in Part C of some degree of interdiffusion taking place at the coating - substrate interface. This phenomena is more pronounced in Figure 4-66 which illustrates the 4000 hour sample. This sample was taken from a different batch of Incoloy 800. The sample is tapered, and was etched during the metallographic examination. The Alonized coating was intact around the sample. The higher magnification, Part C, indicates that the

Figure 4-63. Visual Appearance of Alonized Incoloy 800 Samples in "As Received" Condition and After Exposure to Inlet Reduction Reactor Conditions

100X

Figure 4-64. Cross Section of Alonized Incoloy 800 Sample Prior to Exposure to Inlet Reduction Reactor Conditions

A.

20X

B.

100X

C.

400X

Figure 4-65. Cross Sections of Alonized Incol 800 Sample Exposed 2000 hrs to Inlet Reduction Reactor Conditions at

A.

20X

B.

100X

C.

400X

Figure 4-66. Cross Sections of Alonized Incoloy 800 Sample Exposed 4000 Hours to Inlet Reduction Reactor Conditions at 871°C

interdiffusion zone noted after 2000 hours at the coating-substrate interface had progressed further into the substrate. The sample exposed for 6000 hours and shown in Figure 4-67, illustrate one of the difficulties associated with the coating of substrates. This sample apparently was not adequately coated on one side or the coating spalled off during exposure or subsequent handling. The Alonized coating which covered three of the four sides is shown in Part C, where as the top layer as shown in Part A appears as shown in Parts B and D. If the coating had spalled during exposure or handling at the 2000 and 4000 hour interruptions, the apparently small sample weight change relative to the other test results could be accounted for. If the sample had just been improperly coated on that one side only, the results are encouraging since the specimen did not corrode catastrophically. The photomicrographs B and D show some localized oxidation at grain boundaries, but on the whole the sample seem to have held up quite well under the circumstances.

The Carpenter 20 Cb 3 samples are shown in Figure 4-68 "as removed" from the test furnace along with an "as received" sample for comparison. A cross section of the "as received" sample is shown in Figure 4-69. The cross sections of the exposed samples are shown in Figures 4-70, 4-71, and 4-72. The Carpenter 20 Cb 3 alloy samples were not Alonize coated. The 2000 and 4000 hour samples exhibited significant weight losses during exposure indicating that the nonadherent oxide layer was spalling off during exposure and during thermal cycling. The 6000 hour sample displayed a weight gain which is attributed to gross oxidation evident at one end of the samples as shown in Part A. This behavior could possibly indicate the onset of catastrophic corrosion for longer exposure times. The penetration of oxides at grain boundaries and subsequent spalling of surface oxide layers is not untypical corrosion behavior.

The Alonized Hastelloy G samples are shown in Figures 4-73 along with an "as received" sample cross section in Figure 4-74. The Alonized Hastelloy G samples "as removed" from the test facility show a mottled appearance unlike the Alonized Incoloy 800 samples. The Alonized layer shown in Figure 4-74, exhibits a two layer zone with the darker layer at the substrate-coating interface much thinner than the outer layer. The 2000, 4000, and 6000 hour exposure

A.

20X

B.

400X

C.

400X

D.

400X

Figure 4-67. Cross Sections of Alonized Incoloy 800 Sample Exposed 6000 Hours to Inlet Reduction Reactor Conditions at 871°C

Figure 4-68. Visual Appearance of Carpenter 20 Cb-3 Samples in "As Received" and After Exposures to Inlet Reduction Reactor Conditions

Figure 4-69. Cross Section of Carpenter 20 Cb-3 Sample Prior to Exposure to Inlet Reduction Reactor Conditions

A.

20X

B.

100X

C.

400X

Figure 4-70. Cross Sections of Carpenter
20 Cb-3 Sample Exposed 2000
Hours to Inlet Reduction
Reactor Conditions at 871°C

4-144

A.

20X

B.

100X

C.

400X

Figure 4-71. Cross Sections of Carpenter
20 Cb Sample Exposed 4000
Hours to Inlet Reduction
Reactor Conditions at 871°C

A.

20X

B.

100X

C.

400X

Figure 4-72. Cross Sections of Carpenter
20 Cb-3 Sample Exposed 6000
Hours to Inlet Reduction
Reactor Conditions at 871°C

Figure 4-73. Visual Appearance of Hastelloy G Samples in "As Received" Condition and After Exposure to Inlet Reduction Reactor Conditions

Figure 4-74. Cross Section of Alonized Hastelloy G Sample Prior to Exposure to Inlet Reduction Reactor Inlet Conditions

samples are shown in Figures 4-75, 4-76, and 4-77. In each case the Alonized coating appears to have remained intact. With the progression of exposure time, multiple diffusion zones within the coating and substrate have become distinct. One end of the 6000 hour sample shows signs of progressive attack. This condition may have existed prior to testing as a result of the Alonizing process. Since nondestructive processes must be used to examine samples prior to exposure, it is very difficult to detect flaws in the coating prior to testing. None of the samples displayed excessive grain boundary penetration or gave indication of gross attack of the Alonized layer. Weight change data are consistent with the Alonized Incoloy 800 data.

The SS 444 samples that were removed from test after 2000 hours are shown in Figure 4-78. Cross sections of two of the samples are shown in Figure 4-79. The SS444 alloy which displayed reasonably good compatibility with the process stream up to 1000 hours in the screening tests, was grossly attacked in test in less than 2000 hours. An incubation period for the observed behavior was apparently required. The SS444 alloy was not coated and in this condition is not compatible with the process stream.

The silicon carbide sample which was substituted in the final 2000 hours of the test run is shown in Figure 4-80. The silicon carbide that tested was produced by the chemical-vapor-deposition (CVD) process. This material is fully dense as opposed to material made by pressing and sintering. The sample exhibited essentially no weight change as a result of exposure in the process stream. The fragmented surface layer is produced by the cutting and polishing process and is not believed to be associated with the test environment. The data are consistent with the 1000 hour screening test results and indicate the inert nature of silicon carbide in this particular test environment.

4.6.5.2 Conclusions

Based on the endurance and acknowledgement of qualitative nature of the test results, the limited evaluation of test samples; the following conclusions were drawn:

Figure 4-75. Cross Sections of Alonized
Hastelloy G Exposed 2000
Hours to Inlet Reduction
Reactor Conditions at 871°C

A.

20X

B.

100X

C.

400X

Figure 4-76. Cross Sections of Alonized Hastelloy G Sample Exposed 4000 Hours to Inlet Reduction Reactor Conditions at 871°C

A.

20X

B.

100X

C.

400X

Figure 4-77. Cross Sections of Alonized
Hastelloy G Sample Exposed
6000 h to Inlet Reduc-
tion Reactor Conditions at
871°C

Figure 4-78. SS 444 Samples After 2000 Hours Exposure to Inlet Reduction Reactor Conditions at 871°C

A.

20X

B.

20X

Figure 4-79. Cross Sections of SS 444 After 2000 Hours Exposed to Inlet Reduction Reactor Conditions at 871°C

Figure 4-80. Before and After, and Cross Section of Silicon Carbide Samples Exposed to Inlet Reduction Reactor Conditions

- Alonizing has a significant beneficial effect on the corrosion behavior of samples exposed to the vaporized 80 weight percent sulfuric acid environment provided by the test facilities described in this report.
- Alonized Incoloy 800 and Alonized Hastelloy G displayed good resistance to attack 6000 hours, based on the qualitative results of the endurance test, it is recommended that Alonized Incoloy 800 be carried forward as the primary metallic reduction reactor structural material.
- Silicon carbide was essentially unaffected for times up to 2000 hours under the test condition and should be considered as a candidate ceramic structural material for the reduction reactor.
- The performance of the carpenter 20 Cb 3 alloy was not encouraging. Indications of gross reactions with the process stream on additional exposure cause the material to be dropped from further consideration.
- The SS444 alloy suffered catastrophic attack under 2000 hours of exposure and is not considered as a viable reduction reactor structural material.

4.6.5.3 Recommendations

- Larger test samples that have been well characterized as to coating thickness and integrity must be tested for longer times (>10,000 hours) under pressurized conditions in order to qualify a given candidate reduction reactor material.
- The effect of prolonged exposure on the mechanical properties of Alonized material (particularly ductility) must be determined.
- Silicon carbide continued to display excellent compatibility with vaporized 80 weight percent sulfuric acid and should be included in a confirmatory test program to determine compatibility under pressurized conditions for longer times, >10,000 hours.
- A critical components test program is recommended in which scaled-down models of reduction reactor components can be treated under conditions which approximate design conditions of temperature and pressure.

4.7 SOLAR RECEIVER/REDUCTION REACTOR CONCEPT

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 4-81. 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 were to perform a concept study on the solar receiver/reduction reactor, including preliminary trade-off evaluations, and to prepare a conceptual design of a full-scale solar driven reduction reactor.

Figure 4-81. Schematic of Acid Vaporization/Reduction Equipment

4.7.1 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)

4.7.2 DESCRIPTION OF SELECTED CONFIGURATION

Based on the results of trade studies (discussed in Section 4.7.3), 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 4-82.

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:

- 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).

Figure 4-82. Receiver R-1 Air Heat Transport System

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 4-15 and a sketch of the unit is shown in Figure 4-83.

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

TABLE 4-15
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 4-83. Decomposition Reactor

in materials tests at Westinghouse, ISPRA and General Atomic. Alonized Inconel 625, which also was tested under this contract, was identified as a backup 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.

4.7.3 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, SO_2 and O_2 would then be regeneratively cooled and sent to various condensation, separation and extraction systems. The SO_2 recovered would be recycled back to the SO_2 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 SO_3 into SO_2 and O_2 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 4-16.

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.

TABLE 4-16

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.

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 to the receiver by a conveyor, heated by a solar radiation, and returned to the reduction reactor. The general arrangement is shown in Figure 4-84. 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 4-17 and 4-18 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).

Figure 4-84. Solids Heat Transport Concept

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 4-18

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	--	--	$M/L \left(H/M \right)^*$	-- $\left(H/L \right)$	-- $\left(H/L \right)$
ACID PIPE RUPTURE	-- $\left(H/M \right)$	--	--	--	--
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.

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 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 4-18, 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 comparable 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 4-19. As discussed above, the indirect system utilizing an air heat transport fluid (Option 6) was the selected configuration.

TABLE 4-19

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

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APPENDIX A

OPERATION OF SO_3 REDUCTION CATALYST SCREENING 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. Provisions are also available to install a thermocouple inside of the catalyst to determine the temperature profile of the catalyst bed.

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

Liquid SO_3 is then gradually heated to $\sim 52^\circ\text{C}$, with a thermometer used to note the temperature of the SO_3 vapor. Gaseous SO_3 passes vertically from the delivery flask through a teflon metering valve, rotameter, and to a differential pressure checkvalve.

Beyond this valve, a constant flow of argon is maintained through the furnace and the balance of the system. The Ar is used as a carrier gas for the process stream.

