

AD A091982

Solar Energy, Vol. 17, pp. 129-136 Pergamon Press 1975. Printed in Great Britain

1

DTIC ELECTED

NOV 25 1980

NRL Reprint 8078

ANALYSIS OF GAS DISSOCIATION SOLAR THERMAL POWER SYSTEM

E. O. Hulburt Center for Space Research, Naval Research Laboratory, Washington, D.C. 20375, U.S.A.

(Received 21 December 1973) in revised form 6 November 1974)

DDC FILE COPY

Abstract—Energy collected at high temperatures in a set of scattered solar furnaces can be delivered to a central facility at intermediate temperature by using a polyatomic gas in a closed cycle circulation system. For example, gaseous SO₃ dissociates at 800 to 1000°C to form SO₂ + O₂ with absorption of heat; the products recombine in the presence of a catalyst at 500 to 600°C liberating the heat of recombination. A system using SO₃ for energy transfer and sealed for production of a continuous 100 MW of electrical power with 3 days of cloudy weather storage is outlined.

Alternate working fluids CH₄ + H₂O, COCl₂ and NF₃ are compared. Selected design options, potential problem areas, and possibilities of utilizing the collected heat for chemical processing are discussed.

NRL REPRINT 8078

INTRODUCTION

The purpose of this paper is to examine solar thermal power system concepts in which energy transfer between individual solar collectors and a central heat storage facility is effected by using reversible chemical reactions in a closed-cycle gaseous working fluid. Typical of such working fluids is SO₃ gas. SO₃ gas is dissociated into SO₂ and O₂ at temperatures in the 800 to 1000°C range with absorption of energy; in turn O₂ and SO₂ can be catalytically recombined at 500 to 600°C to produce SO₃ plus 23 kcal mole⁻¹ of chemical reaction energy. Hence, by passing SO₃ vapor through a dissociation reactor in a high temperature solar furnace, sunlight is converted to chemical energy, which is in turn converted to 500°C heat energy at a central facility. By using individual counter-current heat exchangers on each solar furnace to lower the temperature of the outflowing gas to 100°C and a large counter-current heat exchanger at the central heat storage facility to raise the temperature of the dissociated gas to the 500°C temperature of the recombination reactor and energy storage reservoir, gas circulation piping can be kept at the relatively low temperature of 100°C. With the circulation piping at 100°C, no condensation of SO₃ will occur at a 3 atm absolute working pressure.

In this paper, we think in terms of a central power station providing a continuous 24-hr electrical output of 100 MW and providing energy storage for 72 hr of no-sunlight. We examine a system meeting these requirements. Such a system contains 35,500 solar furnace collectors of 7 m dia. Energy is stored in the form of a molten-solid salt eutectic at 500°C in a cubical reservoir ~45 m on a side. Electrical power is generated using a steam driven turbogenerator whose boiler tubes are immersed in the top of the salt bath. Means are provided for continuously removing mechanically the salt solids that freeze out on the boiler tubes so that these solids settle through the underlying melt to the bottom of the

reservoir. Along the bottom of the reservoir are placed catalytic conversion pipes in which SO₂ and O₂ are passed during the day, so as to recombine, liberating heat and remelting the salt solids that have accumulated at the bottom of the reservoir.

We call a solar energy system of the above type a Solchem system. Sketches illustrating a Solchem solar thermal power plant are shown in Figs. 1-3. Figure 1 shows the set of individual solar furnaces that form the solar energy collection field, the molten-solid salt heat energy reservoir, the gaseous closed-cycle fluid system that transfers energy from the collection field to the energy reservoir, the steam boiler tubes and the turbogenerator for producing electricity. The counter-current heat exchangers and circulation pumps are not shown in the figure for reasons of simplicity. Figure 2 shows conceptually a solar collector with gas dissociation reactor and attached counter-current heat exchanger. Figure 3 shows a possible gas dissociation reactor.

