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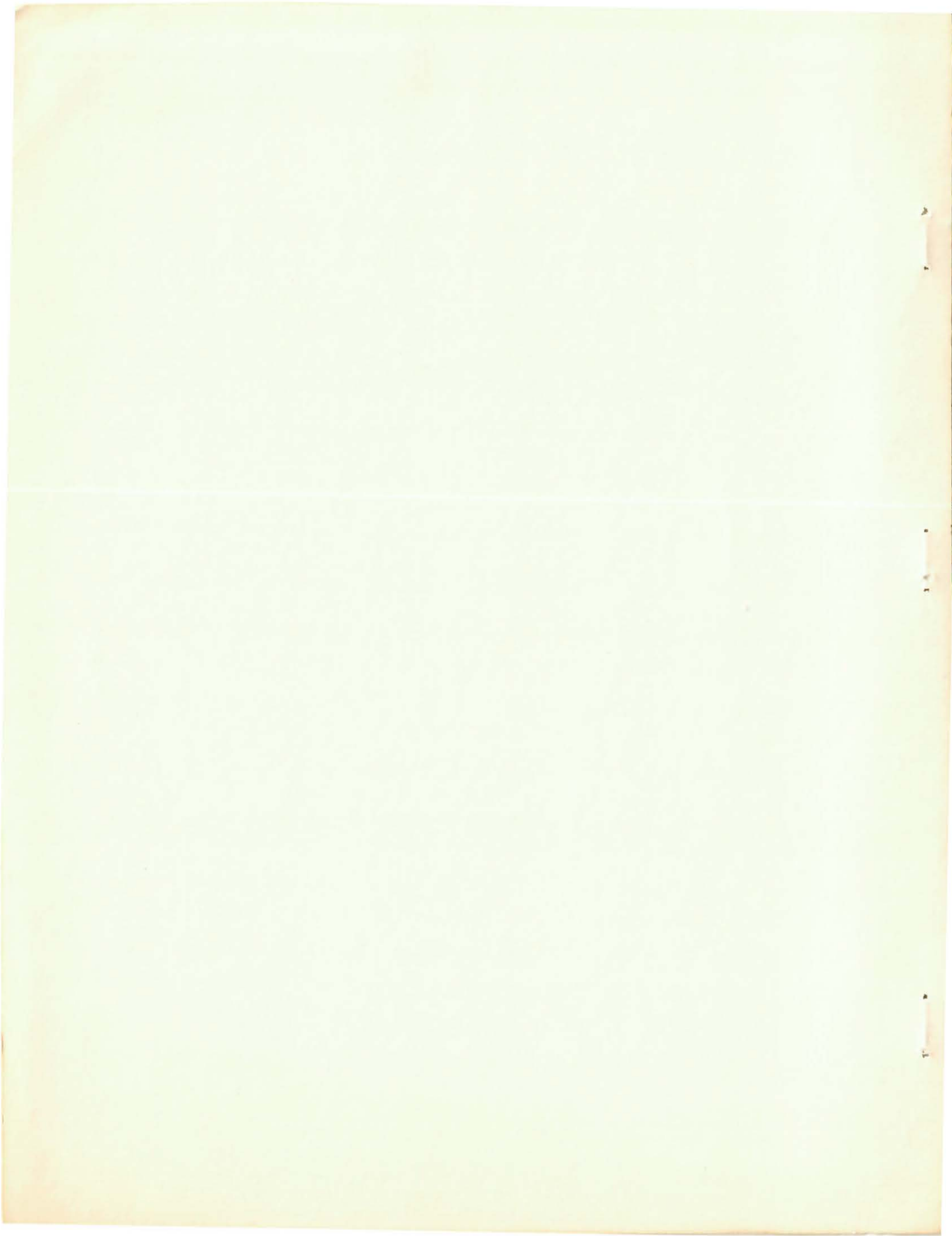
Chemical Energy Transport for Distributed Solar Thermal Electric Conversion

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Printed February 1982

CHEMICAL ENERGY TRANSPORT
FOR
DISTRIBUTED SOLAR THERMAL ELECTRIC CONVERSION

Final Report

RRC 81-R-782

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Under Contract No. 18-2563

July 17, 1981

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ACKNOWLEDGEMENT

ABSTRACT

This study examined the suitability of using reversible chemical reactions to transport energy, via an articulated pipe network, from distributed parabolic dish solar concentrators to a central power generation plant. Of the 85 chemical reactions initially screened, the reversible oxidation of sulfur dioxide (SO_2/SO_3), and the CO_2 reforming of methane were identified as most promising for distributed solar applications. A preliminary process design of a chemical energy transport subsystem based on the SO_2/SO_3 reaction produced a first-law, transport efficiency estimate of 77 percent. Second law considerations reduced this to 62 percent. The SO_2/SO_3 energy transport subsystem capital cost was estimated to be between $160 and $200 per square meter of collector area, which corresponds to $400-490 per $KW_{thermal}$ delivered directly to the power cycle.

1.0 INTRODUCTION

It has been proposed by Chubb (Reference 1, 2) and Carden (Reference 3) to use reversible chemical reactions to transport energy from distributed solar concentrators to central power generation facilities in medium and large scale Solar Thermal Electric Conversion (STEC) facilities. Prior to the work reported herein, under Contract No. 18-2563 to Sandia Laboratories, Livermore (SLL), Rocket Research Company (RRC) carried out a detailed evaluation of the prospects for the use of reversible chemical reactions to store high quality energy at STEC facilities (Reference 4). As an extension of that contract, RRC has carried out a preliminary evaluation of using reversible chemical reactions for energy transport in distributed solar facilities, and this report presents the results of that evaluation.

Background

Presently there are two general types of STEC configurations, central receiver and distributed, being considered by the United States Department of Energy. In the central receiver configuration, sunlight is reflected from a field of accurately aligned concentrators (heliostats) to a receiver placed atop a centrally located tower. In the receiver, the focused sunlight from the entire field of heliostats is converted to thermal energy, and transported by a heat transfer or working fluid to turbomachinery located at the base of the tower for electric power generation.

As in the central receiver configuration, the reflecting surfaces in the distributed configuration consist of an array of individual, tracking concentrators. In contrast to the central receiver systems, in which the heliostats are all focused on the receiver atop the central tower, each concentrator in distributed systems is focused on its own receiver, mounted on the same support as the concentrator. Thermal energy may then be converted to electrical energy by means of a thermal engine attached to each receiver, or, as in the cases considered here, it may be transported by means of some fluid in a pipe network, to a centrally located thermal power plant. The distributed concentrators may be point-focusing paraboloidal dishes, line-focusing parabolic troughs, or some variation of these basic types. Paraboloidal dish concentrators which are controlled by two-axis tracking systems generally develop the highest temperatures of all the distributed collector types, and are therefore the prime candidates for distributed solar thermal electric power

generation. The analysis described in this report is therefore based on the use of such concentrators.

Energy may be transported from the distributed receivers to the central power plant by means of the sensible, latent, or chemical energy contained in various transport fluids. Energy transport by sensible or latent heat is conceptually straightforward. For example, water under pressure could be heated in distributed receivers and then transported via insulated pipes to a centrally located thermal power plant. Cool water from the central facility would then be returned by pipeline to the receivers for another cycle. A substantial portion of the cost of such a solar facility would be due to the required pipe network, and reductions in the cost of this network by reducing the temperature (less insulation), pressure (thinner pipe walls) or mass flow rate (smaller diameter pipe), would be desirable. Also desirable would be an increase in the efficiency of the energy transport subsystem, since it would allow a reduction in the costly concentrator area required per unit of energy output. Improvements in these two items, transport system cost and efficiency (which are of course related), are the main reasons that energy transport by reversible chemical reaction, or Chemical Energy Transport (CET), was suggested for distributed solar applications.

Chemical Energy Transport

Figure 1-1 is a schematic representation of a distributed solar power plant with chemical energy transport. Concentrated sunlight, converted to thermal energy, would be used to drive a reversible chemical reaction in the endothermic direction. For example, the reversible reaction, $SO_2 + \frac{1}{2} O_2 = SO_3$, would be driven to the left (production of SO_2 and O_2) by the input of high temperature (say 1,200 K) thermal energy. After the hot reaction products had been cooled by indirect contact with incoming reactants in a recuperator, they would be transported by pipeline to the centrally located exothermic reactor. After the reactants were raised to reaction temperature, the reaction would proceed exothermically (production of SO_3 by recombination of SO_2 and O_2), providing heat for electric power generation by a thermal power cycle. In both the endothermic and exothermic directions, the reactions considered promising for CET applications would require catalysts, so that both endothermic and exothermic reaction would occur only in the reactors, and not at undesirable intermediate points in the transport network.

In practice, the endothermic reactors and associated recuperators would be combined into single units (Reactor/Heat Exchanger, or RHX) mounted at the focal points of the

SCHEMATIC REPRESENTATION OF CHEMICAL ENERGY TRANSPORT
APPLIED TO SOLAR THERMAL ELECTRIC CONVERSION

$$SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$$

$$SO_3 \rightleftharpoons SO_2 + 1/2\ O_2$$

RECUPERATOR

ELECTRIC POWER ← **CENTRAL POWER GENERATION** ← **CENTRAL EXOTHERMIC REACTOR** → → **ENDO-THERMIC REACTOR** ← **CONCENTRATED SOLAR ENERGY**

THERMAL ENERGY

COMPRESSOR

PIPING NETWORK

RECUPERATOR

CONCENTRATOR FIELD LAYOUT

CENTRAL PLANT

INDIVIDUAL CONCENTRATORS

SUNLIGHT

REACTOR/HEAT EXCHANGER

FLUID TRANSPORT LINES

PARABOLIC CONCENTRATOR

SUPPORT STRUCTURE W/TWO-AXIS TRACKING

Figure 1-1

parabolic concentrators. The concentrators would be arranged in a "field" as shown in Figure 1-1, connected to the field's pipe network by pipes called "risers" and "downcomers". The supply and return pipelines would be laid above ground for economy, and insulated to a greater or lesser extent depending on the transport reaction and specific design considerations.

The thermal power cycle used in the central power plant could be a Brayton or a Rankine cycle, depending (among other things) on the maximum exothermic reaction temperature. Previous work (Reference 4) has indicated that the efficiency of chemical cycles suffers greatly when the exothermic and endothermic reaction temperatures are approximately equal. Since a maximum receiver wall temperature of about 1,400 K is achievable with the concentrators and materials considered here, the necessarily lower exothermic reaction temperatures make a steam Rankine cycle the logical choice, and that cycle was used in the preliminary design study described in Chapter 3.

Study Goals

The overall purpose of the study described here was to examine both technical and economic aspects of chemical energy transport as applied to distributed solar power generation. Key specific goals included:

1. Identification of suitable chemical reactions for CET application.

2. Estimation of thermal efficiency and capital cost of an example CET subsystem.

3. Identification of potential technical difficulties associated with the most promising CET reactions.

Study Approach

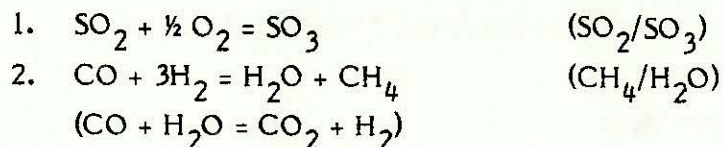The study comprised three main parts:

1. System definition

2. Reaction screening

3. Preliminary CET system design and analysis

The approaches taken for the above segments of the study are described briefly below. In addition, the reaction screening and preliminary design segments are described in more detail in Chapters 2 and 3, respectively.

System Definition -- Due to the limited scope of the study, it was necessary to restrict the reaction screening and preliminary design portions of the project such that they would be pertinent to a specific distributed STEC application. This specific application, or base case, was defined during the early stages of the study. The cost and performance constraints were chosen after a search of pertinent literature and personal communication with investigators familiar with the on-going distributed solar development effort. The baseline system definition is summarized in Table 1-1. While there are certainly other viable configurations for distributed STEC, the one described in Table 1-1 was judged to be representative of program direction at the time the study was begun.

Chemical Reaction Screening -- The starting point for the reaction screening was a list of 85 chemical reactions identified during the study of chemical energy storage (Reference 4, p. 3-8). These 85 reactions were reduced to 19 primarily by eliminating those with constituents which would form solids at temperatures between ambient and the estimated endothermic reaction temperatures.

The intermediate reaction screening considered such reaction characteristics as reversibility, toxicity, corrosivity, and flammability. This intermediate screening reduced the 19 candidate reactions to two:

$$1. \quad SO_2 + \tfrac{1}{2}O_2 = SO_3 \qquad\qquad (SO_2/SO_3)$$
$$2. \quad CO + 3H_2 = H_2O + CH_4 \qquad (CH_4/H_2O)$$
$$(CO + H_2O = CO_2 + H_2)$$

The water gas shift reaction is included parenthetically with the CH_4/H_2O reaction, since the two are inseparable and occur simultaneously. The ammonia synthesis reaction, $N_2 + 3H_2 = 2NH_3$, was initially included with the two above as one of the three most promising reactions. It was eliminated, however, when process engineering difficulties (primarily extremely high pressures), were considered.