At 52°C the vapor pressure of vaporized SO_3 is three to five psig. When the SO_3 vapor pressure equals that of the Ar, the differential pressure checkvalve opens and the SO_3 is carried into the furnace.

When operating under anhydrous conditions, the process stream (92 percent Ar and eight percent SO_3) flows at a constant pressure through the reaction tube containing the catalyst. The SO_3 is then catalytically decomposed into SO_2 and O_2 , which, along with any unreacted SO_3 , exits the furnace and flows through a water cooled condenser. Here the unreacted SO_3 is condensed out and collected and the product stream flows to a three way teflon solenoid valve.

At this point the flow is normally directed through a liquid trap and a gas scrubber (used to remove any residual SO_3) then vented to the atmosphere. Alternately, the product stream may be diverted, by actuating the solenoid valve, to the SO_2 analyzer. The stream passes through the photometric analyzer, to a bubble flowmeter, where the volumetric flow is measured, and finally to a scrubber and then vented.

The analyzer reads the percent of SO_2 in the gas stream and is insensitive to Ar, O_2 , etc. By measuring the volumetric flow rate of the gas stream and knowing the percentage of SO_2 , and the SO_3 flowrate, it is possible to quickly calculate the conversion percent of SO_3 to SO_2 . The analyzer is equipped with an internal calibration that provides a rapid and accurate calibration of the analyzer.

When testing is done in the wet environment, the steam generator is activated. The steam is delivered through a teflon metering valve, rotameter, and differential pressure checkvalve. When the steam pressure equals the argon pressure, the checkvalve opens and steam is admitted to the system and entrained in the argon. In order to ensure a constant steam flow, the steam generator is equipped with a pressure relief valve.

By controlling the steam/ SO_3 flowrates, it is possible to simulate a wide range of H_2SO_4 acid concentration.

In order to prevent condensation of sulfuric acid prior to the catalyst bed, (this will occur if the Ar/ SO_3 /steam stream is allowed to drop below $\sim 340^\circ\text{C}$), the SO_3 is introduced through an injection tube inside the furnace, immediately upstream of the catalyst bed at a location where the temperature is $>600^\circ\text{C}$.

As the wet product stream exits the furnace and passes through the H_2O cooled condenser, the SO_3 /steam is condensed out as dilute sulfuric acid and collected. The remaining gases then pass through the balance of the system as previously described.

To prevent reoxidation of SO_2 and SO_3 , the entire system is constructed of quartz, pyrex, and teflon. All delivery lines are heat traced and insulated to insure adequate temperatures.

APPENDIX B

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 delivered to the acid vaporizer, which is filled with quartz chips to provide a more effective means of heat transfer.

The vaporizer 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 SO_2 and O_2 , after passing through a CaSO_4 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 SO_2 , the stream flow is diverted directly to the SO_2 analyzer where it is photometrically measured for SO_2 content. After leaving the analyzer the flow is measured using a bubble flowmeter and then vented. Conversion rate is calculated using the SO_2 flow method.

If the oxygen content is to be measured, the flow is piped to a liquid nitrogen cooled cryogenic separator. Here the SO_2 is condensed out and the oxygen flow sent to its respective analyzer. Calculations are then performed as described in O_2 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.

APPENDIX C
CATALYST TEST DATA

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

148242	158174
148245	158175
148247	158176
148249	158743
154094	158744
154464	158745
154473	158746
154474	158748
157039	158751
157040	158752
157304	158893
157307	159682
157945	159683
157946	159689
157958	159694
157959	

TABLE C-1

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	59.5
700	29.4	22.6	15.4	13.4	-	68.9
750	38.2	30.8	24.6	-	-	77.5
800	43.8	39.1	36.2	-	-	84.5
850	45.7	-	-	-	-	90.5
900	48.3	47.6	44.5	42.2	35.3	93.1

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 C-2
CATALYST ALFA-4 SERIES 100 TEST RESULTS

TEMP (°C)	ACID FEED RATE	AVG. CONV.	EQUIL. CONV.	EFFICIENCY	LHSV
900	0.588 cc/min	89.1%	90.5%	98%	36.3 hr ⁻¹
900	0.784	89.2	90.5	98	49.0
900	1.02	87.2	90.5	96	66.8
900	1.18	86.7	90.5	96	72.8
850	0.58	82.1	85.0	96	49.0
850	0.973	79.3	85.0	93	61.7
850	1.13	77.1	85.0	91	69.7
800	0.939	69.6	78.0	89	58.0
800	0.964	67.9	78.0	87	61.7
800	1.08	63.2	78.0	81	66.8
750	0.688	56.3	69.0	81	49.0
750	0.987	44.1	69.0	64	61.7
750	1.05	42.0	69.0	61	66.8
700	0.560	31.0	59.5	52	36.3
700	0.775	23.7	59.5	40	49.0
700	0.982	18.9	59.5	32	61.7
700	1.08	17.2	59.5	29	66.8

Catalyst: 20% Fe₂O₃ on Al₂O₃
 Geometry: 3.2 mm right circular cylinders
 Weight: 23.040 g
 Bed length: 3.81 cm
 Reaction tube I.D.: 2.1 cm
 Bulk density: 1.88
 Feed: 80 w/o H₂SO₄
 Total test time: ~233 hours

TABLE C-3
CATALYST ALFA-4 SERIES 200 TEST RESULTS

TEMP (°C)	ACID FEED RATE	AVG. CONV.	EQUIL. CONV.	EFFICIENCY	LHSV
900	1.00 cc/min	86.8%	90.5%	96%	30 hr ⁻¹
900	1.05	87.8	90.5	97	30
900	2.20	83.0	90.5	92	60
900	2.40	82.2	90.5	91	72
900	3.92	77.3	90.5	85	113
750	0.97	49.0	78.0	54	30
750	1.90	38.0	78.0	42	60
750	2.44	32.4	78.0	36	70
750	3.74	25.6	78.0	28	113
700	0.99	18.2	59.5	31	30
700	1.90	12.0	59.5	20	60
700	2.38	8.6	59.5	14	72
700	3.75	3.3	59.5	6	113

Catalyst: 20% Fe₂O₃ on Al₂O₃
 Geometry: 3.2 mm right circular
 Weight: 45.8290 g
 Bed length: 7.62 cm
 Reaction tube I.D.: 2.1 cm
 Bulk density: 1.88
 Feed: 80 w/o H₂SO₄
 Total test time: ~373 hours

TABLE C-4
CATALYST ALFA-4 SERIES 300 TEST RESULTS

TEMP (°C)	ACID FEED RATE	AVG. CONV.	EQUIL. CONV.	EFFICIENCY	LHSV
900	0.51 cc/min	87.0%	90.5%	96%	28.4 hr ⁻¹
900	0.65	86.6	90.5	96	36.3
900	0.98	82.6	90.5	92	54.9
900	1.26	81.0	90.5	90	70.7
900	2.00	70.8	90.5	78	112.3
900	2.61	50.8	90.5	56	146.5
900	3.00	42.1	90.5	47	168.5
900	4.52	32.0	90.5	35	253.9
900	5.07	26.3	90.5	29	284.8
900	0.606	87.6	90.5	97	34.0
900	1.22	79.4	90.5	88	68.5

Catalyst: 20% Fe₂O₃ on Al₂O₃
 Geometry: 3.2 mm right circular cylinders
 Weight: 21.7590 g
 Bed length: 3.65 cm
 Reaction tube I.D.: 2.1 cm
 Bulk density: 1.88
 Feed: 80 w/o H₂SO₄
 Total test time: 330 hours

TABLE C-5

TEST RESULTS OF CATALYST MB-3 IN AN ANHYDROUS ENVIRONMENT

$$SV = 1,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>	<u>Equi.</u>
895	69.26	94.5
844	63.57	91.0
789	56.12	85.0
740	46.69	78.2
679	36.55	68.8
627	25.95	

Ar flow = 153 cc/min

SO₃ flow = 14 cc/min

$$SV = 5,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>	<u>Equi.</u>
889	72.94	94.0
824	68.00	89.0
747	54.94	79.2
704	44.24	72.5
640	32.34	61.0

Ar flow = 767 cc/min

SO₃ flow = 67 cc/min

Catalyst MB-3 - 1% (by weight) Pt on a spherical alumina substrate

Catalyst Volume = 10.00 cc

TABLE C-6

TEST RESULTS OF CATALYST MB-3 IN AN ANHYDROUS ENVIRONMENT

$$SV = 10,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>	<u>Equi.</u>
648	30.32	63.0
699	39.49	71.5
749	50.53	79.5
800	58.49	86.5
848	62.99	91.5
899	66.33	94.5

Ar flow = 337 cc/min

SO₃ flow = 30 cc/min

$$SV = 20,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>	<u>Equi.</u>
650	37.12	63.0
702	46.40	71.6
748	55.02	79.4
796	61.51	86.3
848	66.55	91.5
903	70.02	94.5

Ar flow = 675 cc/min

SO₃ flow = 60 cc/min

Catalyst MB-3 - 1% on a spherical alumina substrate
Catalyst Volume = 2.20 cc

TABLE C-7

TEST RESULTS OF CATALYST MB-3 IN AN ANHYDROUS ENVIRONMENT

SV = 30,000 hr⁻¹SV = 40,000 hr⁻¹

<u>Temperature, °C</u>	<u>Conversion, %</u>	<u>Temperature, °C</u>	<u>Conversion, %</u>
650	28.94	662	31.25
710	37.24	711	40.87
762	44.05	767	45.67
800	49.76	818	52.88
850	55.95	887	61.55
910	59.76	927	62.82
Ar flow = 460 cc/min		Ar flow = 615 cc/min	
SO ₃ flow = 40 cc/min		SO ₃ flow = 52 cc/min	

SV = 50,000 hr⁻¹

<u>Temperature, °C</u>	<u>Conversion, %</u>
686	36.13
706	40.72
777	54.78
811	62.50
862	66.72
911	69.92

Ar flow = 750 cc/min

SO₃ flow = 70 cc/min

Catalyst MB-3 - 1% Pt on a 3.2 mm spherical alumina substrate
 Catalyst Volume = 1.00 cc

TABLE C-8

TEST RESULTS OF CATALYST MB-3 IN A WET ENVIRONMENT

$$SV = 1,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>	<u>Equi.</u>
639	28.94	57.0
672	36.05	63.8
712	42.20	70.8
758	53.25	78.9
821	64.25	87.5
882	71.57	92.7

Ar flow = 105 cc/min

Steam flow = 43 cc/min

SO₃ flow = 18 cc/min

{ This ratio simulates an 80% (by
weight H₂SO₄ concentration

$$SV = 5,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>	<u>Equi.</u>
628	30.30	55.6
678	42.49	64.6
723	49.40	72.7
774	61.19	81.3
812	68.37	86.4
870	76.37	91.7

Ar flow = 525 cc/min

Steam flow = 217 cc/min

SO₃ flow = 92 cc/min

{ This ratio simulates an 80% (by
weight) H₂SO₄ concentration.