Calculations have been carried out relevant to the operation and design of an SO₃ Solchem system. These studies serve to illuminate areas of difficulty and areas where gross system imperfections can be tolerated without important performance degradation. The main body of this paper is concerned with the analysis of a

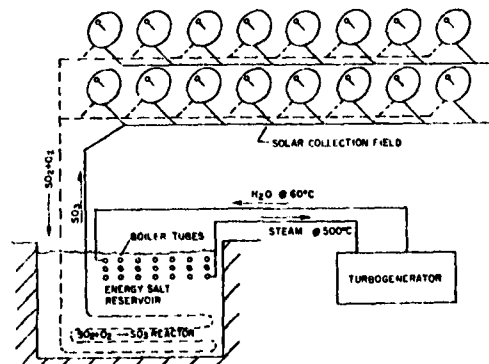


Fig. 1. Outline of gas dissociation solar thermal power plant using SO₃, SO₂ and O₂ in closed cycle energy transfer loop.

*This paper was presented at the International Solar Energy Society's U.S. Section Meeting held in Fort Collins, Colorado, August 1974.

251150 8011 25 98 JLC

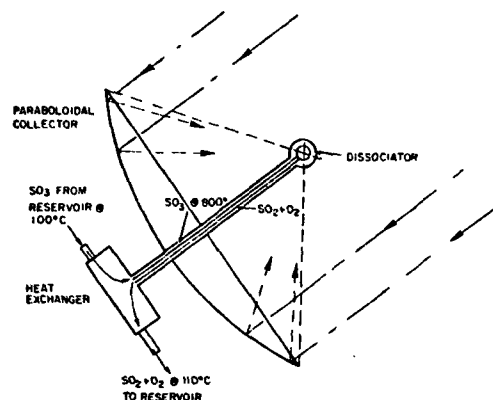


Fig. 2. Outline of solar furnace for gas dissociation solar thermal power plant.

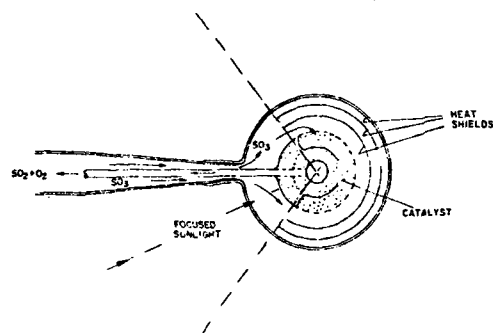
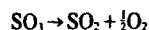


Fig. 3. Globe type gas dissociation reactor for use in solar furnace.

system designed to produce a continuous 100 MW electrical power output.

HEAT OF REACTION AND CHEMICAL EQUILIBRIA

Chemical equilibria are conveniently calculated from the JANAF Thermochemical Tables[1], which provide values of enthalpy H and Gibbs free energy G for SO_3 , SO_2 and O_2 . For the reaction



the heat of reaction ΔH

$$\Delta H = H_{\text{SO}_2} - H_{\text{SO}_3} - \frac{1}{2}H_{\text{O}_2}$$

and the pressure equilibrium coefficient K_p

$$K_p = e^{-\Delta G/RT}$$

are calculated as a function of temperature. The dissociation equilibrium for the SO_3 , SO_2 , O_2 system can be calculated for a system operating at constant temperature as follows:

Let F be the fraction of dissociation, namely

$$F = \frac{P_{\text{SO}_2}}{P_{\text{SO}_2} + P_{\text{SO}_3}}$$

where P_{SO_2} is the partial pressure of SO_2 , and P_{SO_3} is the

partial pressure of SO_3 . The equilibrium coefficient K_p controls the partial pressures of the gaseous mix

$$K_p = \frac{P_{\text{SO}_2}}{P_{\text{SO}_3} \cdot P_{\text{O}_2}^{1/2}}$$

Noting that P_{O_2} is always one-half of P_{SO_2} for a stoichiometric SO_3 feed and that the total pressure P is the sum of the partial pressures, one obtains

$$K_p = \frac{\sqrt{2}(P - 3/2P_{\text{SO}_3})}{P_{\text{SO}_3}^{3/2}}$$

Using values of K_p derived from G values in the JANAF tables for each temperature T , values of P_{SO_3} are found by trial and error. The corresponding dissociation fractions F are plotted vs temperature in Fig. 4 for systems operating at $P = 1$ atm and $P = 3$ atm.