The choice between the final two reactions for subsequent preliminary process design work was a difficult one. One variation of the second reaction shows promise: the CO_2 reforming of methane, or,

$$CO_2 + CH_4 = 2H_2 + 2CO. \qquad (CH_4/CO_2)$$

Table 1-1

BASELINE DISTRIBUTED SOLAR THERMAL ELECTRIC SYSTEM DEFINITION

- Maximum Receiver Cavity Wall Temperature .... 1,400 K

- Power Cycle - Steam Rankine

- Minimum Steam Turbine Inlet Temperature .... 800 K

- Minimum Steam Turbine Inlet Pressure .... 68 bar

- Power Cycle Return Temperature (Boiler Feedwater) .... 526 K

- Power Cycle Efficiency, $kW_e/kW_{thermal}$ 0.333

- Nominal System Peak Power Output .... 10 MW$_e$

- Parabolic Dish Concentrators (two-axis tracking)

  - Diameter .... 11 m

  - Nominal Thermal Input Per Concentrator .... 50 kW

- Endothermic Receiver/Reactor/Heat Exchanger Mounted at Concentrator

  - Maximum Mass .... 1,300 kg

- No Energy Storge

- Reticulated Piping Layout After Caputo (Reference 5)

  - Number of Concentrators 720

  - Minimum Ambient Temperature .... 283 K

This reaction has been proposed by Chubb (Reference 6) for CET applications, and does offer several potential advantages over the SO_2/SO_3 reaction (e.g., fewer corrosion problems, no condensation problem). However, the CH_4/CO_2 reaction may result in two serious problems: 1) the possibility of carbon deposition or coking in reactors during unavoidable thermal transients, and 2) the possibility of iron or nickel carbonyl formation and subsequent catalyst migration. These potentially very serious problems resulted in the choice of the SO_2/SO_3 reaction for further evaluation. This choice should not be construed as an outright rejection of the carbon-based reaction system. A reliable comparison of the two reactions will require preliminary process design work and some bench or pilot scale experimental work for both. The choice of the single SO_2/SO_3 reaction for further study was due to the limited scope of the project.

Preliminary CET Process Design -- A preliminary process design for a CET system was developed, which was based on the SO_2/SO_3 reaction, and which conformed to the performance constraints listed in Table 1-1. The design considered the major components of such a CET system, including:

1. The endothermic reactor/heat exchangers (RHX) to be mounted at the focal points of the concentrators.

2. The piping network connecting the individual receivers to a central exothermic reactor.

3. The exothermic reactor (and recuperator) which generates superheated steam for power generation by steam turbine.

4. The centrifugal compressor required to circulate the fluid reactants.

Temperatures, pressures, and compositions of key process streams were estimated, and the above major process components were sized. From purchase or fabrication cost estimates of these major components, an estimate of the total installed cost of the CET subsystem was generated by a factored cost estimation technique. Finally the thermal efficiency of the SO_2/SO_3 CET subsystem was estimated from the preliminary process design.

The piping network represents a costly and little studied aspect of chemical energy transport subsystems for solar thermal applications. Optimization of such networks is a complex problem, whether the energy transport is to be carried out by means of a reversible chemical reaction, or the sensible or latent heat of a transport fluid such as water/steam. Such an optimization was beyond the scope of the present work, but is

fundamental to a realistic examination of chemical energy transport in this application. Under contract to the Department of Energy, the Pacific Northwest Laboratory of the Battelle Memorial Institute has developed ETRANS, an optimization code for the piping networks associated with sensible and latent heat transport systems for distributed solar facilities. Although ETRANS was not written originally to model chemical energy transport networks, workers at Battelle Northwest were able to adapt ETRANS to this purpose for a short series of runs to examine pressure drop, heat loss, and cost of the piping network in a distributed solar facility with chemical energy transport by the SO_2/SO_3 reaction. The results of these runs are summarized in section 3.2.3.

Finally, it should be emphasized that the study described here was intended as a preliminary evaluation of the prospects for chemical energy transport in distributed solar applications. The scope of the study required much idealization of the systems considered. Perhaps most importantly, the distributed solar case examined here had no storage capability. While actual solar installations for power generation will probably have some storage capability, inclusion of appreciable storage capacity complicates the design and optimization of solar facilities (Reference 4), in this case unnecessarily. The most likely candidates at present for energy storage in solar thermal facilities are sensible storage systems using high temperature oils or molten salts. Chemical energy storage systems, which might interface quite easily with a chemical energy transport system based on the same reaction, are not yet attractive in such applications (again, see Reference 4). The idealized distributed solar configuration used in this study provides an adequate basis for preliminary evaluation of chemical energy transport and comparison of this type of energy transport with other types such as sensible or latent heat systems. However, considerable care should be exercised in using the performance and (especially) cost estimates reported here for chemical energy transport in systems studies of less idealized (e.g., with storage) distributed solar facilities.

2.0 CHEMICAL REACTION SURVEY

The goal of the reaction screening process described in this chapter was to identify a small number of the most promising chemical reactions for CET applications, and from that group to select one reaction for a preliminary process design study of a CET subsystem. The preliminary screening reduced the original list of 85 reactions to one of 19, which was itself reduced to the two most promising reactions by the intermediate screening.

Sections 2.1 and 2.2 below describe the preliminary and intermediate screening processes, and section 2.3 presents a comparison of the two remaining reactions: the reversible oxidation of SO_2, and the CO_2 reforming of methane.

2.1 PRELIMINARY REACTION SCREENING

The starting point for the search for chemical reactions suitable for CET was the list of 85 reactions identified during the search for suitable chemical energy storage reactions carried out at the beginning of the NSF contract (Reference 4). This list is reproduced in Table 2-1. The "rank" and "rating" columns in this table pertain to suitability for energy storage applications and are therefore of no concern here.

The preliminary screening essentially eliminated all those reactions in Table 2-1 for which one or more of the reactants would exist as a solid at the lowest temperature the transport system would be expected to experience (273-283 K). The resulting list of 19 reactions is presented in Table 2-2.
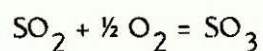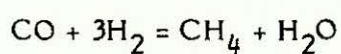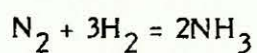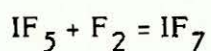
2.2 INTERMEDIATE REACTION SCREENING

The starting point of the intermediate reaction screening was the list of reactions in Table 2-2. Each reaction on this list was briefly evaluated by a team of RRC chemists and chemical engineers. Much of the evaluation was simply application of professional judgment rather than systematic ranking of reactions on some quantitative basis. The reactions which were rejected for CET applications are listed below, along with brief explanations for their rejection. During the screening process, the RRC team made use of information gathered on many of these reactions in the early stages of the CES study contract (Reference 4).

Table 2-1
CANDIDATE REACTIONS FOR CHEMICAL ENERGY STORAGE/TRANSPORT

| Rank	Rating	Reaction	Rank	Rating	Reaction
1	9.010	$CaO + H_2O = Ca(OH)_2$	44	0.978	$NH_3 + HI = NH_4I$
2	8.357	$Li_2O + SO_3 = Li_2SO_4$	45	0.940	$CH_4 + 2Li_2C_2 = 4LiH + 5C$
3	7.474	$K_2O + 3/2 O_2 (AIR) = 2KO_2$	46	0.932	$K_2O + 3/2 O_2 = 2KO_2$
4	6.467	$MgO + H_2O = Mg(OH)_2$	47	0.906	$Li_2C_2 + H_2 = 2LiH + 2C$
5	5.157	$SrO + CO_2 = SrCO_3$	48	0.894	$CuO + H_2O = Cu(OH)_2$
6	5.234	$CaO + CO_2 = CaCO_3$	49	0.870	$2CaCO_3 + 4NO_2 = Ca(NO_2)_2 + Ca(NO_3)_2 + 2CO_2$
7	5.275	$ZnO + SO_3 = ZnSO_4$	50	0.856	$2CO = C + CO_2$
8	5.126	$2NH_3 + H_2O + SO_3 = (NH_4)_2SO_4$	51	0.767	$H_2 + 2Na = 2NaH$
9	4.930	$NH_3 + H_2O + SO_3 = NH_4HSO_4$	52	0.723	$CS_2 + 4H_2 = CH_4 + 2H_2S$
10	4.610	$NiO + SO_3 = NiSO_4$	53	0.699	$Li + 1/2 H_2 = LiH$
11	4.379	$Na_2O + 2NO_2 + 1/2 O_2 = 2NaNO_3$	54	0.675	$2NO + SO_2 = N_2O + SO_3$
12	4.299	$H_2O + SO_3 = H_2SO_4$	55	0.631	$C_6H_6 + 3H_2 = C_6H_{12}$
13	4.234	$CuO + SO_3 = CuSO_4$	56	0.591	$H_2 + CO = C + H_2O$
14	3.887	$Li_2O + CO_2 = Li_2CO_3$	57	0.550	$CO + Cl_2 = COCl_2$
15	3.596	$NH_3 + HCl = NH_4Cl$	58	0.547	$Na_2O + 3/2 O_2 = 2NaO_2$
16	3.474	$CS_2 = C + 2S$	59	0.526	$Mg + H_2 = MgH_2$
17	2.956	$NH_3 + HBr = NH_4Br$	60	0.500	$4HCl + O_2 = 2H_2O + 2Cl_2$
18	3.332	$Li_2O + 2NO_2 = LiNO_3 + LiNO_2$	61	0.504	$Li_2CO_3 + 2NO_2 = LiNO_2 + LiNO_3 + CO_2$
19	3.322	$BaO + 2NO_2 + 1/2 O_2 = Ba(NO_3)_2$	62	0.502	$CdO + CO_2 = CdCO_3$
20	3.321	$MgO + CO_2 = MgCO_3$	63	0.476	$CO + 3H_2 = CH_4 + H_2O$
21	3.132	$NH_3 + HF = NH_4F$	64	0.481	$FeO + CO_2 = FeCO_3$
22	2.837	$2NaOH + 2NO_2 = NaNO_2 + NaNO_3 + H_2O$	65	0.471	$3NO = N_2O + NO_2$
23	2.817	$CaO + 2NO_2 + 1/2 O_2 = Ca(NO_3)_2$	66	0.402	$2NH_3 + 6K = N_2 + 6KH$
24	2.816	$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$	67	0.379	$C + 2H_2 = CH_4$
25	2.503	$2Ca(OH)_2 + 4NO_2 = Ca(NO_3)_2 + Ca(NO_2)_2 + 2H_2O$	68	0.376	$2H_2 + CO_2 = C + 2H_2O$
26	2.286	$MgCl_2 + NH_3 = MgCl_2 \cdot NH_3$	69	0.368	$CH_4 + 4Na = C + 4NaH$
27	2.262	$MnO + CO_2 = MnCO_3$	70	0.358	$SiH_4 + Mg = Si + MgH_2$
28	2.033	$NH_3 + H_3PO_4 = NH_4H_2PO_4$	71	0.339	$2NO + O_2 = 2NO_2$
29	2.006	$NaF + HF = NaHF_2$	72	0.339	$CO + H_2O = CO_2 + H_2$
30	1.905	$KF + HF = KHF_2$	73	0.309	$CO + 2H_2 = CH_3OH$
31	1.585	$2NH_3 + 6Na = N_2 + 6NaH$	74	0.300	$CH_4 + 4K = C + 4KH$
32	1.601	$2NO_2 + 3SO_2 = N_2O + 3SO_3$	75	0.288	$H_2 + 2K = 2KH$
33	1.572	$Na_2S + CO_2 + H_2O = H_2S + Na_2CO_3$	76	0.287	$Cs_2O + SO_3 = Cs_2SO_4$
34	1.451	$CS_2 + H_2S = CH_4 + 4S$	77	0.256	$Ti + H_2 = TiH_2$
35	1.331	$FeCl_2 \cdot NH_3 + NH_3 = FeCl_2 \cdot 2NH_3$	78	0.244	$N_2 + 3H_2 = 2NH_3$
36	1.235	$2LiOH + 2NO_2 = LiNO_2 + LiNO_3 + H_2O$	79	0.186	$2NO + Cl_2 = 2NOCl$
37	1.162	$SO_2 + 1/2 O_2 = SO_3$	80	0.180	$VCl_2 + 1/2 Cl_2 = VCl_3$
38	1.140	$KF + BF_3 = KBF_4$	81	0.167	$CaC_2 + 4H_2 = 2CH_4 + Ca$
39	1.086	$Na_2CO_3 + 2NO_2 = NaNO_2 + NaNO_3 + CO_2$	82	0.077	$2Li_3N + 3H_2 = N_2 + 6LiH$
40	1.067	$C + 2Cl_2 = CCl_4$	83	0.058	$N_2 + 3F_2 = 2NF_3$
41	1.070	$4HF + SiO_2 = SiF_4 + 2H_2O$	84	0.019	$IF_5 + F_2 = IF_7$
42	1.020	$ZnO + CO_2 = ZnCO_3$	85	0.013	$SiH_4 + 4Na = 4NaH$
43	0.990	$Ca + H_2 = CaH_2$			

Table 2-2
REACTIONS WHICH PASSED FIRST SCREENING FOR
CHEMICAL ENERGY TRANSPORT APPLICATIONS

$$H_2O + SO_3 = H_2SO_4$$

$$CS_2 + 4H_2 = CH_4 + 2H_2S$$

$$CS_2 + H_2S = CH_4 + 4S$$

$$2NO + SO_2 = N_2O + SO_3$$

$$2NO_2 + 3SO_2 = N_2O + 3SO_3$$

$$3NO = N_2O + NO_2$$

$$2NO + O_2 = 2NO_2$$

$$2NO + Cl_2 = 2NOCl$$

$$CO + Cl_2 = COCl_2$$

$$CO + 2H_2 = CH_3OH$$

$$C_6H_6 + 3H_2 = C_6H_{12}$$

$$C_2H_4 + H_2 = C_2H_6$$

$$4HCl + O_2 = 2H_2O + 2Cl_2$$

$$N_2 + 3F_2 = 2NF_3$$

$$IF_5 + F_2 = IF_7$$

$$N_2 + 3H_2 = 2NH_3$$

$$CO + 3H_2 = CH_4 + H_2O$$

$$CO + H_2O = CO_2 + H_2$$

$$SO_2 + \tfrac{1}{2} O_2 = SO_3$$

$\underline{H_2O + SO_3 = H_2SO_4}$
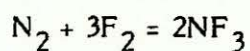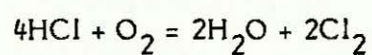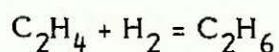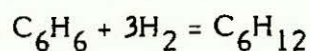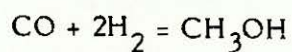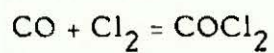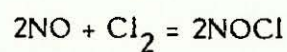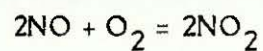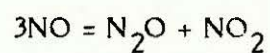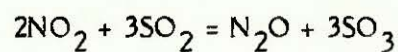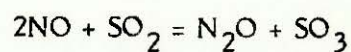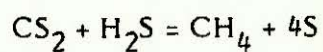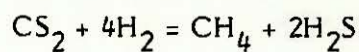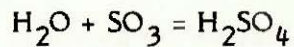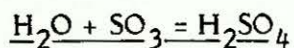
There is at present no known way of separating H_2O and SO_3, and the reaction proceeds non-catalytically in both directions. Therefore, the endothermic reaction (H_2SO_4 dissociation) would automatically reverse itself as the reaction was cooled from endothermic reaction temperatures. Thus, from a practical standpoint, the reaction is irreversible.