Catalyst MB-3 - 1% Pt (by weight) on ~3.2 mm spherical alumina
substrate

Catalyst Volume = 10.00 cc

TABLE C-9

TEST RESULTS FOR CATALYST MB-3 IN A STEAM ENVIRONMENT

$$SV = 30,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>
649	30.66
717	45.02
751	51.97
799	57.49
845	65.45
908	70.33

Ar flow = 320 cc/min

Steam flow = 130 cc/min
 SO_3 flow = 57 cc/min

{ This ratio simulates an 80 w/o
 H_2SO_4 feed stream.

$$SV = 40,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>
659	36.69
700	43.90
748	51.64
801	58.52
853	69.88
901	72.80

Ar flow = 420 cc/min

Steam flow = 173 cc/min
 SO_3 flow = 73 cc/min

{ This ratio simulates an 80 w/o
 H_2SO_4 feed stream.

$$SV = 50,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>
640	33.97
699	47.44
740	56.67
801	64.58
847	72.99
904	78.60

Ar flow = 525 cc/min

Steam flow = 217 cc/min
 SO_3 flow = 92 cc/min

{ This ratio simulates an 80 w/o
 H_2SO_4 feed stream.

Catalyst MB-3 - 1% Pt on a 3.2 mm spherical alumina substrate
 Catalyst Volume = 1.00 cc

TABLE C-10
COMPARISON OF ANHYDROUS TEST RESULTS FOR CATALYST MB-3

Temperature °C	Conversion %						
	1,000 hr ⁻¹	5,000 hr ⁻¹	10,000 hr ⁻¹	20,000 hr ⁻¹	30,000 hr ⁻¹	40,000 hr ⁻¹	50,000 hr ⁻¹
650	30.9	32.8	30.3	37.0	28.9	30.3	32.6
700	40.0	44.2	39.5	46.4	35.5	36.2	41.6
750	47.8	55.0	50.5	55.0	43.6	44.6	50.3
800	57.1	62.7	58.5	61.5	49.8	51.3	58.5
850	63.8	70.0	63.0	66.6	56.0	57.5	65.4
900	69.4	75.7	66.3	70.0	60.9	62.5	74.1

Catalyst MB-3 - 1% Pt on 3.2 mm spherical alumina substrate at all space velocities gas stream consisted of 92% Ar, 8% SO₃. Testing done on three separate catalyst volumes:

One for 1,000 and 5,000,
one for 10,000 and 20,000,
one for 30,000, 40,000 and 50,000.

TABLE C-11
COMPARISON OF TEST RESULTS FOR CATALYST MB-3 IN A STEAM ENVIRONMENT

Temperature °C	Conversion %				
	1,000 hr ⁻¹	5,000 hr ⁻¹	30,000 hr ⁻¹	40,000 hr ⁻¹	50,000 hr ⁻¹
650	32.0	34.9	30.7	35.0	36.3
700	42.3	45.4	41.1	43.9	47.4
750	52.3	55.7	52.0	51.6	58.1
800	61.3	64.1	57.5	58.5	64.5
850	69.0	73.3	66.2	69.8	73.0
900	75.1	79.8	70.5	72.8	78.6

Catalyst MB-3 1% Pt on 3.2 mm spherical alumina substrate

Gas steam composition - 63% Ar, 26% steam, 11% SO₃

The steam/SO₃ ratio simulates an 80 w/o H₂SO₄ feed stream

Catalyst volumes tested same as described in Table 2-3

TABLE C-12

COMPARISON OF ANHYDROUS AND WET TEST RESULTS FOR CATALYST MB-3

Temperature, °C	Conversion %						Temperature, °C	Conversion %			
	SV = 1000 hr ⁻¹		SV = 5000		SV = 30,000			SV = 40,000		SV = 50,000	
	Anhydrous	Wet	Anhydrous	Wet	Anhydrous	Wet		Anhydrous	Wet	Anhydrous	Wet
650	30.9	32.0	32.8	34.9	28.9	30.7	650	30.3	35.0	32.6	36.3
700	40.0	42.3	44.2	45.4	35.5	41.1	700	36.2	43.9	41.6	47.4
750	47.8	52.3	55.0	55.7	43.6	52.0	750	44.6	51.6	50.3	58.1
800	57.1	61.3	62.7	64.1	49.8	57.5	800	51.3	58.5	58.5	64.5
850	63.8	69.0	70.0	73.3	56.0	66.2	850	57.5	69.8	65.4	73.0
900	69.4	75.1	75.7	79.8	60.9	70.5	900	62.5	72.8	74.1	78.6

Catalyst MB-3 = 1% Pt on 3.2 mm Spherical Alumina Substrate

Anhydrous Gas Stream Ratio = 92% Ar - 8% SO₃

Wet Gas Stream Ratio = 63% Ar - 26% Steam - 11% SO₃. The Steam/SO₃ Ratio Simulates an 80 w/o H₂SO₄ Feed Stream.

Catalyst Volumes Test as Described in Appendix B, Table 11.

TABLE C-14

OBSERVED TEMPERATURES AT 5,000 HR⁻¹ CATALYST MB-3

<u>Prior to SO₃</u> <u>Injection</u>		<u>During SO₃</u> <u>Evaluations</u>	
<u>External Temp.</u>	<u>Catalyst Temp.</u>	<u>External Temp.</u>	<u>Catalyst Temp.</u>
889°C	862°C	900°C	863°C
824°C	798°C	823°C	798°C
747°C	728°C	747°C	728°C
704°C	689°C	704°C	689°C
640°C	618°C	641°C	617°C

Catalyst Volume = 10.00 cc

Catalyst Bed Length = 12.70 cm

Catalyst Mass = 45.20 g

Reaction Tube O.D. = 25 mm

Reaction Tube I.D. = 22 mm

Temperatures measured using a Pt-Pt 10% Rh thermocouple with
a Fluke Model 8600A multimeter

SO₃ flow = 67 cc/min

Ar flow = 767 cc/min

TABLE C-15

COMPARISON OF THE INTERNAL CATALYST BED TEMPERATURE
WITH THE REACTION TUBE OUTSIDE SURFACE TEMPERATURE
FOR CATALYST MB-3, SPACE VELOCITY = 10,000 hr⁻¹

<u>TEST 1</u>		
Reaction Tube Surface Temp. (°C)	Prior to Introduction of SO ₃ (°C)	During Evaluations Internal Catalyst Bed Temp. (°C)
648	648	641
699	698	693
749	750	742
802	802	793
850	850	843
<u>TEST 2</u>		
800	800	794
848	847	841
899	899	892
<u>TEST 3</u>		
850	850	844
900	900	892
850	851	842
800	800	792
750	749	743
700	699	694

Temperature measured using a Pt/Pt - 10% Rh thermocouple and a Fluke Model 8600A multimeter

TABLE C-16

COMPARISON OF THE INTERNAL CATALYST BED TEMPERATURE
WITH THE REACTION TUBE EXTERNAL SURFACE TEMPERATURE
FOR CATALYST MB-3, SPACE VELOCITY = 20,000 hr⁻¹

TEST 1

Reaction Tube Surface Temp. (°C)	Prior to Introduction of SO ₃ (°C)	During Evaluations Internal Catalyst Bed Temp. (°C)
650	649	638
702	702	688
748	748	735
796	796	783
848	846	835
903	903	890

TEST 2

653	652	640
707	706	694
756	756	742
805	805	793
849	849	836
899	899	897

Temperatures measured using a Pt-Pt 10% Rh thermocouple with a Fluke
Model 8600A multimeter

TABLE C-17
ANHYDROUS TEST RESULTS OF CATALYST MB-2
SV = 1,000 hr⁻¹

<u>Temperature, °C</u>	<u>Conversion, %</u>
650	30.72
700	39.13
750	45.58
800	52.77
850	55.79
900	59.50

Ar flow = 133 cc/min
SO₃ flow = 12 cc/min

SV = 10,000 hr⁻¹

<u>Temperature, °C</u>	<u>Conversion, %</u>
640	37.37
700	42.48
750	49.35
800	60.50
850	50.41
900	49.75

Ar flow = 639 cc/min
SO₃ flow = 56 cc/min

Catalyst MB-2 - 1% Pt on a spherical alumina substrate

TABLE C-18

TEST RESULTS OF CATALYST MB-2 IN A STEAM ENVIRONMENT

$$SV = 1,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>
652	33.03
700	41.99
750	48.28
800	59.00
850	66.86
900	70.80

Ar flow = 91 cc/min

Steam flow = 38 cc/min } This ratio simulates an 80 w/o
 SO_3 flow = 16 cc/min } H_2SO_4 feed stream.

$$SV = 5,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>
651	35.86
700	46.97
750	54.01
803	63.83
850	69.95
900	81.40

Ar flow = 455 cc/min

Steam flow = 190 cc/min } This ratio simulates an 80 w/o
 SO_3 flow = 80 cc/min } H_2SO_4 feed stream.

$$SV = 10,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion, %</u>
650	29.88
700	36.27

Ar flow = 438 cc/min

Steam flow = 181 cc/min } This ratio simulates an 80 w/o
 SO_3 flow = 76 cc/min } H_2SO_4 feed stream.

Catalyst MB-2 - 1% Pt on a spherical alumina substrate

TABLE C-19
COMPARISON OF ANHYDROUS TEST RESULTS FOR CATALYST MB-2

<u>Temperature, °C</u>	<u>1000 hr⁻¹</u>	<u>Conversion %</u>	
		<u>10,000 hr⁻¹</u>	<u>Equilibrium</u>
650	30.72	37.00	63.0
700	39.13	42.48	71.5
750	45.58	49.35	79.5
800	52.77	60.50	86.5
850	55.79	50.41	91.5
900	59.50	49.75	94.5

Catalyst MB-2 - 1% Pt on a spherical alumina substrate.

TABLE C-20

COMPARISON OF TEST RESULTS IN A STEAM ENVIRONMENT FOR CATALYST MB-2

<u>Temperature, °C</u>	<u>Conversion %</u>			<u>Equilibrium</u>
	<u>1,000 hr⁻¹</u>	<u>5,000 hr⁻¹</u>	<u>10,000 hr⁻¹</u>	
650	33.03	35.86	29.88	59.5
700	41.99	46.97	36.27	68.9
750	48.28	54.01		77.5
800	59.00	63.83		84.5
850	66.86	69.85		90.5
900	70.80	81.40		93.1

Catalyst MB-2 - 1% Pt on a spherical alumina substrate.