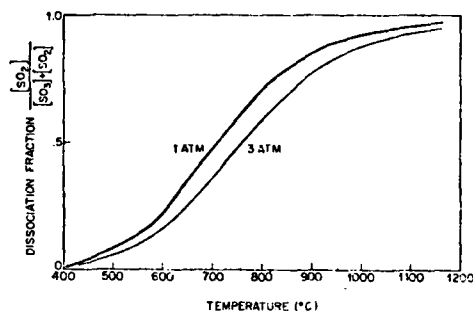


Fig. 4. Equilibrium fraction $[\text{SO}_2]/([\text{SO}_2] + [\text{SO}_3])$ vs temperature for reaction $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3$, under condition that total pressure is kept constant.

FLOW REQUIREMENTS FOR A 7m SOLAR FURNACE

In calculating flow requirements we assume that an unscattered solar flux of $1.2 \text{ cal cm}^{-2} \text{ min}^{-1}$ is incident on a 7 m dia. concentrator which reflects 85 per cent of the incident flux into the focal region of a solar furnace. We assume that 80 per cent of this collected energy is converted into chemical energy by the dissociation process. We also assume that the entering working fluid is a gas mix stoichiometrically equivalent to pure SO_3 , but containing SO_3 , SO_2 and O_2 in proportions corresponding to chemical equilibrium at $T = 500^\circ\text{C}$ and $P = 3$ atm, namely, 91.5 per cent (molar) SO_3 , 5.6 per cent SO_2 and 2.8 per cent O_2 .

The gas flow required to remove the solar energy from the hot zone of a solar furnace by endothermic reaction depends on the reactor temperature. For the conditions given above, results are summarized in Table 1.

HEAT RECOVERY FROM GAS EXITING THE GAS DISSOCIATION REACTOR

The Solchem concept envisages many gas dissociation solar furnaces connected to a central reservoir by means of near-ambient-temperature lines. For an SO_3 system at 3 atm, a 90°C collection line temperature is adequate to prevent SO_3 condensation. The heat content of the gas mix exiting a gas dissociation reactor at 900°C is a substantial fraction of the energy converted by the

Table 1. Flow requirements for a 7 m solar furnace

Flow requirement	Reactor temperature T (°C)			
	700	800	900	1000
Mole input (mole sec ⁻¹)	.750	.433	.322	.282
Mole output (mole sec ⁻¹)	.862	.545	.434	.394
Volume input @ 100°C (l. sec ⁻¹)	7.66	4.42	3.28	2.88
Volume output @ 100°C (l. sec ⁻¹)	8.80	5.54	4.42	4.02
Volume input @ T (l. sec ⁻¹)	19.9	12.7	10.3	9.84
Volume output @ T (l. sec ⁻¹)	23.0	16.0	13.9	13.7

Conditions: energy removed: 5234 cal sec⁻¹
 pressure: 3 atm
 feed composition: stoichiometrically SO₂ @ 500°C equilibrium composition

reactor into chemical energy, hence an efficient operation requires that this energy be used to heat the entering gas feed. To be specific, for each mole of sulfur containing molecules (0.23 mole SO₃, 0.77 mole SO₂, 0.39 mole O₂) exiting a reactor at 900°C equilibrium, 11.65 kcal is released by cooling the gas to 100°C. This compares with 16.75 kcal converted to chemical energy. Hence the gas dissociation approach would introduce substantial energy inefficiency were it not possible to recover most of the gas heat content of the exiting gas by transferring the heat to the incoming gas stream. The heat capacity of the inflowing gas stream exceeds that of the outflowing stream, even though fewer moles of inflowing gas are involved, so that if all of 11.65 kcal per sulfur mole available were transferred to the incoming stream, the temperature of the inflowing gas passing through the heat exchanger would be raised from 100 to 805°C.

Each solar furnace in the system is equipped with a

counter-current heat recovery unit. The heat exchangers can be designed in accord with principles described in the Kirk-Othmer Encyclopedia of Chemical Technology [2]. Suitable solutions exist for designs based on both turbulent flow and viscous flow regimes. The turbulent flow design uses a moderate number of long pipes embedded in an envelope containing counter-flowing gas. The viscous flow design uses a great many smaller pipes of small diameter and shorter length, again in an envelope containing counter-flowing gas. An important consideration that potentially simplifies design is that minor leakage between inflowing and outflowing gas streams can be tolerated without significantly degrading system performance.