$\underline{CS_2 + 4H_2 = CH_4 + 2H_2S}$
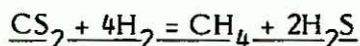
Very high endothermic reaction temperature required ($T* = 1,450 \, K$[1]). Toxicity and flammability of reactants/products is high.

$\underline{CS_2 + H_2S = CH_4 + 4S}$
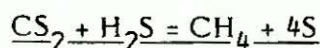
Very low exothermic reaction temperature available ($T* = 450 \, K$). Toxicity is again a problem, as well as the fact that elemental sulfur would have to be transported, most likely as a liquid, resulting in added heat losses (or initial capital expense for insulation) and decreased cycle efficiency due to requirement to vaporize sulfur at the endothermic reactor.

$\underline{2NO + SO_2 = N_2O + SO_3}$
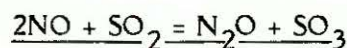
The primary problem with this and the next two reactions is the probability of some N_2 formation. In any reaction in which a N-N bond within a molecule (such as N_2O) must be broken and formed, it is probable that some diatomic nitrogen will be formed -- N_2 is thermodynamically favored over the nitrogen oxides. Formation of N_2 is effectively irreversible in these reactions, and even small amounts of N_2 formed per reaction cycle would, over the course of several hundreds or thousands of cycles, render useless CET systems based on these reactions.

In addition to the problem of N_2 formation, the above reaction suffers from the additional problem that its occurance has not been documented (or if it has, it is apparently not well known).

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[1] $T*$ is the turning temperature, or that temperature at which $\Delta G^o = 0$. Thus $T* = \dfrac{\Delta H^o}{\Delta S^o}$.

$\underline{2\,NO_2 + 3SO_2 = N_2O + 3SO_3}$
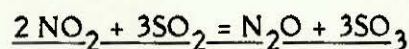
Same as above. A third reaction ($NO_2 + SO_2 = NO + SO_3$) not listed in Table 3-1, would probably be competing with these two reactions, and would suffer from the same N_2 formation problem.

$\underline{3NO = N_2O + NO_2}$
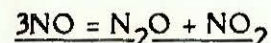
N_2 formation problem same as above. This reaction may not be reversible as written, regardless of any N_2 formation.

$\underline{2NO + O_2 = 2NO_2}$
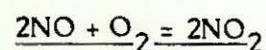
Although no N-N bonds are formed or broken as written, N_2 formation may still be a problem. In addition, the products of the endothermic reaction, NO and O_2, are difficult to separate, and they recombine readily, even at room temperature, so the reaction would probably be irreversible in practice.

$\underline{2NO + Cl_2 = 2NOCl}$
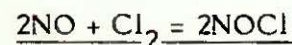
NO and Cl_2 will be difficult to separate without energy-consuming chilling equipment. Nitrocyl chloride, analagous to phosgene, $COCl_2$, is highly toxic, and is corrosive to many metals. Nitrocyl chloride can be dissociated by photolysis as well as thermally, although only thermochemical reactions are considered here.

$\underline{CO + Cl_2 = COCl_2}$
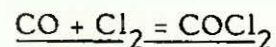
Separation, toxicity, and corrosion problems similar to those for the preceding reaction plague this reaction as well.

$\underline{CO + 2H_2 = CH_3OH}$
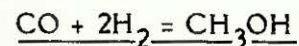
Exothermic reaction temperature too low for present purposes (T* = 415 K), and exothermic reaction pressure required for acceptable reaction kinetics is extremely high.

$\underline{C_6H_6 + 3H_2 = C_6H_{12}}$
$\underline{C_2H_4 + H_2 = C_2H_6}$
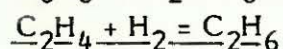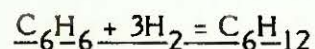
Even with the best catalysts available, unwanted side reactions will cause both of these reactions to be effectively irreversible in an application requiring many reaction cycles, such as the CET systems considered here.

$$\underline{4HCl + O_2 = 2H_2O + 2Cl_2}$$
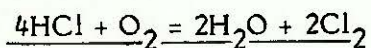
The oxidation of HCl by oxygen to produce chlorine was once used commercially and was known as the Deacon process. In spite of this background, no kinetic information was found in a preliminary search. Wet chlorine atmosphere would present severe corrosion problems for pipe network.

$$\underline{N_2 + 3F_2 = 2NF_3}$$
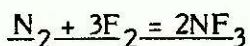
NF_3 cannot be produced from N_2 and F_2 by thermochemical means alone at reasonable temperatures. Additional excitation energy, such as ionizing radiation, must be provided, and even then yields are low, with only traces of NF_3 formed. Moreover, elemental fluorine is extremely reactive, so that handling and corrosion problems would be prohibitive for CET applications.

$$\underline{IF_5 + F_2 = IF_7}$$
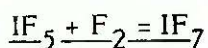
Handling and corrosion problems similar to preceding reaction. This reaction is not well characterized, and no information could be found on its reaction kinetics.

$$\underline{N_2 + 3H_2 = 2NH_3}$$
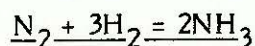
While the ammonia synthesis reaction was originally included as one of the three most promising reactions, it was eliminated when process engineering difficulties were taken into account. Due to the stability of the N_2 molecule, fixation of nitrogen (e.g., NH_3 synthesis) is very difficult. The main difficulties with the $NH_3/H_2/N_2$ system, therefore, are in the ammonia synthesis reaction. While low temperatures favor the synthesis reaction thermodynamically, higher temperatures (>700 K) are required for acceptable reaction kinetics with all known catalysts. These high temperatures dictate very high pressures (References 7 and 8) in order to get acceptable yields, and even at the 40-100 bar synthesis pressures currently used industrially, one-pass yields of less than 50 percent are common. Recycle of unreacted nitrogen and hydrogen is therefore imperative. Such recycle is a troublesome source of inefficiency due to difficulties with recuperation of heat between reactant and product streams, and penalizes the $NH_3/N_2/H_2$ system heavily as far at CET applications are concerned.

The extremely high pressures required for the exothermic (NH_3 synthesis) reaction would cause endothermic equilibrium yields to be low, so operation of the endothermic reactor at a lower pressure would probably be necessary. The compression work required (only

partially recoverable with turboexpanders) for operation of the two modes at different pressures will constitute another substantial source of inefficiency for the CET system.

Finally, the generally high pressures which would be used throughout an $NH_3/H_2/N_2$ system (say 300 bar in the exothermic mode, 100 bar in the endothermic mode) would lead to high capital cost requirements for high pressure equipment, and troublesome containment problems.

In the opinion of the RRC team, all of the above considerations, taken together, serve to eliminate the ammonia synthesis reaction from consideration in the present study.

2.3 FINAL REACTION SCREENING

The reactions remaining after the above screening process were:
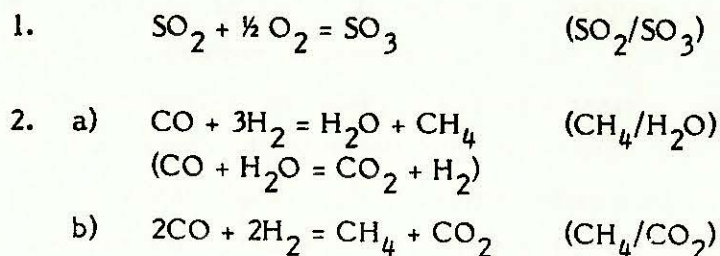
1. $$SO_2 + \frac{1}{2} O_2 = SO_3 \qquad (SO_2/SO_3)$$

2. a) $$CO + 3H_2 = H_2O + CH_4 \qquad (CH_4/H_2O)$$
$$(CO + H_2O = CO_2 + H_2)$$

   b) $$2CO + 2H_2 = CH_4 + CO_2 \qquad (CH_4/CO_2)$$

The water gas shift reaction is included parenthetically with the CH_4/H_2O reaction, since the two are inseparable and occur simultaneously.

The two reactions listed under 2a above form the basis of the complex Carbon/Hydrogen/Oxygen system. Linear combinations of these two reactions result in a number of derivative reactions corresponding to different stoichiometries for the same basic system. In particular, addition of these two equations results in equation 2b.* Denoted the "CO_2 reforming of methane", as opposed to the "steam reforming of methane" (2a above), reaction 2b has been proposed by Chubb as a replacement for the SO_2/SO_3 reaction in the SOLCHEM system, and therefore deserves consideration here.

The CH_4/H_2O reaction and the CH_4/CO_2 reaction share several key potential problems with respect to CET applications. Of the two, the CH_4/H_2O reaction has received considerably more study concerning CET applications, and is therefore discussed in some

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*Reaction 2b represents the stoichiometry in which the ratio of hydrogen to carbon monoxide is about 1:1 (Reference 9).

detail in section 2.3.1. Following that examination the CH_4/CO_2 reaction is briefly examined in section 2.3.2. Finally the reasons for selecting the SO_2/SO_3 reaction for further study are summarized in section 2.3.3.

2.3.1   The Methanation/Steam Reforming Reaction

The CH_4/H_2O reaction has been and is currently being studied for use in Chemical Heat Pipe (CHP) applications. Much of the discussion of this reaction presented below is based on the work at KFA Julich (References 10-13) and at General Electric (Reference 9).

The CHP applications considered by GE and KFA Julich differ in several important respects from the distributed solar applications considered here. The most obvious difference is in the type of heat source. Potentially, higher temperatures are available from a solar source than from the nuclear reactor. Perhaps most important, the input from the solar source will be intermittant (diurnal at best), so that the luxury of long periods of steady-state reformer operation will not be possible. Due to the different texture of the solar input, the entire transport network, and especially the steam reformer, must be able to stand significant, rapid, input-temperature excursions and show no permanent ill effects. Since the reformer must be mounted at the focus of a solar concentrator, there will be rather severe mass and geometric constraints on its design which are not present in the GE and KFA applications. Furthermore, no power plant will be located adjacent to the reformers in the solar applications, so that turbine extraction streams at convenient temperatures will not be available to provide needed process heat.

The nuclear long-distance energy transport systems, as designed by GE and KFA, were considered applicable to distances of approximately 160 km, so that separation of excess H_2O vapor by condensation at the reaction sites was economically attractive since it eliminated the need for one gas pipeline, allowed the remaining ones to be smaller, and reduced compression work. In a typical 100 MW_e distributed solar facility, average transport distances will not be more than one-half mile or so, so that the value of potential reductions in pipe size and compression work will be less than that of maximizing the efficiency of the entire CET system. It is therefore quite possible that the optimum CET system for a distributed solar network based on the CH_4/H_2O reaction would not involve separation or recycle (at least at the reformer), and that any excess water vapor present for reasons of chemistry would never be condensed, and would simply be carried around the entire system with the reacting gases. Such a design could suffer

from problems with H_2O condensation during shutdown. The condensation problem and possible solutions are discussed with respect to the SO_2/SO_3 reaction in section 3.3.

Excess Water in the Methanation/Steam Reforming System

Reaction systems involving carbon oxides and hydrogen are unique in the complexity of their stoichiometry. Not only can synthesis of paraffins, olefins, and alcohols occur, but also the water gas shift reaction as well as several reactions which produce elemental carbon. Important reactions in the system of interest here include:

$$CH_4 + H_2O = CO + 3H_2 \qquad (1)$$

$$CO + H_2O = CO_2 + H_2 \qquad (2)$$

$$2CO = C + CO_2 \qquad (3)$$

$$CO + H_2 = C + H_2O \qquad (4)$$

$$CO_2 + 2H_2 = C + 2H_2O \qquad (5)$$

$$CH_4 = C + 2H_2 \qquad (6)$$
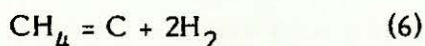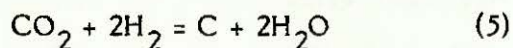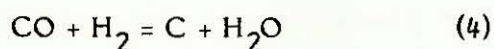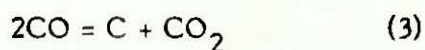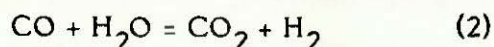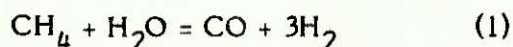
The first two reactions together are the primary energy storage reactions, and are reversible. The last four result in solid carbon deposition which can inactivate high-temperature methanation and reforming catalysts. The carbon deposits can be removed by exposure of the coked catalyst to a hydrogen atmosphere at elevated temperature and pressure by reversing reaction (6). However, such a decoking process would be time consuming and energy intensive, and the capability to carry it out might well require substantial additional capital equipment. Catalyst coking would therefore be a major problem in these systems.

To avoid catalyst coking, the GE report (Reference 9) recommends $H_2O:CH_4$ ratios of 3:1 in the reformer and 1.5:1 in the methanator (stoichiometric ratio is 1:1). Other sources (References 7 and 14) indicate a ratio of at least 3:1 may be necessary in both the reforming and methanation stages.

In industrial steam reforming and methanation, water is generally separated from reactor exit streams and recycled. The KFA and GE chemical heat pipe designs include such recycle, since, as discussed above, the transport distances involved make it attractive. An advantage of recycle in the event that the optimum $H_2O:Carbon$ ratios are different for the methanation and steam reforming reactors is that operation at the optimum ratio is

allowed in both reactors. In addition, recycle allows minimization of the water mole fraction, and therefore the dew point, in the vapor phase transport streams, so that the pipeline temperature can be near ambient.

Recycle at either reactor requires repeated vaporization and condensation of water. Since the enthalpy of vaporization of water is substantial compared to sensible heating requirements, and even to the enthalpy of reaction, poor recuperation between reactor input and output streams could result in severe availability losses. For more thorough discussions of this point, see References 9 and 4.