TABLE C-21

COMPARISON OF ANHYDROUS AND WET TEST RESULTS FOR CATALYST MB-2

$$SV = 1,000 \text{ hr}^{-1}$$

<u>Temperature, °C</u>	<u>Conversion %</u>	
	<u>Anhydrous</u>	<u>Wet</u>
650	30.72	33.03
700	39.13	41.99
750	45.58	48.28
800	52.77	59.00
850	55.79	66.86
900	59.50	70.80

Catalyst MB-2 = 1% Pt on a spherical alumina substrate

Catalyst Volume = 8.70 cc

Anhydrous Composition = 92% Ar, 8% SO_3

Wet Composition = 63% Ar

26% Steam	} This ratio simulates an 80 w/o H_2SO_4 feed stream
11% SO_3	

TABLE C-22

COMPARISON OF ANHYDROUS AND WET TEST RESULTS FOR CATALYST ENG-1 AT SV = 10,000 hr⁻¹

<u>Temperature, °C</u>	<u>% Conversion</u>	
	<u>Anhydrous</u>	<u>Wet</u>
650	35.07	35.74
700	44.05	43.34
750	53.06	47.70
800	59.13	53.13
850	---	54.44
900	62.87	58.29

Catalyst ENG-1 - .5% Pt on a 3.2 mm Cylindrical Alumina Substrate

Anhydrous flow - Ar flow = 116 cc/min

SO₃ flow = 12 cc/min

Wet flow - Ar flow = 81 cc/min

Steam flow = 33 cc/min

SO₃ flow = 14 cc/min

} This ratio simulates an 80 w/o
H₂SO₄ feed stream.

TABLE C-23
ANHYDROUS AND WET TEST RESULTS FOR CATALYST CE-1

Temperature °C	ANHYDROUS 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%

Temperature °C	WET CE-1		Equilibrium Conversion
	1000 hr ⁻¹	5000 hr ⁻¹	
650	5.3%	1.6%	59.5
700	9.0%	2.5%	68.9
750	20.7%	7.3%	77.5
800	35.6%	19.6%	84.5
850	38.9%	32.3%	90.5
900	42.7%	38.2%	93.1

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 C-24

ANHYDROUS AND WET TEST DATA FOR CATALYST ALFA-2

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

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

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 C-25

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 C-26

CATALYST ALFA-2 TEST RESULTS (LHSV = 7.8 hr^{-1})

TEMP (°C)	ACID FEED RATE	AVG. CONV.
900°C	0.625 cc/min	86.0%
850	0.622	79.4
800	0.620	70.4
750	0.597	60.6
700	0.609	45.2
650	0.601	12.6

Catalyst: 0.5% Pd on Al_2O_3
Catalyst weight: 32.66 g
Bed length: 6.35 cm
Bulk density: 1.89
Reaction tube I.D.: 2.1 cm
Feed: 80 w/o H_2SO_4

TABLE C-27
ANHYDROUS AND WET TEST RESULTS FOR CATALYST ALFA-3

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

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

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 C-28

CATALYST ALFA-3 TEST RESULTS
(LHSV = 5.7 hr^{-1})

TEMP (°C)	ACID FEED RATE	AVG. CONV.	EQUIL. CONV.	EFFICIENCY	ACCUMULATED TEST HOURS
900°	0.860 cc/min	89.8%	90.5%	99%	6.8 hrs
900	0.945	82.5	90.5	91.2	12.4
900	0.779	79.2	90.5	87.5	18.8

Catalyst: 15% Cr_2O_3 on Al_2O_3
 Catalyst weight: 29.23 g
 Bed length: 5.72 cm
 Bulk density: 2.92
 Reaction tube I.D.: 2.1 cm
 Feed: 80 w/o H_2SO_4

TABLE C-29

ANHYDROUS AND WET TEST RESULTS FOR CATALYST ALFA-5

ANHYDROUS

TEMPERATURE, °C	CONVERSION %	
	1000 hr ⁻¹	5000 hr ⁻¹
650	-	-
700	-	-
750	-	-
800	-	-
850	-	-
900	25.9	32.1

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

WET

TEMPERATURE, °C	CONVERSION %	
	1000 hr ⁻¹	5000 hr ⁻¹
650	-	-
700	-	-
750	-	-
800	-	-
850	-	-
900	7.7	6.6

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

TABLE C-30
CATALYST ALFA-5 TEST RESULTS
(LHSV = 4.5 hr⁻¹)

TEMP (°C)	ACID FEED RATE	AVG. CONV.	EQUIL. CONV.	EFFICIENCY
900	1.01 cc/min	12.0%	90.5	13%

Catalyst: MgO
 Catalyst weight: 34.4961 g
 Bed length: 6.71 cm
 Bulk density: 3.58
 Reaction tube I.D.: 2.1 cm
 Feed: 80 w/o H₂SO₄

TABLE C-31
CATALYST KAT-1 TEST RESULTS
(LHSV = 13.4 hr⁻¹)

TEMP (°C)	ACID FEED RATE	AVG. CONV.	EQUIL. CONV.	EFFICIENCY
900	0.713 cc/min	40.0%	90.5%	44.2%
850	0.872	32.1	85.0	37.8
800	0.812	17.3	78.0	22.2
750	0.643	5.2	59.5	7.5
700	0.668	1.2	60.0	2.0

Catalyst: Al₂O₃
 Catalyst weight: 33.7942 g
 Bed length: 6.35 cm
 Bulk density: 1.81
 Radiation tube I.D.: 2.1 cm
 Feed: 80 w/o H₂SO₄

TABLE C-32

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 C-33

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 D

TEST RESULTS AND SAMPLE PHOTOGRAPHS
FROM ACID VAPORIZER MATERIALS EVALUATION

TABLE D-1

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	V	- 0.79	-11.2 c	- 13.2	
	I	-77.2	-238. c	-333.	
	L	-235.	-441. c	-510.	
Tantalum, Preanodized	V	0.21			
	I	-367.8			
	L	-528.8			
Sialon 80	V	-55.9	-130.		
	I	-39.6	-85.2		
	L	- 0.03	-79.3		
Sialon 81	V	-190.	-297.		
	I	-70.4	-163.		
	L	-10.1	-72.1		
Sialon 88	V	a			
	I	-22.8	-139.		
	L	- 2.12	-46.4		
Titanium Diboride	V	a			
	I	a			
	L	a			
SS-18-18-2	V	-210.	-292. b	a,c	
	I	-148.	-220. b	a,c	
	L	-57.2	-87.9 b	a,c	
SS 310	V	-61.7	-157.	a,c	
	I	-53.3	-229.	a,c	
	L	- 4.5	-139.	a,c	
Cartech Type 20 Cb-3	V	-71.8	a		
	I	-38.6	-945.		
	L	- 5.86	a		

TABLE D-1
ACID VAPORIZER TEST RESULTS AT 361°C
(Continued)

MATERIAL	SAMPLE LOCATION	Δ WEIGHT/AREA mg/cm ²			
		250 Hours	500 Hours	750 Hours	1000 Hours
W - Plate	V	-30.6	-209.	-312.	
	I	-77.0	-343.	-367.	
	L	-56.4	-460.	-548.	
W - Powder, sintered, swaged	V	-101.	-106.		
	I	- 65.3	- 84.3		
	L	- 39.6	- 73.9		
Hastelloy C-276	V	-133.	-397. c	a	
	I	-133.	-491. c	a	
	L	- 1.38	-403. c	a	
Incoloy 825	V	76.6	-347. c	a	
	I	- 41.7	-464. c	a	
	L	- 1.26	-339. c	a	
Inconel 657	V	- 14.9	-161. c	-453.	
	I	- 73.8	-246. c	-610.	
	L	- 90.3	-241. c	-608.	
Inconel 625	V	- 51.5	-499.		
	I	-122.	a		
	L	-173.	a		
Alonized Inconel 625	V	- 31.9	-463.		
	I	- 93.8	-518.		
	L	-152.	a		

TABLE D-1
ACID VAPORIZER TEST RESULTS AT 361°C
(Continued)

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

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

SAMPLE LOCATION: V - Exposed to Vapor Phase Only
I - Exposed to Liquid/Vapor Interface
L - 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.

TABLE D-2

ACID VAPORIZER TEST RESULTS - ENDURANCE TESTS AT 450°C

SAMPLE ID	ORIGINAL WT	WEIGHT @ 1500 HRS.	Δ WT	% CHANGE
AV-01	0.9919g	1.0074g	+.0155g	+1.5%
AV-02	1.2446	1.2494	+.0048	+.4
AV-03	1.1670	1.1778	+.0108	+.9
AV-04	1.0305	1.0414	+.0109	+1.1
AV-05	0.9891	1.0010	+.0119	+1.2
AV-06	1.2418	1.2437	+.0019	+.1
AV-07	0.9445	0.9488	+.0043	+.5
AV-08	1.2214	1.2237	+.0023	+.2
AV-09	0.8379	0.8532	+.0153	+1.8
AV-10	1.4652	1.4672	+.0020	+.1
AV-11	.9599	.9660	+.0061	.6
AV-12	1.3326	1.3323	-.0003	0

0 Hours

1000 Hours

VAPOR
PHASELIQUID/VAPOR
INTERFACELIQUID
PHASE

Figure D-1. Visual Appearances of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C

0 Hours

1000 Hours

Figure D-2. Visual Appearances of Samples After Exposure to 98 w/o Sulfuric Acid at 361°C

ALUMINUM
SILICATE

VITREOUS
CARBON

0 Hours

ALUMINUM
SILICATE

VITREOUS
CARBON

TOP

1000 Hours

VAPOR
PHASE

LIQUID/VAPOR
INTERFACE

LIQUID
PHASE

Figure D-3. 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 D-4. Visual Appearance of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C

500 Hours

750 Hours

LEGEND:

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

VAPOR
PHASELIQUID/VAPOR
INTERFACELIQUID
PHASE

Figure D-5. 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.)

Figure D-6. Visual Appearances of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C.
(The TiB_2 was completely disintegrated after 250 hours exposure.)

Figure D-7. Visual Appearance of Samples Before Exposure to 98 w/o Sulfuric Acid at 361°C.

250 Hours

500 Hours

VAPOR
PHASE

LIQUID/VAPOR
INTERFACE

LIQUID
PHASE

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

Figure D-9. 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.)

LEGEND:

625 - Inconel 625

625A - Alonized Inconel
625

Figure D-10. Visual Appearance of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C.

0 Hours

500 Hours

VAPOR
PHASE

LIQUID/VAPOR
INTERFACE

LIQUID
PHASE

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

Figure D-11. Visual Appearances of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C.