Heat exchanger designs based on turbulent and non-turbulent flow are compared in Table 2. Examination of Table 2 shows that introduction of a heat exchanger into the flow system at each solar furnace causes negligible pressure drop and can effectively recover the heat content of the gas leaving the solar furnace. For turbulent flow designs, a spiral configuration of plate stampings appears attractive; for viscous flow units, concepts involving an intricately folded sheet metal membrane between streams and use of crimped seals at the ends may provide a low cost alternative to designs based on assemblies of small diameter tubes. In both cases it is desirable that the heat exchanger be made part of a combined reactor-heat recovery unit so as to reduce thermal conduction losses to the environment.

At the central station a large heat recovery unit is required to recover heat values contained in the gas stream leaving the catalytic recombination reactor. The exiting gas stream, as it cools from 500 to 100°C, provides 6.25 kcal per sulphur mole. To heat the entering gas

Table 2. Heat exchanger designs based on turbulent and nonturbulent flow for a 7 m furnace

Quantity	Turbulent	Nonturbulent
Number tubes	24	2500
D = tube diameter (cm)	1.27	.254
L = tube length (cm)	1162	62.2
Total molar flow (moles sec ⁻¹)	.542	.542
G = Mass flow per cm ² (gm cm ⁻² sec ⁻¹)	1.026	.247
Reynold's Number (DG/μ)	4203 ^a	202 ^a
Prandtl Number (c _p /k)	.64 ^b	.64 ^b
Nusselt Number (hD/k)	15.70 ^c	2.55 ^d
h = heat flow per cm ² -deg (cal sec ⁻¹ cm ⁻² deg ⁻¹)	.00125	.00102
Total surface area, all pipes (cm ²)	111300	124100
Heat flow per deg temp difference gas → wall (cal sec ⁻¹ deg ⁻¹)	139	126
$\bar{\Delta T}$ reqd. to transfer 3257 cal sec ⁻¹ g → wall + wall → g (°C)	46.0	50.6
v = gas velocity (cm sec ⁻¹)	424	112
2 Δp = two path pressure drop (atm)	.026 ^e	.0009 ^e
ΔT ₁ = temperature difference high end	95 + ΔT ₂	95 + ΔT ₂
ΔT ₂ = temperature difference low end	13.6 ^f	16.9 ^f
Ratio heat lost to 6542 cal sec ⁻¹ collected	.011	.013

a) μ = viscosity ≈ .00031 poise at mean temperature [3]

b) k = thermal conductivity ≈ .000101 cal cm⁻¹ sec⁻¹ deg⁻¹ based on values for CO₂ reduced by sq. rt. of molecular weight ratio for CO₂/SO₂ [4]; c = spec. heat ≈ .207 cal gm⁻¹ deg⁻¹ @ 480°C [1]

c) (hD/k) = .023 (DG/μ)^{0.6} (c_p/k)^{0.4} [2]

d) (hD/k) = 1.86 (DG/μ)^{0.55} (c_p/k)^{0.45} (D/s¹)^{0.55}; s¹ = uninterrupted flow length, made 12.7 cm [2]

e) Δp = 2fρv²/D, ρ = density = .00277 gm cm⁻³ @ 480°C, f = friction factor = 0.000775 + 0.0675 (DG/μ)^{-0.55} [3]

f) $\bar{\Delta T} \approx (\Delta T_1 - \Delta T_2) / \ln (\Delta T_1 / \Delta T_2)$ [2]

stream from 100 to 500°C requires only 6.14 kcal per sulphur mole. Hence, use of a perfect heat exchanger will still result in an energy unbalance of 110 cal per sulphur mole. This energy unbalance will not cause an energy loss if one operates the gas lines running back to the solar furnaces about 7 deg warmer than the lines exiting the furnaces, provided that a temperature drop of at least 7 deg occurs during the round trip circulation of the fluid. Similarly, the energy excess in gas exciting imperfect heat exchangers does not cause an energy loss provided that the energy excess is less than the conductive energy loss associated with the circulation piping.