The GE report (Reference 9) demonstrates convincingly that even with low ΔT's in the recuperators, and therefore with large heat transfer areas, it is not possible to reclaim a satisfactory amount of the heat of condensation of water for use in the reactor feed stream, due to temperature mismatches. The workers at GE "solved" this problem with the invention of their "mixed-feed evaporator". The thermodynamic arguments justifying use of such a device are clever and compelling. However, no such device has been built, and even if, as GE claims, the heat transfer area required for such a device is not much greater than that of an ordinary recuperator, it is doubtful that such an evaporator could be incorporated into the cramped geometry of a receiver/reformer at the focal point of a solar concentrator.

If proved successful, the mixed-feed evaporator could be included in the methanator end of the transport system, where space and mass are not severely constrained. However, the largest availability losses from poor recuperation would occur at the reformer, due to the decrease in moles of H_2O on reforming. So the efficiency penalty associated with recycle would be quite high for a CET system without a mixed-feed evaporator at the reformer end. No attempt has been made here to estimate the efficiency of such a system, but in light of the discussion in Chapter 5 of the GE report, it is likely that it would be unacceptably low. Therefore, recycle of unreacted gases at either the reformer or methanator would probably not be advisable for CET systems based on the CH_4/H_2O reaction.

Carbonyl Formation

Another serious drawback to the use of the methane/steam reforming reaction for CET is the potential for carbonyl formation. Carbon monoxide reacts with both iron and nickel to form carbonyls, according to: (Reference 9)

$$Fe + 5CO = Fe(CO)_5$$
$$Ni + 4CO = Ni(CO)_4$$
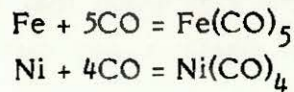
Both of these reactions occur in the temperature range 420-590 K. Iron carbonyl formed in other parts of the system will decompose at methanation and reformer reaction temperatures, depositing iron at catalyst surfaces. This deposited iron would not only interfere with the reaction which should be taking place, but would also promote the deposition of carbon. Appendix I of the GE report states:

"Thus, it can deposit carbon under operating conditions that normally would not produce carbon in the iron's absence. Such transfer of iron can be prevented only by proper equipment design and metallurgy selection upstream of the methanators."

Iron deposition by this process may occur at surfaces other than those of the catalyst, resulting in coking of surfaces of reactor outlets, heat exchangers, etc. Moreover, prevention of iron carbonyl formation may require exotic materials which could substantially increase the capital cost requirements for the system.

The formation of the gaseous nickel carbonyl results in depletion of catalyst (generally a promoted nickel catalyst) within the reactors. According to Appendix I of the GE report, "The sole means of avoiding the depletion of nickel from methanation catalysts is by minimizing exposure of the catalyst to carbon monoxide at the appropriate temperatures."

Methanators and steam reformers in industry are generally run continuously, at steady state, and at temperatures high enough to avoid carbonyl formation. In the solar applications addressed here, however, the temperatures of both of the reactors and of the attached piping and heat exchanger will cycle, at least diurnally, through the 420-590 K range in which carbonyl formation occurs. Short lived occultations caused by the passage of clouds will probably cause temperature excursions through this "danger zone" more frequently, even with some buffer storage. Moreover, preliminary calculations indicate that at system operating pressures between 10 and 40 bar, the minimum dew point in the piping network is within the "danger zone", so that $Fe(CO_5)$ formation could occur continuously in the pipelines. It appears, then, that migration of Ni and Fe to places they ought not to be, and subsequent, irreversible degradation of system performance, may be very difficult to avoid.

The preceding paragraphs lead to the conclusion that due to potential problems with transport efficiency, condensation in pipelines, and carbonyl formation with associated complications, the CH_4/H_2O reaction should be eliminated from further consideration for CET applications.

2.3.2 The Methanation/CO_2 Reforming Reaction

The CH_4/CO_2 reaction promises at least one key advantage over the CH_4/H_2O reaction: the dew point in all lines would be well below the minimum ambient temperature expected, so that condensation in the transport lines would not be a problem. This advantage would reduce the insulation requirements and thus the capital cost of the piping network.

Brief examination of the CH_4/CO_2 reaction system indicates, however, that it may suffer from the same major shortcoming as the CH_4/H_2O reaction: carbon deposition and resultant loss of catalyst activity. As in the CH_4/H_2O system, carbonyl formation, related to the carbon deposition problem, could prove to be a major problem.

Again, the gaseous carbonyls which are most likely to form are $Fe(CO)_5$, from ferrous containment equipment such as heat exchangers and reaction vessels, and $Ni(CO)_4$ from the most prominent methanation/reforming catalyst, Ni. Iron carbonyl formation could be troublesome because $Fe(CO)_5$ may decompose in the methanation reactor, depositing Fe at the catalyst surface. This iron promotes the carbon deposition reactions, and could therefore lead to coking under conditions which would not ordinarily produce it. Formation of gaseous nickel carbonyl would result in steady migration of valuable catalyst material from the catalyst bed where it belongs to surfaces throughout the system where it would be useless.

With clever process design, carbonyl formation during steady-state operation can probably be avoided. However, the intermittant nature of the solar input to a real CET subsystem would make the critical temperature range for carbonyl formation very difficult to avoid, and therefore present vexing temperature control problems.

2.3.3 The SO_2/SO_3 Reaction

The SO_2/SO_3 reaction was the one first proposed by Chubb for the SOLCHEM systems, and has probably received more study than any other reaction for energy storage/transport applications. The key reasons for this attention are:

1. Freedom from side reactions

2. Endothermic reaction temperature (at reasonable pressures) is good match with present high temperature solar technology

3. Reaction readily reversible

4. Reaction catalytic in both directions, allowing good reaction control. Catalysts well known.

5. Considerable experience in handling reactants, although they are corrosive and toxic.

The SO_2/SO_3 reaction also has drawbacks for CET applications, including:

1. Corrosivity

2. Toxicity

3. Relatively high dew point of exothermic reaction products (from stoichiometric mixtures) at practical pressures (greater than 1 bar).

4. Lack of intrinsic rate data for endothermic reaction, or for even the exothermic reaction of SO_2 with pure O_2 rather than air.

The CH_4/CO_2 reaction system, on the other hand, offers some important advantages over the SO_2/SO_3 system, including:

1. Fewer corrosion problems.

2. Low dew point for both supply and return compositions, so that condensation problem is eliminated.

Each of these two reactions thus has apparent advantages and disadvantages for CET applications, and adequate comparison of the two will require more detailed process design work as well as some experimental work. The difficult choice between the two was necessary, however, because the scope of the present contract limited subsequent parts of the study to one reaction only. Thus, the SO_2/SO_3 reaction was chosen for further analysis. The CH_4/CO_2 reaction was eliminated due primarily to uncertainty concerning catalyst poisoning by carbon deposition, as well as carbonyl formation. Uncertainty is the key word here, since it may be possible to avoid carbon deposition, even with the variable temperatures/compositions which will undoubtedly be encountered in solar-driven reactors.

Further study, probably experimental, may show that carbon deposition and/or carbonyl formation may be readily avoided in practice, thus making the CH_4/CO_2 reaction the most attractive for CET applications. Even if this occurs, the choice of the SO_2/SO_3 reaction, and subsequent analysis based on it, will not have been in vain, since the primary goal of the overall effort was a preliminary evaluation of CET for distributed solar applications, rather than a detailed comparison of suitable chemical reactions.

3.0 THE SO_2/SO_3 CHEMICAL ENERGY TRANSPORT SUBSYSTEM PRELIMINARY PROCESS DESIGN

3.1 SYSTEM DEFINITION AND DESIGN APPROACH

As noted in the Introduction, the limited scope of the study made it necessary to restrict the preliminary CET process evaluation to a specific distributed STEC application. This specific case, representative of the distributed solar program direction at the time the study was begun, is summarized in Table 1-1 (Page 1-6).

The endothermic reactor/recuperator design used here was adapted from a spiral-flow design based on ceramic extrusion technology, proposed by Chubb (Reference 15) and analyzed by Li and Schmidt (Reference 16). Other designs for the combined reactor/heat exchanger (RHX) have been proposed (References 15, 16, 17), and there is some question as to whether the novel extruded ceramic units can be fabricated to meet cost and performance specifications. Nonetheless, the ceramic, spiral flow design appears to be representative for performance and cost purposes, and therefore adequate for a preliminary evaluation of CET.

The concentrator field layout was patterned after that of Caputo (Reference 5), and the pipe field design optimization and performance estimate were carried out by Battelle Northwest Laboratory using the ETRANS code (which is also based on the Caputo layout). The average thermal input to the receivers was assumed to be 50 KW_t per concentrator, defined at the receiver aperture. The entire transport subsystem was sized to handle this 50 KW_t input continuously, although variation in insolation would of course cause the actual transport power to vary during the course of a day's operation. The field was designed to contain 720 concentrators, which was the initial estimate of the number necessary to achieve a nominal plant output of 10 MW_e (assuming 50 KW_t average input per concentrator). The final estimate of nominal plant output, based on the more reliable transport efficiency estimate resulting from the preliminary process design, is 12.5 MW_e from the 720 dish field.

The preliminary transport process design was carried out at the major component level, including:

1. Reactor/Heat Exchangers
2. Transport Network
3. Compressor
4. Central Recuperator
5. Central Exothermic Reactor

These major components were sized and their purchase or fabrication costs were estimated. Total installed cost of the transport subsystem was then estimated from the component costs by a factored estimating technique. All costs are expressed per square meter of concentrator area as well as per KW_t of nominal transport power.

3.2 Preliminary Process Design

The preliminary process design for the CET subsystem based on the SO_2/SO_3 reaction is depicted schematically in Figure 3-1, while key stream characteristics are given in the accompanying table. The key design assumptions for the process shown are as follows:

1. A nominal operating pressure of 3 bar was assumed. Estimates of pressure drops through process components would result in pressures between about 2.5 and 3.5 bar in various parts of the system. Thermodynamic equilibrium calculations were carried out for a pressure of 3 bar, even though the pressure in both reactors could vary slightly from this value. The value of 3 bar was chosen because it provided a good match between design constraints for endothermic and exothermic reaction temperatures and convenient extents of reaction in both reactors, while allowing a reasonably low dew point in the supply side of the piping network.

2. The endothermic reactor/heat exchanger was assumed to perform as modeled by Li and Schmidt (Reference 16), with respect to such parameters as heat loss, pressure drop, and conversion.

3. Actual converison in both the endothermic and exothermic reactors was assumed to be 90 percent of the theoretical conversion attainable at 3 bar at the reactor exit temperatures. This assumption agrees reasonably well with the analysis of Li and Schmidt.

SO₂/SO₃ CHEMICAL ENERGY TRANSPORT SUBSYSTEM
PRELIMINARY PROCESS SCHEMATIC
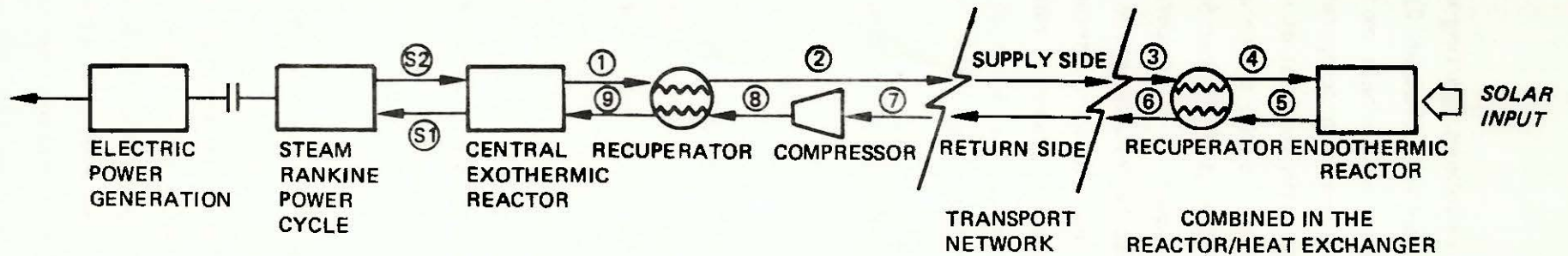
Stream	Flow Rate (moles/mole S)	Temp. (K)	Pressure (bar)	State	Composition (mole fraction)		
					SO_3	SO_2	O_2
1	1.0	580	3.3	ν	0.91	0.06	0.03
2	1.0	420	3.2	ν	0.91	0.06	0.03
3	1.0	343	2.9	ν	0.91	0.06	0.03
4	1.4	*	2.9	ν	0.16	0.56	0.28
5	1.4	1,273	2.8	ν	0.16	0.56	0.28
6	1.4	440	2.7	ν	0.16	0.56	0.28
7	1.4	363	2.4	ν	0.16	0.56	0.28
8	1.4	400	3.6	ν	0.16	0.56	0.28
9	1.4	560	3.5	ν	0.16	0.56	0.28
S1	—	800	68	ν	—	Steam	—
S2	—	526	68	ℓ	—	Water	—

*Not estimated. Reactor/heat exchanger assumed to perform as predicted by Li and Schmidt (Reference 16)

The process depicted in Figure 3-1 may be described briefly as follows, starting with the supply side exit from the central recuperator to the pipe network (Stream 2). After distribution by the network, the SO_3-rich stream enters the reactor/heat exchangers mounted at individual concentrators, where it is heated to reaction temperature by indirect contact with reaction products, reacted catalytically with the heat of reaction coming from concentrated solar-thermal energy, and cooled to pipeline temperature in the recuperators. After collection by the return-side pipe network, the combined SO_3-lean streams are compressed in a centrifugal compressor, preheated in a recuperator by indirect contact with hot reaction products, and reacted exothermically in the central reactor. This reactor is a series of packed-bed adiabatic reactors with interbed heat exchangers. On the tube side of the interbed heat exchangers, steam is raised and superheated for use in the steam turbine for power production. The SO_3-rich stream leaving the reactor is then cooled in the recuperator, and distributed for another cycle.

The designs and performance estimates of the major process components are described in the following paragraphs.