0 Hours

250 Hours

VAPOR PHASE

LIQUID/VAPOR
INTERFACE

LIQUID PHASE

Figure D-12. 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

0 Hours

250 Hours

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

500 Hours

750 Hours

Figure D-14. Visual Appearance of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 361°C

LEGEND: Cb-3 - Cartech 20 Type CB-3
HG - Hastelloy G

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

0 HOURS

250 HOURS

VAPOR PHASE

LIQUID PHASE

VAPOR PHASE

LIQUID PHASE

Figure D-16. Visual Appearance of Samples Before and After Exposure to 90 w/o Sulfuric Acid at 452°C for 250 Hours

Figure D-17. Visual Appearances of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 452°C for 500 Hours

0 HOURS

750 HOURS

Figure D-18. Visual Appearances of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 452°C for 750 Hours

Figure D-19. Visual Appearances of Samples Before and After Exposure to 98 w/o Sulfuric Acid at 452°C for 1000 Hours

Figure D-20. Visual Appearance of Test Set 2 Samples Before and After Exposure to 98 w/w Sulfuric Acid at 452°C for 250 Hours (Vapor Phase Samples are the Larger Samples)

Figure D-21. Visual Appearance of Test Set 2 Samples Before and After Exposure to 98 w/o Sulfuric Acid at 452°C for 500 Hours (Vapor Phase Samples are Larger Samples on Left Side)

APPENDIX E

PTU SELECTION PROCESS DETAILS

NUMERICAL EVALUATION OF EACH CRITERION

The most difficult feature of the evaluation process is the conversion of comparative worth within a criterion into a numerical value. Optimally, this can be done by specifying a given quantifiable characteristic of the configuration under study which represents the whole of each criterion. If a single quantitative value cannot be defined, then a set of such values, each characteristic of one or more of fully representative dimensions or measures within each criterion, can be combined to give a characteristic value for that criterion, and for each candidate configuration. Unfortunately, even under these less restrictive conditions a strictly quantitative characterization of a configuration cannot be found in each criterion. Other means of obtaining valuation in each criterion configuration couple must be found. However, it is clear that each criterion must have measures defined within it so that the final result of judging the worth of a configuration is a numerical value. These values must be arrived at in a fashion which assigns the highest value to the configuration of the highest worth, if the evaluation is to be consistent. Hence, the definition of measures and valuations within each criterion must be attended to with this simple relationship in mind.

The following subsection defines the measures and valuation process used for each criterion.

CRITERION 1 - INHERENT DEGREE OF RISK

This criterion was selected to represent the degree of risk associated with a given PTU configuration in two distinct areas important to achieving the mission objectives. These areas are: integration of the sulfur cycle with a solar heat source, and development of the sulfur cycle itself. Risk is normally represented in terms of a probability/consequence couple, with well defined system designs permitting failure rate calculations for probability, and specified social/system

effects forming the basis of the consequence calculation. For a system such as the PTU, however, the lack of detailed design and operating experience precludes the use of such a risk measure. To deal with this type of criterion on developmental systems, AESD engineers developed certain methods rising a so-called Equipment Application Rating Matrix, which describes and classifies systems or individual pieces of equipment in terms of their developmental status. The matrix assigns equipment into four different development classifications as shown in Table A-1, and these classifications may be used as a rough estimate for the probability of failure of each piece of equipment. For the instant case, it may be assumed that failure of any one of the major components of a system results in a similar consequence for each PTU configuration considered, that is, failure of the entire PTU program. Thus, the risk is a function of the probability of failure, and may be evaluated numerically (i.e., on a relative basis) by comparing the relative development status of the major components in each candidate configuration, given an acceptable "mapping" of the alphabetic classifications into numerical values.

The specific method of application used for PTU evaluation is described below.

1. The list of major components for each candidate PTU configuration is drawn up. Specific equipment related to the solar heat source systems is included to permit an estimate of the total system failure rate.
2. The development status of each component is assigned by reference to the equipment application rating matrix.
3. The alphabetic status indicator is converted to a numerical value by use of the arbitrary mapping.

A = 10

B = 7

C = 4

D = 1

4. For each PTU configuration, the assigned values for all components are summed directly.
5. The resulting sum is normalized by division by the number $[10 \times (\text{total number of components considered})]$. This results in a value equal to or less than 1.0 for the Risk Criterion Value, designated C_{IN} for the N^{th} PTU configuration.

CRITERION 2 - INFORMATION PAYOFF

This criterion is defined to be a measure of how capable each PTU candidate configuration is expected to be in providing information in certain areas judged important to the development of solar-driven by hydrogen generation processes. It is anticipated that some configurations could provide more/better data than others. A true quantitative evaluation cannot be made, but a summary comparison/valuation method, based on fixed information areas, has been delineated.

The important information areas are the same for each configuration, and are

- Materials evaluation potential
- Catalyst evaluation potential
- Component design feature evaluation potential
- Sulfur cycle process characteristics evaluation potential
- Integrated system operational characteristics evaluation potential.

For the PTU evaluation process, an information area which cannot be addressed in a certain configuration is given a 0 valuation; for partial addressing capability, a 1/2 valuation is assigned. For an area which can be fully addressed, a 1 valuation is assigned. The total value for a configuration within this criterion is therefore arrived at in the following manner:

1. Appropriate values (0, 1/2, 1) for each area and each configuration are assigned, according to the scheme discussed above.
2. For each separate candidate configuration, all area values are summed.
3. The resulting sum is divided by 5 to normalize the final value, which is designated C_{2N} for the N^{th} candidate PTU configuration.

CRITERION 3 - EXPERIMENTAL FLEXIBILITY

This criterion was selected as part of the PTU evaluation scheme because of the necessity for providing some leeway in the system design for equipment or parameter changes, due to the current sketchy knowledge of the Sulfur Cycle operational characteristics. To date, all knowledge of cycle parameters has been based on theoretical considerations and/or bench scale or laboratory testing. A pilot-scale device which attempts to fully integrate the cycle and the solar heat

source may be expected to require some basic system or component changes (in sizing, process parameters, etc.) before it can perform satisfactorily. Therefore, flexibility is very important. Such flexibility also permits the evaluation of different types of unit operations modules, catalysts, etc., without major expense.

Several areas in which flexibility is desirable have been defined as measures within this criterion. These measures are individually valued 0, 1/2 or 1 if they can be: never provided for (0); partially provided for (1/2); or fully considered (1) in a given candidate configuration. The areas in question are:

- Reactor operating mode
- Reactor thermal power control
- Reactor temperature control
- Vaporizer thermal power control
- Electrolyzer acid concentration
- Reactor acid inlet concentration
- Thermochemical system pressure control
- Diurnal energy input simulation (or control) .

Evaluation of this criterion for a given PTU configuration is carried out in this manner:

1. Values 0, 1/2, 1 are assigned in each measure, as appropriate.
2. All values are summed.
3. Sum of all values is divided by 8 to normalize.

The normalized value for configuration N is called C_{3N} .

CRITERION 4 - PERFORMANCE POTENTIAL

This criterion can be virtually completely represented by a quantifiable (directly calculable) value characteristic of each candidate configuration - the efficiency. Depending upon the specific application of a solar - hydrogen system, one may wish to consider the overall thermal efficiency (if co-generation is proposed, for

example). However, for this PTU evaluation it was felt that a more appropriate measure would be the simple hydrogen production efficiency (HPE), defined as

$$\text{HPE} = \frac{\text{kW derivable from H}_2, \text{ HHV basis}}{\text{KW}_{\text{TOT}} \left(\text{thermal input} + \frac{\text{kWe}}{0.395} \right)} \times 100$$

The HPE for various candidate configurations does not vary widely, always being $\leq 40\%$. To normalize the HPE to C_{4N} , therefore, it was decided to divide each HPE by 40.

CRITERION 5 - SAFETY AND ENVIRONMENTAL ASPECTS

This criterion was selected because it is important to estimate how well each candidate configuration can be expected to do with respect to safety and environmental requirements. Critical areas (which are used as measurement bases within the criterion) were determined to be

- SO_2 emission control
- Acid mist control
- Public hazard level
- Occupational hazard level

Certain PTU candidate configurations provide at least the theoretical possibility of containing SO_2 and acid mist within a structure even if system rupture would occur - other configurations (which have collector - mounted thermal decomposition reactors) do not provide such a high level of emission control. Basic considerations such as these are evaluated here. A full safety evaluation is clearly beyond the scope or capability of this study.

For those safety/emission measures which can be fully provided for a configuration receives a 1; for those which can only be partially addressed by configuration design features, a 1/2 is assigned. The criterion evaluation is carried out as follows:

1. Assign values (1/2, 1) in each measure area
2. Sum all values for each configuration
3. Divide sum by 4 to normalize

For the Nth candidate configuration, the normalized sum in number 3 (above) is C_{5N} .

CRITERION 6 - CAPITAL COSTS

Even a summary evaluation of the costs associated with each PTU candidate configuration is difficult if these must be derived by making operations/materials tests and then costing on a per pound and per hour (or operation) basis. The detail available is insufficient to support such an effort. However, the results of previous costing studies for larger-scale solar-hydrogen systems can be used to evaluate costs on a relative basis, and get numerical values for use in the "figure-of-merit" for each configuration. A baseline PTU configuration will be defined, and have a relative relation of the three major subsystems associated with a Sulfur Cycle process system will be taken from a previous study which did get cost numbers. The reference study selected was the NASA Hydrogen Sulfur Study performed by Westinghouse in 1976.

The reference study showed that the following (very rough) breakdown for Sulfur Cycle process equipment was obtained;

Acid Heating & Vaporization Electrolyzer, Pumps, Tanks

comprised 60%

of total cost of system.

Decomposition Reactor - 25% of cost, including initial catalyst charge SO_2/O_2
Separation - 15% of cost.

(The costs of the solar heat source itself will not be considered, since it is being furnished by the government for the PTU development program.)

The following scaling laws are thought to apply:

- Costs of electrolyzer, pumps, etc., will scale linearly with acid mass flow ($\dot{M}_A$) in thermochemical section
- Costs of decomposition reactor scale linearly with volumetric flow out of reactor ($\dot{V}_A$).
- Costs of SO_2/O_2 separation equipment scale linearly as conversion ratio in reactor (CR).

Using these scaling laws, the definition of the baseline design configuration (Configuration "I"), and the relative costs of the major equipments raw numerical value of the criterion 6 measure can be thus defined for configuration "N"

$$\tilde{C}_{6N} = \frac{1.0}{0.6 \frac{\dot{M}_{AN}}{\dot{M}_{AI}} + 0.25 \frac{\dot{V}_{AN}}{\dot{V}_{AI}} + 0.15 \frac{CR_N}{CR_I}}$$

To normalize for use in the FOM, determine the highest raw value $\tilde{C}_{6H}$. Then

$$C_{6N} = \frac{\tilde{C}_{6N}}{\tilde{C}_{6H}} \quad \text{for} \quad \tilde{C}_{6H} > 1.0$$

or

$$C_{6N} = \tilde{C}_{6N} \quad \text{for} \quad \tilde{C}_{6H} \leq 1.0$$

C-2 DETAILED VALUATION OF C_{JN} 's

Calculation of C_{IN} 's

The calculation of the risk values is based upon the number of critical components in each configuration and their development status, as previously stated.

Configuration 1 - Reference System. Uses a single process pressure and a shell/u-tube evaporator.

<u>Critical Components</u>	<u>Dev. Status</u>	<u>Mapped Value</u>
Electrolyzer	C	4
Reduction Reactor (Indirect Solar Htg.)	C	4
Acid Preheater	B	7
Acid Vaporizer	C	4
Solar Heat Source Coupling	C	4
Total Value		23

$$C_{11} = \frac{23}{50} = 0.460$$

Configuration 2 - Single process pressure, direct contact vaporizer. Here a high temperature acid flow control subsystem is required.