ENERGY REQUIREMENT FOR FLUID CIRCULATION

The Solchem concept requires a network of closed circulation piping to carry the gaseous working fluid back and forth between scattered solar furnaces and the central power station. The question arises as to whether the power required to pump the working fluid through the system consumes most of the power produced. To examine this question, we imagine the solar collectors to be split into groups of 1000 furnaces located at a mean distance of 0.80 km from the central station. Gas is carried in large header pipes 60 cm in diameter. Again we consider furnaces of 7 m dia, an operating pressure of 3 atm absolute and an operating temperature of 900°C. The total closed circuit length of piping is 1.60 km. The flow for each header is 542 moles per sec⁻¹ from furnaces to central station and 402 moles per sec⁻¹ from central station to solar furnaces. The output and input flow velocities at 100°C are 1955 cm sec⁻¹ and 1450 cm sec⁻¹, so that the round trip circulation period is 96 sec. Calculating as per Table 2, the round trip pressure drop is 0.09 atm. Increasing the circulation pipe size to 90 cm decreases the pressure drop to 0.013 atm.

Let us now compare the work required to provide pumping power with the electrical output produced. We assume that 20 per cent of the sunlight collected ends up as electrical energy. On this basis, using 60 cm piping, pumping power equals ~0.6 per cent of system electrical power output.

REACTOR HEAT LOSSES AND HEAT TRANSFER PROBLEMS

Heat loss from the hot reactor is ultimately limited by radiation loss from the reactor entrance aperture or receiving plate since conduction losses from reactor walls can be adequately controlled by layers of insulation. Radiant heat loss depends on the strategies employed in implementing the Solchem concept. In order that collector costs be minimized, it is desirable that specifications as regards perfection of the optical reflectors be kept loose. The reactor concept outlined below is based on a focus requirement that the image focus diameter be not more than three times the size of that produced by a perfect on-axis optical system at perihelion. For a 7 m F/0.5 paraboloid this means that the reactor entrance aperture must be 20.7 cm and permitted angular departures of the reflector surface from an ideal figure $\pm 0.27^\circ$. With this size aperture the radiation loss for optical absorptivity α equal i.e. emissivity ϵ is 14 per cent of the energy absorbed.

The cavity type of reactor appears to be particularly well suited to Solchem since heat transfer problems are reduced to manageable proportions by the optical dilution which occurs before the radiation hits the reactor walls. A conservative size consists of a cavity of diameter 60 cm and height 100 cm, with walls, top, and bottom made up of blackened cermet tubing of 1.111 cm o.d. and 0.794 cm i.d. This tubing carries the working fluid. At the ~920°C temperature of the reactor interior, all portions of the cavity surface are at approximately the same temperature due to efficient redistribution of heating by radiative transfer. The interior surface of such a cavity contains 24,200 cm² and is subject to a mean radiation flux of 0.271 cal cm⁻² sec⁻¹. This compares with a flux of 19.5 cal cm⁻² sec⁻¹ passing through the entrance aperture and greatly simplifies heat transfer to the working fluid. The conductive temperature drop [6] from the illuminated outside of the tube to the interior tube wall is 0.9°C. Radiative transfer of half the heat across the tubing interior requires a temperature drop of 15°, so that each tube can be considered approximately isothermal around its circumference. Transfer of heat into the working fluid is carried out by arranging the tubing in 36 parallel flow circuits each of 605 cm length. The mean temperature difference between walls and gas is then 40.1°C, which means that the gas exits the reactor at a temperature 13.9°C below cavity wall temperature. Ignoring the drag effect of contained catalyst, the pressure drop is 0.024 atm. The total volume available for dissociation is 12.8 l, which means that only a small packing density of catalyst is required.

The reactor outlined above is of larger size than really needed. The heat loss by conduction to the atmosphere is calculated at 4.6 per cent of the 5620 cal sec⁻¹ collected, based on *American Institute of Physics Handbook* [4] conductivity values for diatomaceous firebrick 20 cm thick. By designing the heat exchanger to be imbedded in the insulation blanket, some of this leakage heat should be recoverable.