3.2.1 Endothermic Reactor/Heat Exchanger

Li and Schmidt modeled the performance of two types of RHX suggested by Chubb for SO_2/SO_3 service. The design and performance of the RHX used for the present analysis is patterned after the "9-layer gapped" design, as analyzed by Li and Schmidt. The 9-layer gapped design is based on ceramic extrusion technology and consists of spiral ceramic passages wound around a cylindrical cavity (see Figures 3-2 through 3-5). The innermost passage, its walls coated with platinum or iron catalyst, serves as the chemical converter, and the remaining passages as the heat exchanger. Chubb has suggested that the device be fabricated with extruded cordierite although silicon carbide or silicon nitride may also be used.

Both the front and the end plates are well insulated, but with an aperture on the front plate to receive the reflected sunlight from the collector. Quartz tubes fill the aperture to inhibit convection losses and provide partial blockage of long wave length IR radiation. The major part of the design is the 9 spiral layers wound around the cylindrical cavity. Each layer contains 60 in-flow passages and 59 out-flow passages arranged in a staggered pattern along two separate rows. The out-flow passages are in the inner row, while the in-flow passages are in the outer row. A high-temperature resistant ceramic fiber insulation fills the gap separating the layers. The purpose of installing the insulation gap is to

INSULATING
BACK FACE

CERAMIC SPIRAL

SO_3 IN

$SO_2 + O_2$ OUT

ENTRANCE
APERTURE

FRONTISPIECE

THE 9-LAYER GAPPED REACTOR/HEAT EXCHANGER

INSULATION

INLET, OUTLET

B

B

QUARTZ TUBES
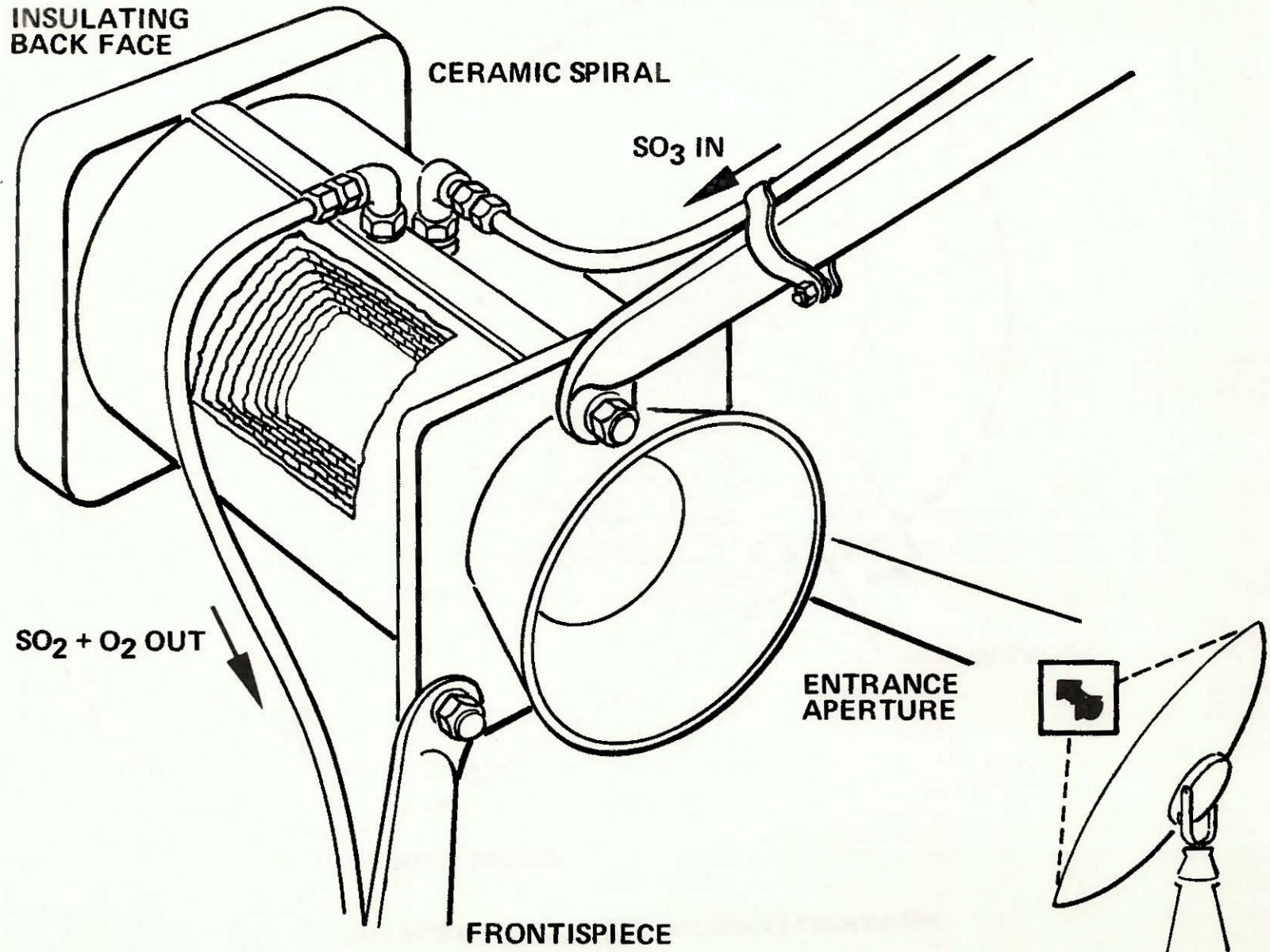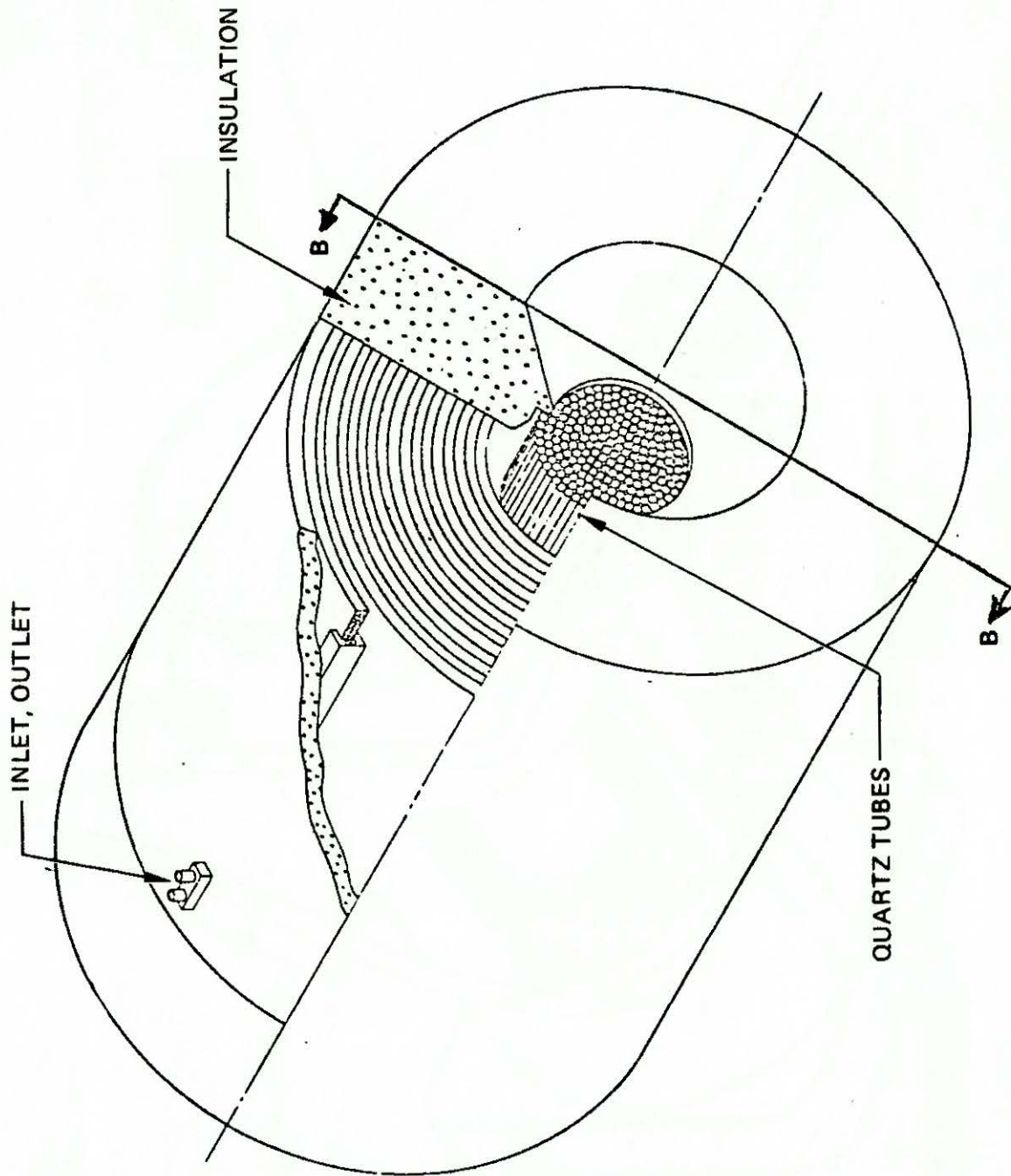
Figure 3-4

RADIAL CROSS SECTION OF THE 9-LAYER GAPPED REACTOR/HEAT EXCHANGER

INSULATION
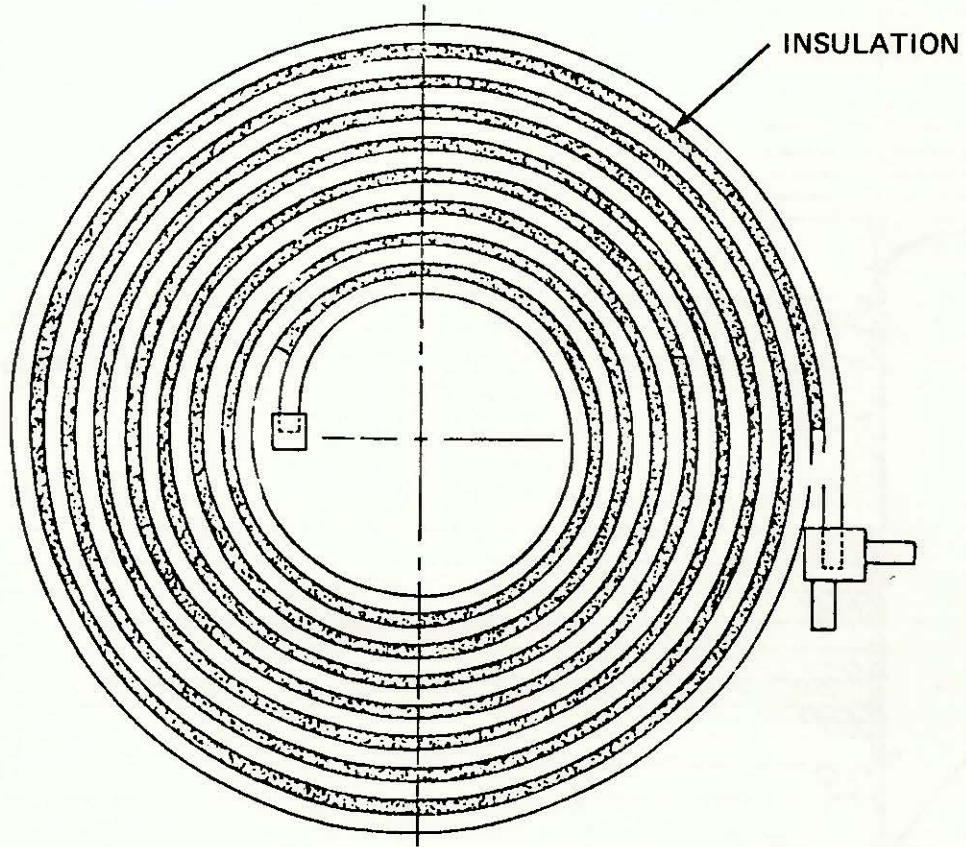
AXIAL CROSS SECTION OF THE 9-LAYER GAPPED REACTOR/HEAT EXCHANGER

INSULATION

SUNLIGHT

QUARTZ TUBES
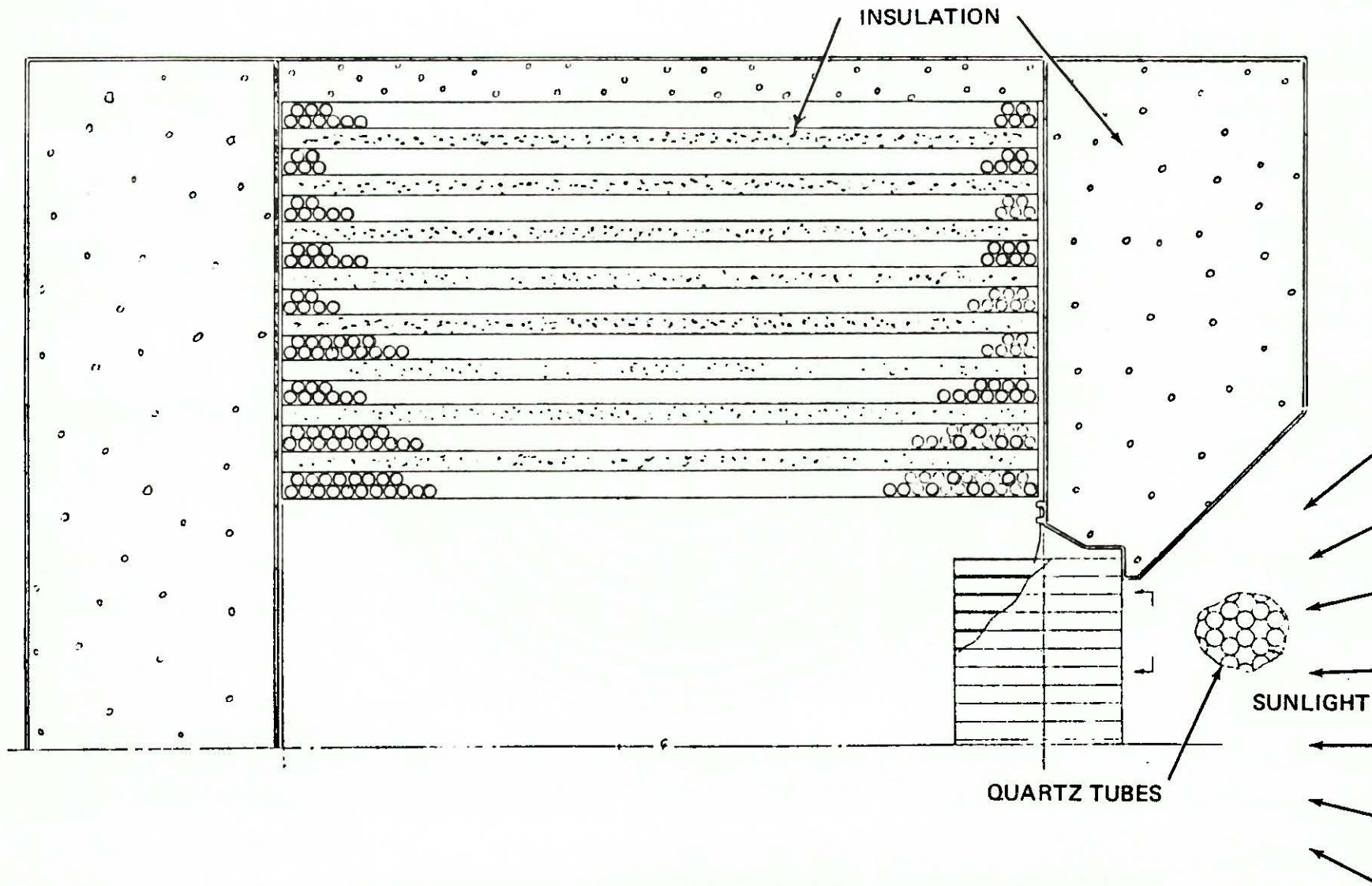
Figure 3-5

minimize the heat cross flow from the inner layer toward the outer layer, and thus keep the performance as close to countercurrent heat exchange as possible.