<u>Critical Components</u>	<u>Dev. Status</u>	<u>Mapped Value</u>
Electrolyzer	C	4
Reduction Reactor	C	4
Direct Contact Evap. (Adiabatic Tower)	C	4
Vaporizer	C	4
High Temp. Acid Flow Control	D	1
Solar Heat Source Coupling	C	4
Total Value		21

$$C_{12} = \frac{21}{60} = 0.350$$

Configuration 3 - Dual process pressure, shell/u-tube evap.

There is no obvious difference between configurations 1 and 3 at this level of detail. Thus

$$C_{13} = C_{11} = 0.460 .$$

Configuration 4 - Dual process pressure, direct contact vaporizer.

$$C_{14} = C_{12} = 0.350 .$$

Configuration 5 - Direct solar heating of reduction reactor, single process pressure.

<u>Critical Components</u>	<u>Dev. Status</u>	<u>Mapped Value</u>
Electrolyzer	C	4
Decomp R _x (direct heating)	D	1
Acid Vaporizer	D	1
Acid Preheater	B	7
Acid Pumping	C	4
Solar Heat Source	D	1
Total Value		<u>18</u>

Normalized Value $C_{15} = \frac{18}{60} = 0.300$

In this configuration, medium-temperature acid pumping equipment is required to lift acid to tower. This has been developed and used in the past.

Configuration 6 - Direct solar heating, dual pressure

Same as Configuration 5 - $C_{16} = C_{15} = 0.300 .$

C_{2N} 's - INFO PAYOFF

- a) For metal evaluation, only the direct solar heating cases (5 & 6) limit choices. This is because metal for reactor and vaporizer must not only be good for holding hot pressurized acid, but must suffer rapid transients caused by direct radiation impinging on exterior.

b) Catalyst evaluation - no difference among cases.

c) Component design features

Vaporizer/reactor geometry for Configurations 5 & 6 constrained by requirement that radiation be collected for heating.

d) Sulfur Cycle process characteristics

For adiabatic tower cases (2 & 4) the requirement for pumps on high-concentration, high-temperature outlet of tower means a free choice of flows/pressures/temperatures cannot be made.

For direct solar heating cases, (5 & 6), the choice of flows/temperatures/reactor operating mode is constrained by collector design requirements. Since simulation of 85 kW solar collection is difficult, full range of sulfur cycle tests cannot be done.

e) Integrated system characteristics

Can't evaluate transient characteristics of entire system for direct solar heating on a controlled basis. Indirect coupling design permits use of combustion heater to drive process.

<u>Measure</u>	<u>Final Matrix</u>					
	<u>Configurations</u>					
	1	2	3	4	5	6
Materials Evaluation	1	1	1	1	1/2	1/2
Catalyst Evaluation	1	1	1	1	1	1
Component Design Evaluation	1	1	1	1	1/2	1/2
Sulfur Cycle Process Characteristics	1	1/2	1	1/2	1/2	1/2
Integrated System Characteristics	1	1	1	1	1/2	1/2
$C_{2N} =$						
	1	0.9	1	0.9	0.600	0.600

C_{3N} - EXPERIMENTAL FLEXIBILITY

<u>Measure</u>	<u>Configurations</u>					
	1	2	3	4	5	6
Reactor Operating Mode	1	1	1	1	1/2*	1/2*
Reactor Power Control	1	1	1	1	1/2**	1/2**
Reactor Temp. Control	1	1	1	1	1/2***	1/2***
Vaporizer Power Control	1	1	1	1	1/2***	1/2***
Acid Conc. In Electrolyzer	1	1	1	1	1	1
Acid Conc. in Reactor	1	1/2@	1	1/2@	1	1
Thermochem Sys. Press. Control	1	1	1	1	1	1
Diurnal Energy Input Control	1	1	1	1	1/2 ^x	1/2 ^x
C _{3N} =	1	0.94	1	0.94	0.69	0.69

* Control of adiabatic/isothermal modes not complete with direct heating option.

** Partial power control by shutters. May be limited in extent.

*** Depends on vaporizer design.

@ Function of adiabatic tower design and power level/flow.

x Artificial insolation facility for 85 kW input not (feasible) available.

C_{4N} - PERFORMANCE POTENTIAL

<u>Configuration</u>	<u>Calculated Efficiency</u>
1	36.7%
2	37.0%
3	38.0%
4	38.3%
5	36.7%
6	38.0%

$C_{41} = 36.7/40$	0.950	0.918
$C_{42} = 37/40$		0.925
$C_{43} = 38/40$		Not a very sensitive measure
$C_{44} = 38.3/40$		0.958
$C_{45} = 36.7/40$		0.918
$C_{46} = 38/40$		0.950

C_{5N} - SAFETY AND EMISSIONS CONTROL (ENVIRONMENTAL)

Measure	Configurations					
	1	2	3	4	5	6
SO ₂ Emissions	1	1	1	1	1/2*	1/2*
Acid Mist Emissions	1	1	1	1	1/2*	1/2*
Public Hazard Level	1	1	1	1	1/2**	1/2**
Occupational Hazard Level	1/2@	1/2@	1	1	1/2@	1
C_{5N}	0.875	0.875	1	1	0.500	0.625

- * SO₂ and acid mist emissions from failed reactor at foci of collectors.
- ** Liquid acid sprayed over large area if riser to reduction reactor fails.
- @ All piping at single high pressure. Dual-pressure systems have lower operating pressure in piping in certain areas.

C_{6N} - CAPITAL COSTS

Baseline plant: Configuration 1

$\dot{M}_{A1} = 380 \text{ lbm/hr}$	$CR_1 = 67.02\%$
$\dot{V}_{A1} = 12.9 \text{ holes/hr}$	$\tilde{C}_{61} = 1.0 \text{ by definition}$

<u>Configuration</u>	<u>M_{AN}</u>	<u>V_{AN}</u>	<u>CR_N</u>
1	380	12.9	67.02
2	355	7.0	60.80
3	360	24.7*	73.60
4	336	17.88*	66.00
5	380	12.9	67.02
6	360	25.80*	73.60

*Based on reduction reactor pressure of 10 atm.

$$\tilde{c}_{62} = 1.202$$

$$c_{61} = 0.832$$

$$\tilde{c}_{63} = 0.825$$

$$c_{62} = 1.000$$

$$\tilde{c}_{64} = 0.976$$

$$c_{63} = 0.686$$

$$\tilde{c}_{65} = 1.000$$

$$c_{64} = 0.812$$

$$\tilde{c}_{66} = 0.811$$

$$c_{65} = 0.832$$

$$c_{66} = 0.675$$

$$FOM = 0.225 (c_{1N} + c_{2N}) + 0.175 (c_{3N}) + 0.125 (c_{4N} + c_{5N} + c_{6N})$$

1	.460	1.000	1.000	0.918	0.875	0.832
2	.350	0.900	0.940	0.925	0.875	1.000
3	.460	1.000	1.000	0.950	1.000	0.686
4	.350	0.900	0.940	0.958	1.000	0.812
5	.300	0.600	0.690	0.918	0.500	0.832
6	.300	0.600	0.690	0.950	0.625	0.675

FINAL RANKING

1	0.832	2
2	0.796	3
3	0.833	1
4	0.792	4
5	0.605	6
6	0.605	6

tie

Since 1000's place means little, we can select either Configuration 1 or 3.
Configuration 1 was chosen as basis.

APPENDIX F

This appendix contains a detailed listing of each test series along with materials identification and test environment - Table F-1, tables of weight change data for each test series - Tables F-2 through F-20, and photographs of test samples "before" and "after" exposure - Figures F1 to F19.

TABLE F-1
REDUCTION REACTOR MATERIAL SAMPLES TESTED

TEST SERIES	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 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 Titanium Diboride
		RR 482HI5	Duro Acid-Proof Brick Duriron Vitreous Carbon Durichlor 51 Aluminum Silicate M-120 Inconel 617 Tungsten

TABLE F-1 (CONTINUED)
REDUCTION REACTOR MATERIAL SAMPLES TESTED

TEST SERIES.	TEST ENVIRONMENT	RUN IDENT.	MATERIALS TESTED
1.3	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	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 Stainless Steel 310
		RR 650H03	Sialon 80 Sialon 81 Sialon 88 Hastelloy C-276 Cartech Type 20Cb3 Tungsten
1.4	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	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

TABLE F-1 (CONTINUED)
REDUCTION REACTOR MATERIAL SAMPLES TESTED

TEST SERIES	TEST ENVIRONMENT	RUN IDENT.	MATERIALS TESTED
1.4	Furnace Temperature, °C - 871 80 w/o H ₂ SO ₄ Flow Rate, cc/min - 1.0 SO ₂ Flow Rate, scc/min - 0 O ₂ Flow Rate, scc/min - 0 Ar Flow Rate, scc/min - 0	RR871DI1	Carpenter Type 20 Cb3 Hastelloy C-276 SS 444 SS 316 Alonized SS 316 Alonized CS 1018
		RR 871DI2	SS 18-18-2 Inconel 617 Incoloy 825 Alonized Incoloy 825 Hastelloy G Alonized Hastelloy G
		RR 871DI3	IN 793 Alonized IN 793 Incoloy 800 Alonized Incoloy 800 Alonized Inconel 625 Alonized Inconel 671

TABLE F-1 (CONTINUED)

REDUCTION REACTOR MATERIAL SAMPLES TESTED

	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
		RR 871D01	Incoloy 825 Alonized Incoloy 825 Inconel 625 Alonized Inconel 625 Hastelloy G Alonized Hastelloy G
	Furnace Temperature, °C - 871 48.5 w/o H ₂ SO ₄ Flow Rate, cc/min - 0.5 SO ₂ Flow Rate, scc/min - 276 O ₂ Flow Rate, scc/min - 138 Ar Flow Rate, scc/min - 0	RR 871D02	Carpenter Type 20 Cb3 Inconel 617 IN 793 Alonized IN 793 Alonized SS 316 Alonized CS 1018
		RR 871D03	SS 444 Alonized SS 444 Incoloy 800 Alonized Incoloy 800 Inconel 671 Alonized Inconel 671

TABLE F-2

REDUCTION REACTOR MATERIALS SCREENING
TEST RESULTS IN ANHYDROUS ENVIRONMENT
(RUN RR 482A11)

SAMPLE	Δ Wt/Area, mg/cm ²					APPEARANCE AFTER 525 HRS
	115 hrs	212 hrs	308 hrs	425 hrs	525 hrs	
Hastelloy C-276	0.041	0.041	0.137	0.178	0.320	Black with white waxlike patches
Cartech Type 20 Cb-3	0.194	-0.111	-0.028	0.207	0.540	Black with white flaky corrosion
Incoloy 825	0.221	0.179	0.262	0.345	0.608	Reddish black with white patches
Inconel 625	0.096	0.124	0.179	0.248	0.262	Gray-black
SS 310	0.598	-0.667	-0.459	-0.334	0	Gray-black with red and white patches
SS 18-18-2	0.365	0.352	0.392	0.509	0.914	Gray-black
<u>CONDITIONS:</u> Furnace Temperature: 755°K SO₃ Flask Temperature: 326°K SO₃ Flow Rate: 11 SCC/min Argon Flow Rate: 130 SCC/min						