An alternative, windowed reactor design has been considered in which the incident sunlight is imaged directly onto the catalytic surface on which dissociation reactions occur. In such a design it is easy to provide two passes of the working gas through the catalytic medium. The window can be sealed to the reactor housing with a gasket which can be kept at low temperature by water cooling or by directing a small fraction of 100°C SO₂ at the gasket area. The radiant heat loss of this type of reactor is about the same as encountered with the cavity reactor. The small size of the reactor makes reduction of conductive heat loss easier to control than for the cavity type. Windowed reactors are particularly attractive for light-sensitive working fluids such as COCl₂.

Reactors can be designed for collectors providing a lower energy density image, e.g., on-axis collectors with looser optical specifications, off-axis scoop-like paraboloidal collectors designed to provide largely upward-directed cones of light, and multiple mirror collectors using tower mounted reactors [7]. Such reactors require α/ϵ ratios of 2-3 to keep radiation energy losses at a reasonably small fraction of collected energy. Emissivity control requires

that light be received on a more or less flat blackened metallic surface through which the received heat must be conducted to the interior of the reactor. Energy flow densities are high so that the receiving plate must be thin to avoid excessive temperature drop, and the received energy must subsequently be efficiently distributed to a much larger surface area to provide adequate heat flow to the working fluid. This energy redistribution requires use of metallic vapor heat piping. To be specific, an efficient reactor with a 28 cm dia orifice receiving plate can be designed to receive the upward-directed cone of light from an off-axis 7 m dia paraboloidal reflector. Such a reactor uses a sodium vapor heat pipe to transfer heat from the receiving plate to the exterior walls of stainless steel tubing which carries the working fluid. With $\alpha/\epsilon = 3$ radiation loss is about 11 per cent of the energy collected.

HEAT LOSS IN CIRCULATION PIPING

It is envisaged that Solchem circulation lines are insulated from a 20°C ambient environment by 10 cm of sawdust. Conduction loss in 1.6 km of 60 cm collection lines is then about 0.6 per cent of the chemical energy collected.

REQUIREMENTS FOR A 100 MW ELECTRICAL CONTINUOUS OUTPUT POWER PLANT WITH MOLTEN EUTECTIC ENERGY STORAGE

A commercial, scale power plant based on the Solchem approach is envisaged as having 20 m dia collectors scattered over 7 km² of land area. Each collector delivers 85 per cent of a mean incident 1.2 cal cm⁻² min⁻¹ of unscattered solar radiation to a reactor in which 80 per cent of the incident flux is converted to chemical energy. We assume that total thermal losses in the piping system and thermal storage reservoir amount to 10 per cent of the collected energy. Under these conditions each 20 m collector provides at the central station 38500 cal sec⁻¹ of 500°C heat. We assume that with an optimal southwest U.S. location this energy is available an effective 8 hr per day. We assume that the 500°C heat is convertible to

450°C high-pressure steam, and that a turbo-electric generator efficiency of 80 per cent of that of a Carnot engine operating between 450°C and 60°C is realizable. With these assumptions, and assuming 0.6 per cent of produced electricity goes into fluid pumping, a single 20 m collector ends up contributing 23 kW to continuous electrical generation. Thus for 100 MW continuous electrical output, 4350 collectors are required. The total area of these collectors facing the sun is 1.37 km², so that 20 per cent of the 7 km² collector field area would be covered by collectors. The overall efficiency for conversion of unscattered sunlight into electrical energy is 26 per cent.

Table 3 summarizes requirements for a continuous 100 MWe system with 3 day salt eutectic energy storage. The storage system has been sized based on data on NaCl, CaCl₂ eutectic[8] using a heat of fusion of 6.8 kcal mole⁻¹[9]. Storage of gaseous chemical dissociation products is an alternate approach to the energy storage problem, but requires very large storage volumes. Another alternative is pumped-water storage using Colorado river dams.

GAS DISSOCIATION AND RECOMBINATION REACTION RATES

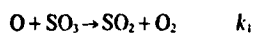
For a gas to operate as a suitable working fluid for recovering solar energy, it must be capable of dissociating rapidly at the solar furnace temperature, and it must not recombine extensively in the heat exchanger as it drops to collection line temperature. SO₂ meets these requirements provided a catalyst is used to accelerate the dissociation reaction. Purely gas phase reactions are too slow to provide sufficiently rapid SO₂ dissociation rates.