Li and Schmidt analyzed a 9-layer gapped RHX sized for use with a 7-meter diameter paraboloidal dish concentrator. For the purposes of this analysis, the design on which their analysis was based was scaled up by a simple procedure so that it would handle the heat flux and reactant flow rates associated with the larger 11 m concentrators. This scale-up was constrained such that the pressure drop through the RHX and the heat loss to the surroundings would be approximately the same as those for the smaller RHX analyzed by Li and Schmidt.

Although catalyst coating of the walls of only the innermost passage was proposed by Chubb and considered here, temperatures in the first several inner passages would be high enough to cause reaction in the presence of a catalyst. Coating of these passages as well would be relatively inexpensive and could result in near-equilibrium conversions, thus increasing subsystem efficiency.

Thus, the RHX may be characterized as follows:

1. Flow rate through each receiver:

    0.68 moles S^*/sec

    or

    54.4 g/sec

2. RHX pressure drop: 0.2 bar

3. Heat loss to surroundings: 0.13 kcal/mole S

4. No buffer storage

No buffer, or short term, energy storage was included in the RHX design, nor were the effects of insolation transients on transport system performance examined. While designs for solar receivers with attached thermal engines (e.g., Sterling engines) generally require some buffer storage to smooth the insolation profile, such storage may not be necessary with fluid transport systems. The flow rate of the fluid itself can be varied to achieve

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*While the molar flow rates of the reaction constituents, SO_3, SO_2, O_2, vary with extent of reaction, the flow rate of total moles of sulfur (S) is constant, and is therefore used as the basis for all flow rates.

constant or slowly varying heat removal from the receiver, thus protecting hardware from unacceptable thermal shock. The viability of such arrangements in chemical energy transport systems can best be tested by experiment. The reliability of the cost estimate for CET will not be affected greatly by the presence or absence of a buffer storage requirement.

3.2.2   Exothermic Reactor

The production of heat by recombination of SO_2 and O_2 occurs in the central exothermic reactor. This reactor consists of a series of 8 adiabatic, packed-bed reactors with intermediate cooling (Figure 3-6). Steam for the power plant is raised and superheated in the heat exchangers, flowing countercurrent to the reacting gas stream. Preheated reactants enter the first packed bed at 560 K, leave the last packed bed at 600 K (approximate ignition temperature with platinum catalyst) and the last heat exchanger at 577 K. Boiler feedwater enters the last (low temperature) heat exchanger at 526 K and leaves the first (high temperature) heat exchanger at 800 K (68 bar). The reactor diameter was estimated to be 18 feet, although several smaller diameter reactors, rather than one large one may be necessary for adequate turndown capability.

The adiabatic reactor beds are packed with supported catalysts. The high temperature beds (T > 873 K) would use an iron oxide catalyst -- good high temperature stability, low cost and adequate catalytic activity at these temperatures (Reference 18). The down-stream, lower temperature beds would use vanadium pentoxide or, where necessary, platinum catalysts, because these two are more active than iron at lower temperatures.

The exothermic reactor design was based on the assumption that the platinum catalyst in the final catalyst bed would be operable at temperatures as low as 600 K. At such low temperatures even the platinum catalyst requires a substantial bed depth to achieve the required conversion. The additional extent of reaction obtainable by operating the last bed at low temperature may not be economically justifiable due to the expense of platinum catalyst. Elimination of the last (platinum catalyst) bed, and use of only iron oxide (T > 873 K) and vanadium pentoxide (700 K < T < 873 K) catalyst beds would reduce somewhat the extent of reaction in the exothermic reactor, with the result that more material would have to be circulated per unit of energy transported by the system. However, equilibrium calculations indicate that the reduction in conversion would be small, and the subsystem efficiency reported below would not change significantly. Elimination of the last catalyst bed may therefore be economically attractive.

SCHEMATIC OF EXOTHERMIC REACTOR CONFIGURATION

INCOMING REACTANTS

STEAM TO TURBINE

ADIABATIC PACKED-BED REACTORS (8 REACTORS IN BASE CASE DESIGN)

INTERBED HEAT EXCHANGERS

PREHEATED BOILER FEEDWATER

TO RECUPERATOR AND SUPPLY SIDE PIPE NETWORK
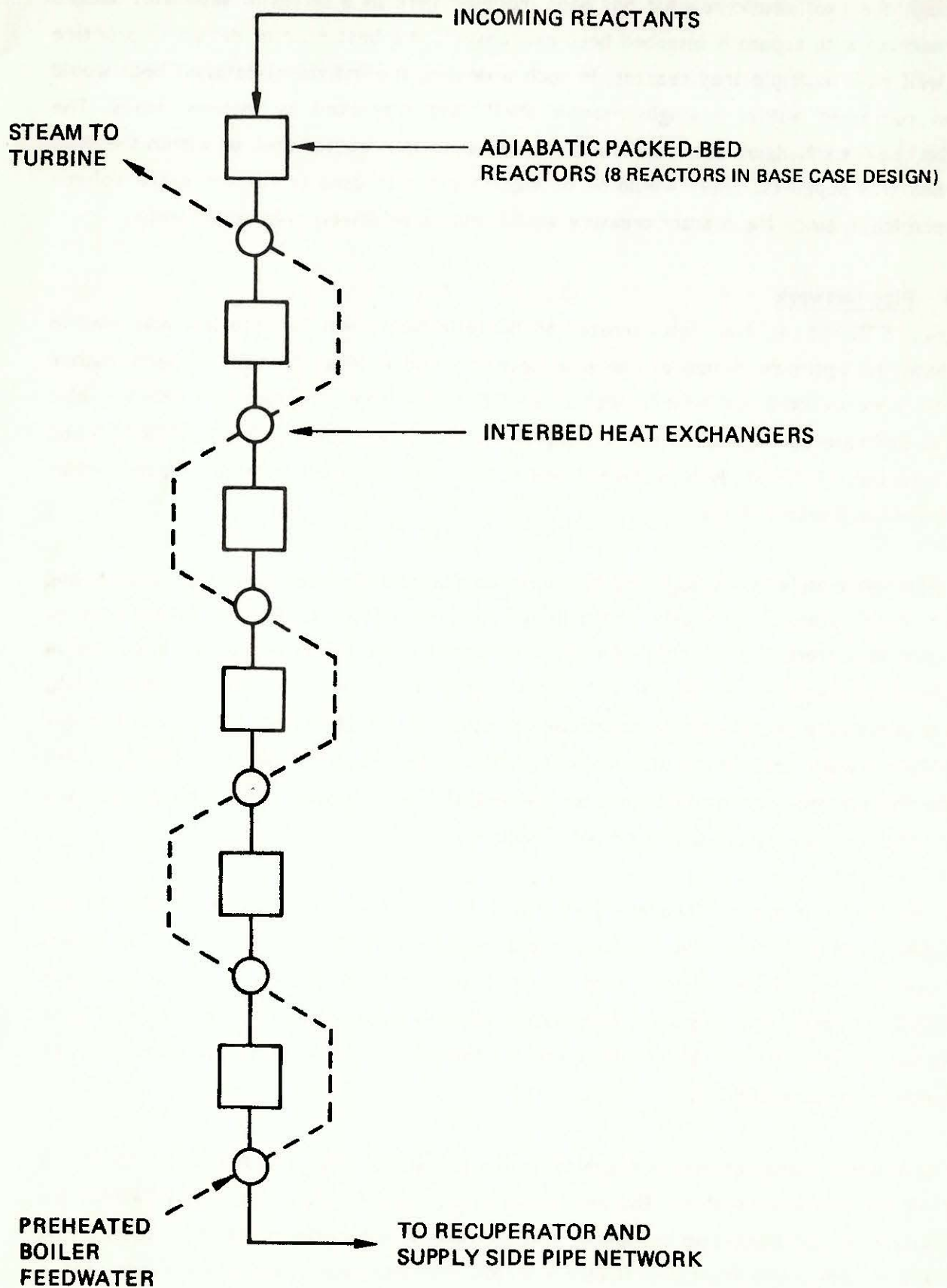
Although the exothermic reactor has been modeled here as a series of separate, packed bed reactors with separate interbed heat exchangers, the best reactor design in practice may well be a multiple tray reactor. In such a design, the individual catalyst beds would all be contained within a single reactor shell, and supported by internal trays. The interbed heat exchangers could be located external to the reactor shell or within the shell between tray supports. There would be no significant cost penalty for the extra volume between trays, since the reactor pressure would require relatively thin vessel walls.

3.2.3 Pipe Network

Program ETRANS, written and operated by Battelle Northwest Labortories, was used to estimate the optimum design of the pipe network, and to characterize its performance (system pressure drop and heat losses) in the CET subsystem. Program ETRANS was also used to estimate the capital cost of the pipe network. A brief description of ETRANS and its adaptation to this study is presented below. For more detailed information, the reader is referred to Reference 19.

The ETRANS code was developed to assess the capital and operating costs for sensible and latent energy transport networks in distributed solar installations. The field layout used by the code is patterned after that of Caputo (Reference 5). The power plant is located in the center of a square field of dish collectors (Figure 1-1). Since the field is symmetrical, only a one-eighth section of the total field is optimized by ETRANS. Such a section for the CET network analyzed in this work is shown in Figure 3-7 along with the arbitrary numbering system used by ETRANS for individual pipe segments. The field supply and return pipelines are collinear and supported above ground.

Each section in the main headers (sections 1-10 and 65-74 in Figure 3-7) and in the branches emanating from the headers, is optimized individually by ETRANS. The risers and downcomers which connect each concentrator/receiver module with the adjacent pipelines are optimized in groups. The design includes gate valves on either side of each collector so that it can be isolated for maintenance, and a valve in each riser or downcomer for flow control.

The optimized piping network is taken to be the one which results in the lowest life cycle cost for the transport system. The key independent variables considered by ETRANS are pipe diameter and insulation thickness, and the objective function to be minimized is the annualized system-resultant cost (Reference 20). The annualized system resultant cost is