NOTE: Negative Values Indicate Weight Loss per Unit Area

TABLE F-3

REDUCTION REACTOR MATERIALS SCREENING
TEST RESULTS IN STEAM ENVIRONMENT
(RR 482H11)

SAMPLE	Δ Weight/Area, mg/cm ²										APPEARANCE AFTER 1007 HRS
	98 hrs	178 hrs	296 hrs	398 hrs	513 hrs	600 hrs	700 hrs	792 hrs	889 hrs	1007 hrs	
Hastelloy C-276	0.227	0.489	0.454	0.436	1.274	0.454	0.419	0.349	0.297	0.262	Whitish-blue on one side, rust hues on other side
Cartech Type 20 Cb-3	0.167	0.584	0.718	0.835	0.718	0.851	0.835	0.868	0.851	0.868	Black with blue hues
SS 18-18-2	0.220	0.744	1.014	1.150	0.896	0.879	0.845	0	0	-0.017	Black with yellow around edges
Inconel 625	0.069	0.347	0.313	0.313	0.278	0.330	0.313	0.208	0.174	0.174	Metallic with gray-blue patches
SS 310	0.515	0.961	1.304	1.475	1.338	1.527	1.527	1.492	1.492	1.492	Black with yellow around edges
Incoloy 825	0.181	0.593	0.742	0.841	0.758	0.709	0.692	0.676	0.709	0.840	Black metallic with rust hues and light blue patches
CONDITIONS: Furnace Temperature: 755°K SO₂ Flask Temperature: 326°K SO₂ 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 F-4
REDUCTION REACTOR MATERIALS SCREENING
TEST RESULTS IN STEAM ENVIRONMENT
RR 482HI2

SAMPLE	Δ Weight/Area, mg/cm ²										APPEARANCE AFTER 1000 HRS
	101 hrs	198 hrs	244 hrs	396 hrs	493 hrs	593 hrs	693 hrs	796 hrs	896 hrs	1000 hrs	
Macor	0.377	0.654	0.793	0.694	0.872	1.407	1.506	1.566	1.823	2.279	Tiny black spot visible on each side
Silicon	0.041	-0.020	0	0	-0.020	0	0	-0.020	-0.020	0	Like as received
Silicon Nitride	0	0	0	0.015	0.015	0.029	0.015	0.029	0.029	0.015	Tiny amount of white residue
Alonized Inconel 625	0.011	0.011	0.011	0.033	0.011	0.067	0.056	0.078	0.078	0.078	Brownish discoloration
Silicon Carbide	-0.014	-0.042	-0.014	0	0.014	0	0.014	0	0.028	-0.014	Tiny amount of white residue
Inconel 657	0.042	0	0.063	0.085	0.085	0.127	0.127	0.127	0.085	0.127	Black opal-like with blue and rust hues
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											

NOTE: Negative Values Indicate Weight Loss per Unit Area

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
 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 F-6

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
 SO₃ FLASK TEMPERATURE - 53°C
 SO₃ 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.

REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - 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 F-8
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.

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 F-10

REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - OUTLET CONDITIONS

RUN RR 650H03

SAMPLE	Δ WEIGHT/AREA, mg/cm ²								VISUAL APPEARANCE AFTER 1000 HOURS
	127 HOURS	216 HOURS	336 HOURS	497 HOURS	639 HOURS	777 HOURS	874 HOURS	1000 HOURS	
Tungsten - Powder, Sintered, Swaged	28.9	44.0	60.7	39.4	31.8	27.0	24.7	23.4	Green, Flaking
Sialon 88	.24	.24	.28	.42	.39	.33	.53	.29	Black
Carpenter Type 20 Cb3	.77	41.0	5.08	5.13	5.02	5.08	5.35	5.38	Black with White and Green Patches
Sialon 80	-.51	-1.40	-2.69	2.37	-3.61	-4.12	-5.16	-4.35	Gray with Black Spots
Sialon 81	-.17	-.88	-1.25	-1.39	-1.52	-2.01	-1.93	-2.29	Gray
Hastelloy C-276	1.03	1.53	3.75	5.68	3.97	3.78	4.15	2.75	Gray

TEST CONDITIONS:

NOTE: Negative values indicate weight loss per unit area.

Furnace Temperature - 871°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

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
Anonized 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 F-12

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 F-13

REDUCTION REACTOR SCREENING TEST RESULTS IN STEAM ENVIRONMENT - INLET CONDITIONS
RUN RR 871H13

SAMPLE	Δ WEIGHT/AREA, mg/cm ²									VISUAL APPEARANCE AFTER 1000 HOURS
	67 HOURS	108 HOURS	222 HOURS	312 HOURS	410 HOURS	546 HOURS	683 HOURS	826 HOURS	1000 HOURS	
Inconel 671	.73	.78	.81	.81	1.18	.75	.40	-.04	-.01	Black with green tint
Alonized Inconel 671	.53	.69	.73	.71	.73	.75	.79	.56	.72	Black with gray patches
Incoloy 800	.47	.72	.79	.80	4.13	1.71	1.50	.63	.24	Black with gray bumps
Alonized Incoloy 800	.21	.70	.97	1.12	1.05	.94	1.00	.71	.86	Brown

TEST CONDITIONS:

Furnace Temperature - 871°C

SO₃ Flask Temperature - 53°CSO₃ 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 F-14

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

SAMPLE	Δ WEIGHT/AREA, mg/cm ²										VISUAL APPEARANCE AFTER 1000 HOURS
	120 HOURS	164 HOURS	259 HOURS	360 HOURS	417 HOURS	529 HOURS	599 HOURS	741 HOURS	901 HOURS	1000 HOURS	
Incoloy 800	1.71	1.69	1.76	2.20	2.06	1.78	1.62	1.48	1.31	1.30	Rust- Black Corrosion
Alonized Incoloy 800	-.49	0	.13	.63	.47	.26	.88	.64	.75	.96	Brown Corrosion
Inconel 671	4.89	4.59	4.97	5.88	4.63	5.27	5.09	4.23	3.97	4.23	Green corrosion layer with white patches
Alonized Inconel 671	2.51	2.66	2.68	2.96	2.67	2.82	3.01	2.65	2.81	2.93	Gray-black

TEST CONDITIONS:NOTE: Negative values indicate weight loss per unit area.

Furnace Temperature - 871°C

SO₃ Flask Temperature - 53°CSO₃ Flow Rate - 25 scc/minSO₂ Flow Rate - 47 scc/minO₂ Flow Rate - 23 scc/min

Steam Flow Rate - 169 scc/min

TABLE F-15
REDUCTION REACTOR SULFURIC ACID DECOMPOSITION MATERIALS RESULTS - INLET CONDITIONS
RUN RR 871DI1

SAMPLE	Δ WEIGHT/AREA, mg/cm ²										VISUAL APPEARANCE AFTER 1000 HOURS
	53 Hours	153 Hours	252 Hours	337 Hours	436 Hours	536 Hours	633 Hours	791 Hours	912 Hours	1000 Hours	
SS 316	2.17	0.38	-2.20	-1.65	-17.4	-28.6	-37.6	-50.3	-57.9	-63.4	Black, flaking
Carpenter Type 20Cb3	0.73	0.29	0.06	0.79	2.27	0.70	0.19	- 0.43	- 0.77	- 1.32	Black with white on edges.
Alonized CS 1018	1.75	1.75	2.39	4.08	4.56	3.58	3.48	3.42	3.30	3.34	Rust-Brown
Alonized SS 316	0.10	1.26	1.23	3.15	3.50	2.45	2.46	2.45	2.45	2.40	Rust-Brown
444	-.15	1.00	0.77	2.16	2.15	2.14	2.05	1.96	1.73	1.73	Black with white and rust patches on edges.
Hastelloy C-276	0.28	-0.27	-0.61	-1.45	-5.04	-7.94	-10.1	-21.0	-36.8	-62.5	Black-Brown, flaking.

TEST CONDITIONS:

Furnace Temperature - 871°C
80 w/o H₂SO₄ Flow Rate - 0.5 cc/min

NOTE: Negative values indicate weight loss per unit area.

TABLE F-16

REDUCTION REACTOR SULFURIC ACID DECOMPOSITION MATERIALS TEST RESULTS - INLET CONDITIONS
 RUN RR 871DI2

SAMPLE	Δ WEIGHT/AREA, mg/cm ²							VISUAL APPEARANCE AFTER 1000 HOURS
	53 Hours	224 Hours	362 Hours	530 Hours	668 Hours	814 Hours	1000 Hours	
Alonized Hastelloy G	0.11	0.49	0.36	0.51	0.71	0.69	0.66	Black
Hastelloy G	-0.47	-0.62	-1.72	-2.43	-2.71	-3.51	-6.28	Black, Flaking Edges
Inconel 617	0.29	0.73	-1.30	0.78	-0.99	0.43	0.54	Gray
18-18-2	0.17	-1.22	-7.89	-13.9	-22.9	-33.2	-37.8	Black, Spalling
Incoloy 825	0.14	-1.07	-2.06	-3.34	-4.30	-5.19	-6.66	Black
Alonized Incoloy 825	0.02	0.53	0.46	0.54	0.70	0.70	0.68	Black

TEST CONDITIONS: Furnace Temperature - 871°C
 80 w/o H₂SO₄ Flow Rate - 0.5 cc/min

NOTE: Negative values indicate weight loss per unit area.

TABLE F-17
REDUCTION REACTOR SULFURIC ACID DECOMPOSITION MATERIALS TEST RESULTS - INLET CONDITIONS
RUN RR 871DI3

<u>SAMPLE</u>	<u>Δ WEIGHT/AREA, mg/cm²</u>							<u>VISUAL APPEARANCE AFTER 1000 HOURS</u>
	<u>146 Hours</u>	<u>316 Hours</u>	<u>485 Hours</u>	<u>606 Hours</u>	<u>753 Hours</u>	<u>877 Hours</u>	<u>1000 Hours</u>	
Alonized IN 793	0.62	0.64	0.83	0.70	0.62	0.72	0.88	Brown, Rust Spot
Alonized Inconel 625	0.77	0.69	0.69	0.58	0.38	0.48	0.64	Black, White Edges
IN 793	-0.38	-0.53	-0.46	-1.42	-2.17	-2.46	-2.96	Black, Brown Spot
Incoloy 800	0.55	-0.20	-1.21	-3.17	-3.77	-6.19	-7.75	Black
Alonized Incoloy 800	0.42	0.44	0.61	0.63	0.49	0.58	0.73	Gray - Black
Alonized Inconel 671	3.50	2.84	2.16	1.62	0.28	-0.72	-1.29	Green with Black Edges and Spots

TEST CONDITIONS: Furnace Temperature - 871°C
80 w/o H₂SO₄ Flow Rate - 0.5 cc/min

NOTE: Negative values indicate weight loss per unit area.