SCHEMATIC OF ONE-EIGHTH SECTION OF SQUARE COLLECTOR
FIELD LAYOUT FOR CET PIPE NETWORK

INDIVIDUAL
CONCENTRATORS

720 COLLECTORS IN ENTIRE FIELD
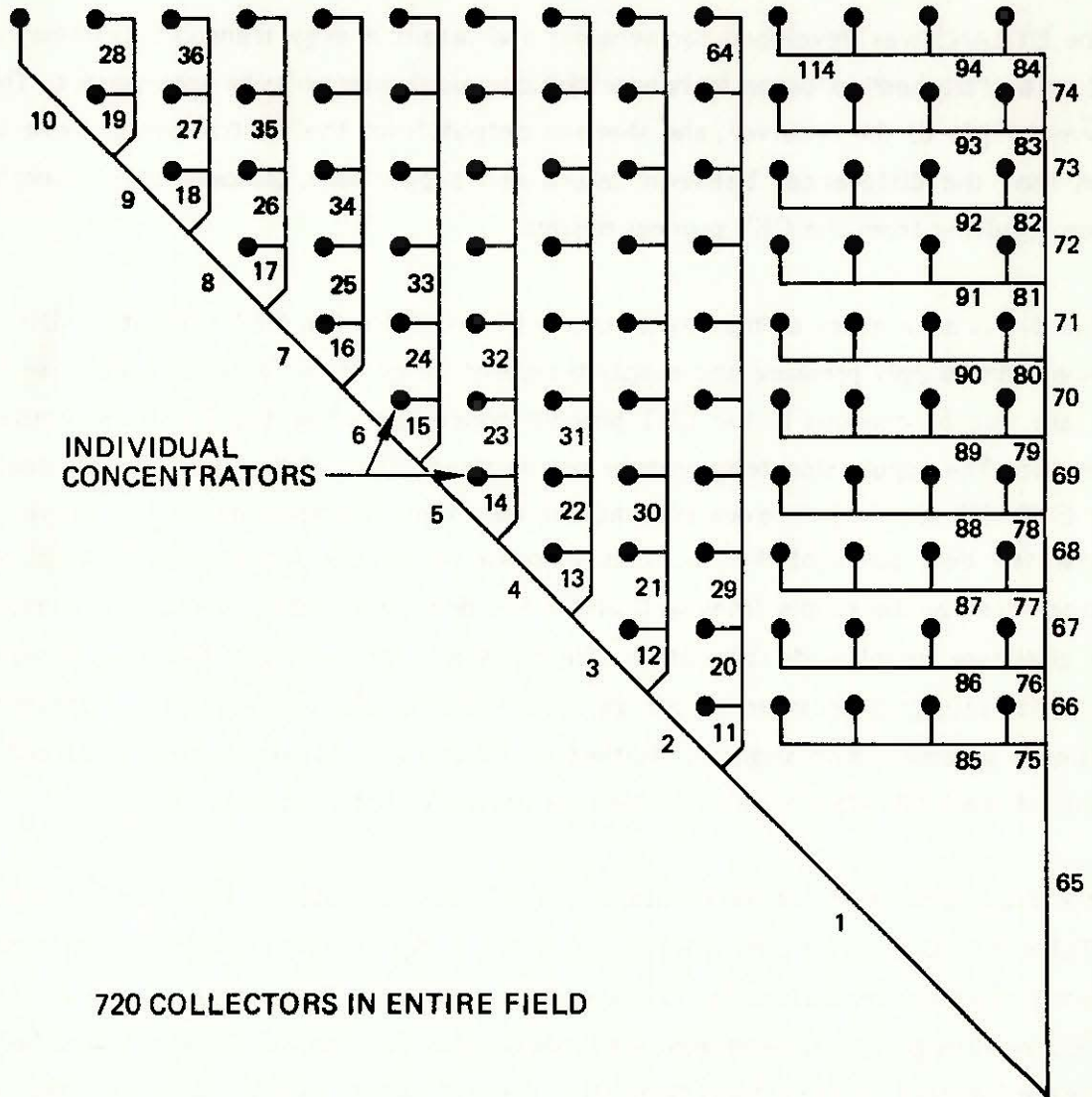
the weighted sum of the present values of the capital investment and operating costs. While there is a small maintenance cost, the key operating costs associated with the pipe network are for compressor energy requirements and for energy dissipated to the surroundings from the pipelines. The relative weight assigned by ETRANS to operating costs is thus a function of two program inputs: the cost of electricity to operate the compressor ($0.090/kWh) and the value assigned to lost energy ($0.030/kWh).

Since ETRANS was developed for sensible and latent energy transport systems, the code had to be "tricked" in order to handle the chemical energy to be transported. Therefore, thermal input to the receiver, and thermal output from the central plant, were specified such that the differences between return and supply side temperatures coincided with those resulting from the CET process design.

Table 3-1 is a summary of the key inputs to ETRANS for the CET simulation. Discrepancies between the supply pressure and supply temperature given in Table 3-1 and those in Figure 3-1 are due to changes in the CET process conditions after the ETRANS simulation had been run. The supply side temperature was increased to 420 K in the process design after the ETRANS simulation revealed that the minimum temperature in the supply side fell below the dew point of 342 K. This increase in supply temperature should keep the temperature in the supply lines well above the dew point during operating hours, although the optimum supply-side insulation thicknesses might change slightly. Similarly, the reduction in supply pressure to 3.2 bar would change the optimum pipe diameters and/or optimum pressure drop slightly. Neither of these changes would greatly affect the key result of the ETRANS simulation: the pipe network capital cost estimate.

Table 3-2 is a summary of the results of the ETRANS simulation based on the inputs given in Table 3-1. One result not listed in Table 3-2 is that the temperature drop in the supply side risers of concentrators far (in pipe distance) from the central plant was as much as $11^{o}C$, resulting in temperatures well below the dew point. As mentioned above, the increased supply temperature from the central plant should eliminate this problem. Thicker insulation (with higher capital cost) should also solve this problem. It is interesting to note, however, that attempts to force ETRANS to opt for more insulation (and thus lower temperature drops through the network) by increasing the value of heat lost had little effect on the minimum supply side temperature. For example, tripling the value of heat lost to $0.09/kWh resulted in an increase of only about $3^{o}C$ in the minimum supply-side temperatures, although the optimum insulation thickness increased one-half

Table 3-1
ETRANS INPUTS FOR CHEMICAL ENERGY
TRANSPORT FIELD SIMULATION

Operating Conditions and Field Specifications

Supply Pressure	4 bar
Supply Temperature	363 K
Flow Per Collector	53.3 g/sec
Compressor Efficiency	60%
Motor Efficiency	90%
Daytime Temperature	303 K (30°C)
Night Time Temperature	283 K (10°C)
Receiver Pressure Drop	20 k Pa
Nominal Collector Power	1.37 kW_t
RHX Supply Pipe Length	23 m
RHX Return Pipe Length	23 m
Expansion Loop Spacing	30 m
Number of Collectors in Field	720
East-West Collector Spacing	18.7 m
North-South Collector Spacing	13.4 m

Financial Data

General Inflation Rate	6%/year
Energy Cost Escalation Rate	8%/year
Plant Life	20 years
Plant Construction Time	4 years
Year of Commercial Operation	2000
Cost of Electricity	$0.09/kWh
Cost of Heat Loss	$0.03/kWh
Capital Recovery Factor	0.196
Fixed Charge Rate	0.282

Table 3-2
ETRANS CET FIELD SIMULATION
SUMMARY OF RESULTS

Overall Field Pressure Drop	0.62 bar
Total Capital Investment (1980 dollars)	$5.95 million
Temperature of Fluid Supplied to Plant	352 K

Piping and Insulation Summary

(Carbon Steel Schedule 40 Pipe and Fiberglass Insulation)

Pipe Diameter		Supply Side		Return Side	
I.D. (cm)	Nominal (in)	Length (m)	Insul. Thickness (cm)	Length (m)	Insul. Thickness (cm)
4.09	1.5	17,974	2.54	19,349	2.54
5.25	2	3,624	2.54	3,054	2.54
7.79	3	4,749	3.81	4,509	3.81
10.22	4	1,733	3.81	1,346	3.81
15.40	6	400	3.81	236	3.81
20.27	8	394	3.81	505	3.81
25.45	10	379	3.81*	333	3.81
30.48	12	948	5.08	796	5.08

*83 meters with 5.08 cm thick insulation.

inch on the smaller pipes and up to one inch on the larger pipes. The corresponding capital cost increase was about 5 percent.

A brief examination of the effects of changes in system pressure on pipe network capital cost indicate that capital cost would be reduced 15 percent to about $5 million at a nominal operating pressure of 10 bar. At present it appears that such operating pressures are not workable because of the higher dew points - condensation in the supply-side lines would be difficult if not impossible to avoid.

A rough comparison of the CET pipe network with a sensible heat transport network was made using ETRANS. A pressurized water transport system serving a 720 collector field identical to the one used for the CET analysis, and delivering the same thermal power to the central plant, was simulated. The operating pressure of the water system was 96 bar, and the temperature of energy delivered to the power cycle was 557 K. The capital cost of this transport network was estimated by ETRANS to be $4.7 million, or $68.7/m^2 of collector area.

Finally, it should be noted that the optimizations described above were performed by ETRANS on the piping network only. Design optimization of the non-network process components was necessarily separate from the ETRANS simulations. An expanded ETRANS, modified to simulate the entire CET subsystem, might opt for changes in some process variables in order to reduce the overall capital cost of the system. Such an analysis is beyond the scope of the present study. The limited excursions described above indicate, however, that cost reductions from such an expanded analysis would be minor, and that the approach taken herein has yielded a good first approximation of the capital cost of this key component of the CET system.

3.2.4   Compressor

The compressor was specified as a one-stage, centrifugal type, with a nominal power rating of 2,200 HP. The compressor is to be driven by an electric motor; during start-up and night time circulation, steam would probably not be available to operate a turbine drive. In calculating the efficiency of the CET system, the thermal equivalent of the electric energy consumed was charged against the system.

3.3 PREVENTION OF CONDENSATION IN PIPE NETWORK

A key problem with the SO_2/SO_3 reaction in CET applications is that condensation of an SO_3/SO_2* liquid mixture may be difficult to avoid in the supply-side pipe network due to the low dew point of the SO_3-rich gas stream. It has already been noted in section 3.2.3 that even during steady-state operation the temperature in the risers of some concentrators approaches the dew point.

Table 3-3 presents the dew points of the supply and return side compositions for the design pressure of 3 bar, as well as for pressures of 10 bar and 1 bar. During night time or extended shutdowns during cold weather, when the network temperature could drop below $0^{\circ}C$, condensation of an SO_3-rich liquid in the supply side lines is certain to occur, even at 1 bar pressure, unless mitigating steps are taken. Such condensation would be undesirable due to increased corrosion problems, and, perhaps more important, would be difficult to reverse in order to bring the system back on line in a timely manner. Condensation in the SO_3-lean return side lines would be unlikely to occur during steady-state operation (dew point ~$40^{\circ}C$). During extended shutdowns in cold weather, however, condensation could be a problem in the return-side as well.

Table 3-3

DISTRIBUTION SYSTEM DEW POINTS** ($^{\circ}C$) AT VARIOUS OPERATING PRESSURES
(STOICHIOMETRIC REACTANT MIXTURES)

	Pressure		
	1 bar	3 bar	10 bar
Supply Side	43	69	107
Return Side	15	38	73

**Ideal gas and solution behavior assumed. Vapor
pressure data from Reference 21.

Possible solutions to the condensation problem include heat tracing of the lines, additional insulation, changing the stream compositions, and the most viable solution, continuous circulation of warm gas through the system during shutdown. Each of these options is discussed below.

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*Predominately SO_3.

Heat Tracing

Although heat tracing may be necessary on some sensible or latent heat transport systems, it is expensive in both initial capital investment and additional operating expenses, and not attractive for the CET system considered here.

Additional Insulation

As noted in section 3.2.3, a reasonable amount of additional insulation may not, by itself, prevent supply side condensation during steady-state operation. Additional insulation, combined with composition changes described below, could possibly increase the number of nights for which supplementary heating would not be required. However, extended periods of downtime during cold weather would cause the pipeline temperature to fall below the dew point eventually, regardless of the amount of insulation, if no other measures were taken. Additional insulation, by itself, will therefore not solve the problem.

Changing Stream Compositions to Decrease Dew Point

The dew point of the streams in the SO_2/SO_3 system may be decreased by decreasing the mole fraction of the higher boiling component, SO_3. Three ways in which this could be done are discussed below:

1. Near the end of an operating day, the transport subsystem could be run in the endothermic mode only, after the exothermic reactor and power plant had been shut down. This shutdown operation would convert the entire network to the return side (SO_3-lean) composition, reducing the dew point for the entire system to $38^{\circ}C$ in the ideal case (3 atm). This would still not be low enough to avoid condensation even at moderate temperatures. Moreover, in actual practice, this operation at constant system volume would cause the system pressure (and therefore the dew point) to increase slightly, so that even the $38^{\circ}C$ dew point would not be achievable. Even if some central storage vessel were provided so that the night time system pressure could be reduced to near 1.2 bar* in addition to the above shutdown procedure, the dew point could only be reduced to about $20^{\circ}C$, still too high. The cost of such a vessel or the

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*System pressures at or below 1 bar are to be avoided due to the possibility of system contamination from the atmosphere.

process details associated with it were not examined. The endothermic shutdown procedure would not, by itself, solve the condensation problem.

2. Instead of attempting to prevent condensation throughout the subsystem during shutdown, it may be more desirable to force condensation to occur in a central condenser. The liquid SO_2/SO_3 mixture could then be stored in a central storage vessel, and vaporized prior to the next operating day using heat from an auxiliary heating source. Some mechanical refrigeration might be required, but much of the required cooling for condensation could probably be provided with air coolers: the cooler the ambient temperature, the more condensation would be required in the central faciity to prevent condensation in the pipe network, and the lower the temperature achievable in the air-cooled condenser. This approach would most likely be combined with the endothermic shutdown procedure described in 1. above, so that the condensed liquid would be primarily SO_2, and the latent heat required for restart would be minimized.

3. The entire CET system could be designed to operate with excess O_2, thereby depressing the SO_3 mole fraction and the dew points of both the supply and return sides. The base case process described in Figure 3-1 was based on a stoichiometric reaction mixture. Calculated dew points for various amounts of excess O_2 are presented in Table 3-4. At a pressure of 3 bar, even the extreme molar ratio of 90/10 (18 times the required O_2) would reduce the dew point to only $23^{\circ}C$, or to $7^{\circ}C$ if the endothermic shutdown procedure were followed. If the shutdown pressure were reduced to 1.2 bar as well, the dew point could be reduced to $-5^{\circ}C$ in the extreme excess O_2 case, but would still be above $0^{\circ}C$ for the less extreme cases. The excess O_2 necessary to avoid condensation during cold shutdown, without auxiliary heating, would result in unacceptable reductions in efficiency (mass circulated per kW of energy transported, higher compression work) and increases in capital cost (increased size of process vessels and pipelines).

Auxiliary Heating During Shutdown

The discussions of each of the preceding "solutions" to the condensation problem indicate that some auxiliary heat source, along with slow, continuous circulation of fluid throughout the transport system, will be required for the SO_2/SO_3 CET subsystem. This

Table 3-4

DISTRIBUTION SYSTEM DEW POINTS[1] ($^{\circ}$C) WITH EXCESS OXYGEN

	O_2/SO_2 MOLAR RATIO[2]				
	33/66[3]	50/50	60/40	80/20	90/10
p = 3 bar					
Supply Side	69	58	52	37	23
Return Side	38	32	28	16	7
p = 1.2 bar					
Return Side	20	16	12	4	-5

[1] Ideal gas and solution behavior assumed. Vapor pressure data from Reference 21.

[2] Ratio in completely dissociated state (no SO_3 present).

[3] Stoichiometric ratio used in base case design.

auxiliary heat source could be a storage system (hot rocks and oil, molten salt, etc.) using heat stored during daytime operation, a fired heater using some fossil fuel, or a waste heat source (only a low grade heat would be required). While heat from a storage subsystem could be used during overnight shutdowns, a fossil fuel heater would be required for longer shutdowns. Such a heater would be required anyway during start-up after extended shutdowns, for heating the exothermic reactor catalyst beds to achieve ignition.

While further design optimization may determine that it is advantageous to alter either pressure or composition in one of the ways described above, there appears to be little doubt that an auxiliary fossil fuel heater will be required for the SO_2/SO_3 CET system, and that extended periods of low power operation of this heater may be required in addition to the short periods of high power operation required for startup. The most likely scenario at present would seem to be a combination of the endothermic shutdown procedure, use of a central air-cooled condenser, and auxiliary heating. The extent to which the condenser would be used would probably vary with meteorological conditions, and would depend on the energy required for vaporization of the liquid sulfur oxide mixture relative to that of continuous heating with circulation. Low level, late afternoon insolation, not usable for power production, could probably be used for the endothermic shutdown procedure.

Finally, it is worth noting again that the CH_4/CO_2 reaction system would not suffer from condensation problems, since the reaction (as written) involves only very low boiling constituents. For this reason and others, if carbon deposition and carbonyl formation can be avoided in CET systems based on the CH_4/CO_2 reaction, this reaction would become a viable candidate for CET.

3.4 TRANSPORT SUBSYSTEM EFFICIENCY

The procedure used to estimate the efficiency of the SO_2/SO_3 energy transport subsystem is outlined in Table 3-5. Both first and second law efficiencies were estimated. The first law efficiency of 0.77 indicates that for every unit of energy which enters the transport subsystem through the receiver cavity wall, 0.77 units are discharged to the central plant power cycle as steam at 800 K, and 68 bar. Taking into account the decrease in availability of transported energy due to the difference between the input and output temperatures reduces the first law efficiency from 0.77 to 0.62. These efficiency estimates do not take into account any auxiliary heat input which might be required as discussed in section 3.3.

3-22

Table 3-5
$\underline{SO_2/SO_3}$ ENERGY TRANSPORT SUBSYSTEM EFFICIENCY

Energy Delivered To Receivers:	17.56 kcal/mole S[*]
Heat Loss To Surroundings From RHX:	0.13 kcal/mole S
Make-up Sensible Heat:	
Endothermic RHX	1.30 kcal/mole S
Exothermic Reactor	0.24 kcal/mole S
Compressor Work:	2.44 kcal/mole S
Total Energy To Operate CET Subsystem:	4.11 kcal/mole S

CET First Law Efficiency, η_1:

$$\frac{17.56 - 4.11}{17.56} = 0.77$$

CET Input Temperature: 1,400 K

Associated Carnot Efficiency, η_I:

$$\frac{1,400 - 298}{1,400} = 0.78$$

CET Output Temperature: 800 K

Associated Carnot Efficiency, η_O:

$$\frac{800 - 298}{800} = 0.627$$

CET Second Law Efficiency (Approximate), η_2:

$$\eta_2 = \eta_1 \cdot \frac{\eta_O}{\eta_I} = 0.62$$

[*]kcal per mole of sulfur circulated in the CET system.

3.5 TRANSPORT SUBSYSTEM COST ESTIMATE

Table 3-6 summarizes the capital cost estimate for the SO_2/SO_3 energy transport subsystem described in Figure 3-1. The pipe network capital cost estimate was taken directly from the ETRANS output. The total installed costs of the other major components were estimated from their purchase prices or fabrication costs by a factored cost estimation technique (References 22 and 23). Fabrication or purchase costs of the exothermic reactor, interbed heat exchangers, recuperator, and compressor were estimated from sizing calculations based on the process design, and using cost data from Reference 23. Cost estimates were updated to the 1980 base year using the Marshall and Swift Equipment Cost Index, published in "Chemical Engineering" magazine. The fabrication costs of the endothermic RHX was estimated to lie between \$1.50 and \$4.00 per lb of ceramic (References 24 and 25).

In converting the capital costs to a collector area basis, each 11 m diameter collector was assumed to have a reflective surface area of 95 m^2. The basis for the values of cost per unit of delivered power (\$/kW$_t$ in Table 3-6) is the power output to the power cycle. In converting the capital costs to a delivered power basis, the thermal power input to the cavity wall of each RHX was taken as a steady 50 kW, which corresponds to 27.7 MW$_t$, at 800 K, to the power cycle from the exothermic reactor.

The results in Table 3-6 indicate that the pipe network will be the major cost item in a chemical energy transport subsystem for distributed solar applications, accounting for as much as one-half of the total subsystem cost of \$400-487/kW$_t$. Hanseth, et al, (Reference 26) concluded that CET subsystem costs would have to be reduced to \$30-40/kW$_t$ in order to compete with dish Sterling (distributed) and central receiver solar power plants. Comparison of the results in Table 3-6 with those of Hanseth, et al, leads to the conclusion that the SO_2/SO_3 CET subsystem, and probably all CET subsystems, cannot compete on a cost basis with dish Sterling or central receiver configurations in solar thermal electric power plants. Moreover, substantial reductions in the CET cost estimates will not change this conclusion.

Finally, it is worth noting that the transport subsystem analyzed here, and therefore the capital cost estimates presented in Table 3-6 pertain to an idealized solar thermal

Table 3-6
PRELIMINARY CAPITAL COST ESTIMATE

SO_2/SO_3 Chemical Energy Transport Subsystem
For A 10 MW_e[1] Solar Thermal Electric Power Plant (No Storage)

Item	Total Installed Cost[2]			% (high side)	% (low side)
	(10^6)	($/m^2$)[3]	($/kW_t$)[4]		
Endothermic RHX	1.4 - 3.8	20 - 55	50 - 137	13	28
Pipe Network	5.9	86	213	53	44
Exothermic Reactor (with heat exchangers)	1.1	16	40	10	8
Recuperator	1.0	15	36	9	7
Compressor	1.7	25	61	15	13
Total	11.1 - 13.5	162 - 197	400 - 487	100	100

1   Power Cycle Efficiency (including electricity generation):   0.36

2   All costs in 1980 dollars.

3   Total concentrator area: 68,420 m^2

4   Basis: kW_t output to power cycle

facility, one which has no explicit* energy storage capability. Previous investigations (Reference 4) have shown that the inclusion of energy storage capability in a solar facility requires that the power-related components upstream from the storage unit be sized to handle the maximum storage charging power plus the direct, nominal power output of the plant. As (central) storage capacity is increased, the absolute cost of the energy transport subsystem will increase (assuming the insolation and power demand profiles remain the same). The cost figures in Table 3-6 should therefore be used with caution in analysis of distributed solar facilities with non-zero storage capacity.

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*The reactants in the return side of the piping network represent a small amount of stored energy.

4.0 CONCLUSIONS

1. Of the 85 thermochemical reactions considered initially, the most promising for chemical energy transport in high temperature distributed solar power plants appear to be:

   a) $SO_2 + \frac{1}{2} O_2 = SO_3$ (SO_2/SO_3)

   b) $2CO + 2H_2 = CH_4 + CO_2$ (CH_4/CO_2)
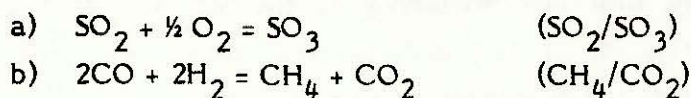
2. The carbon/hydrogen/oxygen reaction system, of which the CH_4/CO_2 stoichiometry is one variation, may suffer from two major problems.

   a. Carbon deposition during transient reactor operation, resulting in catalyst deactivation.

   b. Carbonyl formation and subsequent loss or migration of catalyst.

   These somewhat related potential problems may be avoidable, in which case the CH_4/CO_2 would become at least as attractive at the SO_2/SO_3 reaction for chemical energy transport applications. Experiments will be required to determine the extent (if any) of these problems, and ways to avoid them.

3. In view of the potential problems with the CH_4/CO_2 reaction, the SO_2/SO_3 reaction was judged to be the most viable candidate at present, and was therefore chosen as the basis for a preliminary process design and analysis of a chemical energy transport subsystem for a 10 MW_e distributed solar power plant. Key advantages of the SO_2/SO_3 reaction over other candidates include:

   a. SO_2/SO_3 system is free from irreversible side reactions.

   b. Endothermic and exothermic reaction temperatures (at reasonable pressures) match well with present high temperature distributed solar technology and steam Rankine power generation technology, respectively.

   c. Reaction is readily reversible, and catalytic in both directions, allowing good reaction control. Catalysts are well known.

   d. Considerable industrial experience exists in handling reactants.

Key drawbacks of the SO_2/SO_3 reaction include:

    a.   Reactants are toxic and potentially corrosive.

    b.   Dew points of both the endothermic and exothermic reaction products are high enough that condensation may be a problem during night time or extended shutdowns.

    c.   Intrinsic reaction rate data are not available for endothermic or exothermic reaction with pure O_2 rather than air.

4.   The estimated first law efficiency of the SO_2/SO_3 CET subsystem design developed during this study was 77 percent. Taking into account the temperature drop across the transport subsystem reduced this value to an estimated second law efficiency of 62 percent.

5.   An auxiliary heating source will be required for a distributed solar facility with SO_2/SO_3 chemical energy transport. A fairly high power, high grade energy input will be required to achieve ignition temperature in the exothermic reactor during startup (and possibly to vaporize liquid sulfur oxide mixtures), while a lower power, low grade energy input into a continuously circulating reactant stream will probably be required to prevent condensation of SO_3/SO_2 during extended cold weather shutdowns. An energy storage system (e.g., hot rocks and oil or molten salt) could provide these energy inputs for short periods (overnight), but a fossil fuel fired heater would probably be most economic for longer shutdowns.

6.   Total SO_2/SO_3 energy transport subsystem capital cost was estimated to range from $160-200/m^2 of parabolic dish collector area, which corresponds to $400-490/KW_t$ delivered directly to the power cycle. The major cost item in the transport subsystem was the pipe network, which was estimated to account for roughly 45-55 percent of the total subsystem capital cost.

7.   Preliminary comparison of pipe network costs for sensible (steam/hot water) and chemical (SO_2/SO_3) energy transport subsystems indicated that costs are roughly equivalent for subsystems which are identical on the basis of thermal power delivered to a power cycle. However, the analysis indicated that for equivalent input temperatures, the output temperature of the steam/water

subsystem will be lower than that of the SO_2/SO_3 subsystem, so that the second law efficiency of the latter would exceed that of the former.

8. Comparison with published guidelines based on systems analyses of solar thermal options indicates that the SO_2/SO_3 CET subsystem in particular, and probably CET subsystems in general, cannot compete on a cost basis with either dish Sterling (distributed) or central receiver configurations for solar thermal electric power production.

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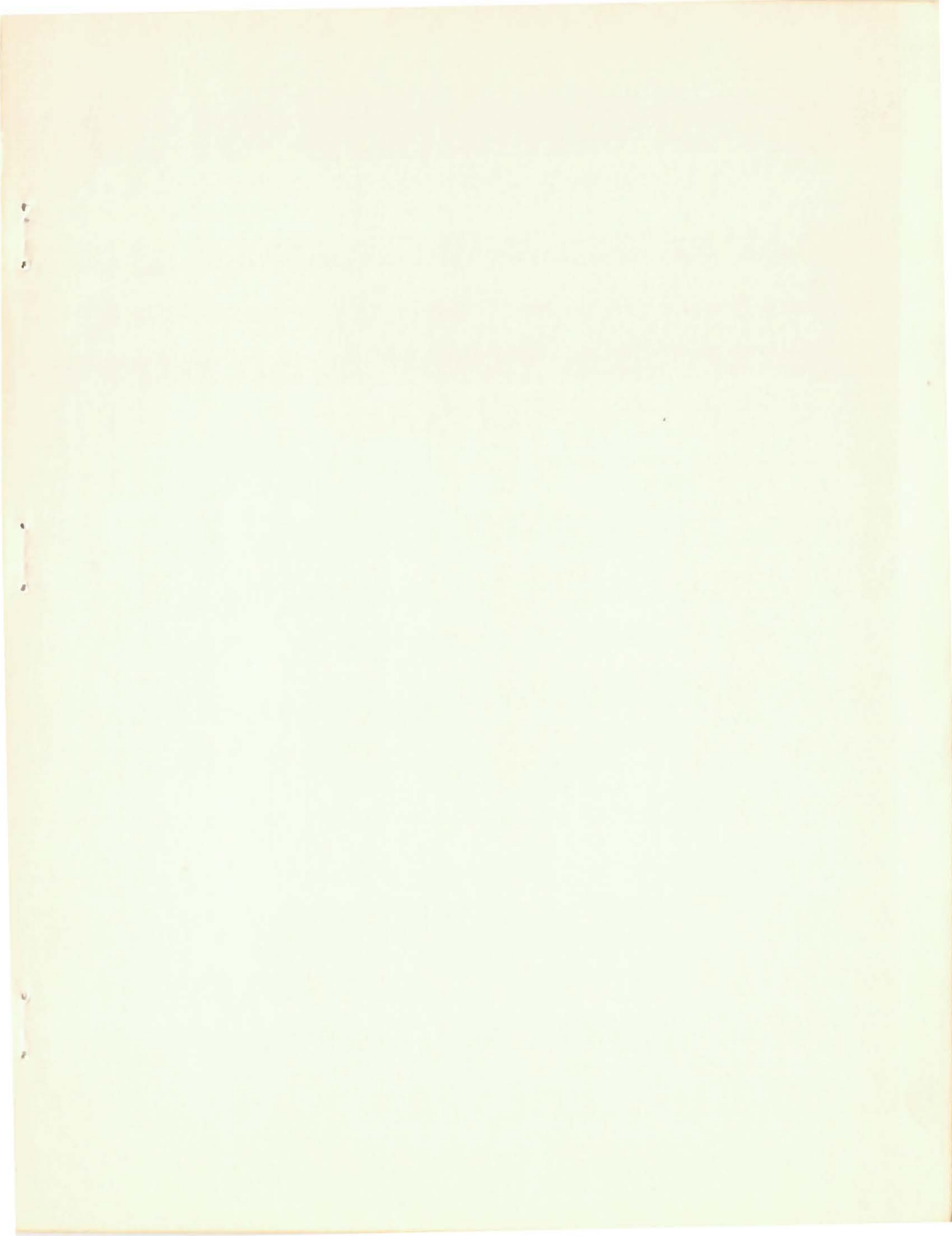   G. Nix
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