TABLE F-18
REDUCTION REACTOR SULFURIC ACID DECOMPOSITION MATERIALS TEST RESULTS - OUTLET CONDITIONS
RUN RR 871D01

SAMPLE	Δ WEIGHT/AREA, mg/cm ²								VISUAL APPEARANCE AFTER 1000 HOURS
	51 Hours	221 Hours	344 Hours	497 Hours	656 Hours	801 Hours	900 Hours	1000 Hours	
Alonized Incoloy 825	0.44	0.51	0.72	0.87	0.97	0.86	0.90	0.71	Brown
Inconel 625	-0.46	-1.44	-1.69	-1.53	-1.93	-2.59	-3.01	-3.72	Black with Brown Edges
Hastelloy G	0.09	-0.90	-1.11	-0.74	-1.09	-2.18	-2.62	-3.24	Black
Incoloy 825	-0.01	-0.67	-1.07	-1.63	-1.38	-2.30	-1.65	-2.04	Black
Alonized Inconel 625	1.13	1.00	1.23	0.73	0.29	0.09	0.10	-0.03	Flaking Green
Alonized Hastelloy G	0.42	0.37	0.70	0.35	0.31	0.07	0.17	-0.09	Brown

TEST CONDITIONS: Furnace Temperature - 871°C
48.5 w/o H₂SO₄ Flow Rate - 1.0 cc/min
SO₂ Flow Rate - 276 cc/min
O₂ Flow Rate - 138 cc/min

NOTE Negative values indicate weight loss per unit area.

TABLE F-19
REDUCTION REACTOR SULFURIC ACID DECOMPOSITION MATERIALS TEST RESULTS - OUTLET CONDITIONS
RUN RR 871D02

<u>SAMPLE</u>	<u>101 Hours</u>	<u>393 Hours</u>	<u>516 Hours</u>	<u>665 Hours</u>	<u>837 Hours</u>	<u>1000 Hours</u>	<u>VISUAL APPEARANCE AFTER 1000 HOURS</u>
IN 793	0.20	0.40	0.08	-0.40	-0.74	-1.20	Gray - Black
Carpenter Type 20 Cb3	0.46	-0.66	-0.93	-1.26	-1.35	-1.59	Black
Alonized SS 316	2.35	5.55	5.69	5.67	5.95	5.94	Gray, Brown Edges
Alonized CS 1018 Sample #1	69.0	219. ^a	-	-	-	-	^a Black, Badly Corroded
Alonized CS 1018 Sample #2	-	3.07	3.96	4.30	4.73	4.89	^b Gray, Rust on One Corner
Alonized IN 793	0.29	0.81	0.85	0.68	0.80	0.71	Black, Gray Patches
Inconel 617	0.75	-1.00	-1.63	-2.40	-2.63	-3.89	Green

TEST CONDITIONS: Furnace Temperature - 871°C
48.5 w/o H₂SO₄ Flow Rate - 1.0 cc/min
SO₂ Flow Rate - 276 scc/min
O₂ Flow Rate - 138 scc/min

NOTES: Negative values indicate weight loss per unit area.

^aSample #1 of Alonized CS 1018 was taken out of test after 169 hours exposure.

^bSample #2 of Alonized CS 1018 began after other samples were tested for 169 hours.
Therefore, subtract 169 hours from column values to get exposure times for Sample #2
of Alonized CS 1018.

TABLE F-20

REDUCTION REACTOR SULFURIC ACID DECOMPOSITION MATERIALS TEST RESULTS - OUTLET CONDITIONS
 RUN RR 871D03

<u>SAMPLE</u>	<u>98 Hours</u>	<u>247 Hours</u>	<u>389 Hours</u>	<u>533 Hours</u>	<u>680 Hours</u>	<u>817 Hours</u>	<u>1000 Hours</u>	<u>VISUAL APPEARANCE AFTER 1000 HOURS</u>
Alonized SS 444	0.90	1.58	2.04	2.56	3.03	3.34	3.72	Gray-Brown Edges White Haze on Sides
SS 444	0.47	2.19	3.20	4.49	4.39	4.25	4.12	Gray, Minor Spalling
Alonized Inconel 671	2.68	1.35	-0.18	-1.27	-2.07	-2.92	-3.29	Gray, Green Patches, Spalling
Alonized Incoloy 800	0.40	0.55	0.70	0.70	0.70	0.68	0.73	Brown
Inconel 671	-0.26	-2.87	-4.19	-5.57	-6.88	-8.15	-9.68	Gray, Green Edges
Incoloy 800	0.22	0.57	0.43	0.53	0.29	-0.09	-0.33	Black, Minor Spalling

TEST CONDITIONS: Furnace Temperature - 871°C
 48.5 w/o H₂SO₄ Flow Rate - 1.0 cc/min
 SO₂ Flow Rate - 276 scc/min
 O₂ Flow Rate - 138 scc/min

NOTE: Negative values indicate weight loss per unit area.

BEFORE

AFTER

Figure F-1 Materials Samples Before and After RR 482AI1

BEFORE

AFTER

Figure F-2. Materials Samples Before and After Run RR 482HI1

BEFORE

0 Hours

AFTER

1000 Hours

Figure F-3. Materials Samples Before and After Run RR 482HI2

0 HOURS

EXPOSURE CONDITIONS:

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

1000 HOURS

LEGEND:

HASTELLOY G - HASTELLOY G
 1018 - CARBON STEEL 1018
 1018A - ALONIZED CARBON STEEL 1018
 316 - STAINLESS STEEL 316
 316A - ALONIZED STAINLESS STEEL 316
 TA - ELECTROCHEMICALLY PREANODIZED TANTALUM

0 Hours

TEST CONDITIONS:

FURNACE TEMPERATURE - 482°C
 SO₂ 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 F-5. Visual Appearance of Samples in Run RR 482HI4

0 Hours

TEST CONDITIONS:

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

RR 482HI5

VITREOUS
CARBON

INC 617

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

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

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 F-7. 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
 Al_2O_3 - 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 82)
 (425 Hours for Stainless Steel 310)

TEST CONDITIONS:

FURNACE TEMPERATURE - $650^{\circ}C$
 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

0 HOURS

1000 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 F-9. Visual Appearance of Samples in Run RR 650H03

RUN RR871HI1

RUN RR871HI1

0 Hours

1000 Hours

TEST CONDITIONS:

FURNACE TEMPERATURE - 871°C
 SO₂ 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

Figure F-10. Visual Appearance of Samples in Run RR 871HI1

0 Hours

1000 Hours

TEST CONDITIONS:

FURNACE TEMPERATURE	-	871°C
SO ₃ FLOW RATE	-	25 scc/min
STEAM FLOW RATE	-	58 scc/min
ARGON FLOW RATE	-	78 scc/min

Figure F-11. Visual Appearance of Samples in Run RR 871HI2

TEST CONDITIONS:

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

Figure F-12. Visual Appearance of Samples in Run RR 871HI3

TEST CONDITIONS:

FURNACE TEMPERATURE - 871°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 F-13. Visual Appearance of Samples in Run RR 871H01

TEST CONDITIONS:

FURNACE TEMPERATURE - 871°C
 80 w/o SULFURIC ACID FLOW RATE - 0.5 cc/min

LEGEND:

316 - STAINLESS STEEL 316
 AL 1018 - ALONIZED CARBON STEEL 1018
 444 - 18Cr-2Mo FERRITIC STAINLESS STEEL, TYPE 444
 CB3 - CARPENTER TYPE 20Cb3
 AL 316 - ALONIZED STAINLESS STEEL 316
 C276 - HASTELLOY C276

Figure F-14. Visual Appearance of Samples in Run RR 871DI1

RR 871DI2

INCOLOY 825

ALONIZED
INCOLOY 825

HASTELLOY G

ALONIZED
HASTELLOY G

INCONEL 617

18-18-2

INCOLOY 825

ALONIZED
INCOLOY 825

HASTELLOY G

ALONIZED
HASTELLOY G

INCONEL 617

18-18-2

0 HOURS

362 HOURS

TEST CONDITIONS:

FURNACE TEMPERATURE - 871°C
80 w/o SULFURIC ACID FLOW RATE - 0.5 cc/min

Figure F-15. Visual Appearance of Samples in Run RR 871DI2

TEST CONDITIONS:

FURNACE TEMPERATURE - 871°C
80 w/o SULFURIC ACID FLOW RATE - 0.5 cc/min

Figure F-16. Visual Appearance of Samples in Run RR 871DI3
(Samples designated Al were Alonized)

RR 871D01

INCOLOY 825

INCONEL 625

HASTELLOY G

ALONIZED
INCOLOY 825 ALONIZED
INCONEL 625 ALONIZED
HASTELLOY G

0 HOURS

RK 871D01

INCOLOY 825

INCONEL 625

HASTELLOY G

ALONIZED
INCOLOY 825 ALONIZED
INCONEL 625 ALONIZED
HASTELLOY G

497 HOURS

TEST CONDITIONS:

FURNACE TEMPERATURE	- 871°C
48.5 w/o SULFURIC ACID FLOW RATE	- 1.0 cc/min
SO ₂ FLOW RATE	- 276 scc/min
O ₂ FLOW RATE	- 138 scc/min

Figure F-17. Visual Appearance of Samples in Run RR 871D01

TEST CONDITIONS:

FURNACE TEMPERATURE - 871°C
 48.5 w/o SULFURIC ACID FLOW RATE - 1.0 cc/min
 SO₂ FLOW RATE - 276 scc/min
 O₂ FLOW RATE - 138 scc/min

LEGEND:

In 793 - IN 793
 C20 Cb3 - CARPENTER TYPE 20 Cb3
 A1 SS 316 - ALONIZED STAINLESS STEEL 316
 A1 CS 1018 - ALONIZED CARBON STEEL 1018
 A1 In 793 - ALONIZED IN 793
 In - INCONEL 617

Figure F-18. Visual Appearance of Samples in Run RR 871D02

RR 871D03

RR 871D03

ALONIZED
INCOLOY 800

ALONIZED
INCONEL 671

ALONIZED
INCOLOY 800

ALONIZED
INCONEL 671

INCONEL 671

INCOLOY 800

INCONEL 671

INCOLOY 800

SS 444

ALONIZED
SS 444

SS 444

ALONIZED
SS 444

0 HOURS

1000 HOURS

TEST CONDITIONS:

FURNACE TEMPERATURE	- 871°C
48.5 w/o SULFURIC ACID FLOW RATE	- 1.0 cc/min
SO ₂ FLOW RATE	- 276 scc/min
O ₂ FLOW RATE	- 138 scc/min

Figure F-19. Visual Appearance of Samples in Run RR 871D03