The chemistry of sulfur-oxygen flames has been studied by many workers (Emelius[10], Fenimore and Jones[11], and Mulcahy *et al.*[12]). Typically, an SO₂/SO ratio of ~ 2 per cent is produced under a wide variety of burn conditions. The SO₂/SO ratio appears not to be determined by thermodynamic equilibrium. Instead, two fast reactions involving atomic oxygen dominate the flame; namely

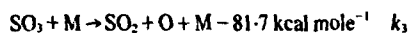
Table 3. Sizing for a 100 MW solar dissociation power plant

Average power plant output (cal sec ⁻¹)	2.389 x 10 ⁷
Unscattered solar flux (cal cm ⁻² min ⁻¹)	1.2
Overall efficiency during sunshine	0.264
Duty cycle of energy collection	0.333
Mean electrical power resulting from single 7m solar furnace (cal sec ⁻¹)	2.82 kw
Number 7m collectors required	35510
Equivalent number of 20m collectors	4350
Storage requirement (cal)	1.436 x 10 ¹³
Volume required for NaCl/CaCl ₂ heat sink (cm ³)	8.786 x 10 ¹⁰
Side of cube having this volume (m)	44.5
Overall efficiency during sunshine	0.26

flame; namely

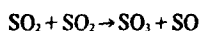


with rate coefficients $k_1 \sim 10^{12} \text{ cm}^3 \text{ mole}^{-1}$ and $k_2 \sim 2 \times 10^{15} \text{ cm}^3 \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1}$. The atomic oxygen responsible for these reactions is produced by the reaction

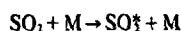


which has been studied by Nettleton and Sterling [13] using shock tube techniques. Extrapolating from k_3 values listed by Kondratiev [14] for 2013°C down to 1000°C using an Arrhenius activation energy of dissociation, one obtains a k_3 value of $10^3 \text{ cm}^3 \text{ mole}^{-1}$, which means that pure SO_3 at 3 atm will disappear with a time constant of $\tau = 0.17 \text{ sec}$. This purely gas phase decomposition time is longer than the residence time of the gas in a practical size reaction-chamber, hence surface reactions must be employed to achieve chemical equilibrium.

On the other hand, purely gas phase recombination rates are too slow to cause significant heat evolution in the heat exchanger. The controlling reaction



has been studied by Gayden *et al.* [15], who conclude that the reaction proceeds by an excited state of SO_2



where SO_2^* is the 3B_1 excited state of SO_2 , about 74 kcal mole $^{-1}$ above the ground state. At 1000°C the relaxation period is estimated at 126 sec, so that little heat is liberated once the gas mix leaves the catalytic dissociation chamber.

Catalysts can provide adequate reaction rates for SO_2 decomposition. For example, platinized asbestos, which is used by industry for production of sulfuric acid, should be suitable for the decomposition process. V_2O_5 is also used for acid production. With V_2O_5 Calderbank [16] quotes an

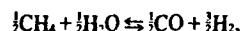
SO_2 dissociation rate of

$$r = e^{-5000/RT} + 22.75 \frac{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}} \text{ moles sec}^{-1} (\text{g catalyst})^{-1/2}$$

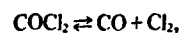
Using 1.7 kg of catalyst, a dissociation rate of 0.31 moles sec $^{-1}$ is produced at 560°C with the reaction rate increasing rapidly with temperature. Unfortunately, V_2O_5 deteriorates at temperatures above 560°C. However, since lesser volumes of platinized asbestos are required than V_2O_5 in sulfuric acid production [17], and since volumes of more than a liter can be accommodated, a suitable catalyst should not be hard to find.

ALTERNATE WORKING FLUIDS

In addition to the SO_2 dissociation cycle $\text{SO}_2 \rightleftharpoons \text{SO}_2 + \frac{1}{2}\text{O}_2$, three additional potentially useful gas phase reaction cycles have been identified, namely: (1) the gas reforming—methanation cycle



the phosgene dissociation cycle



and the nitrogen trifluoride dissociation cycle



Dissociation fraction versus temperature curves are shown in Fig. 5 for SO_2 , $\text{CH}_4 + \text{H}_2\text{O}$, and COCl_2 . The dissociation curve for NF_3 falls closely on that of $\text{CH}_4 + \text{H}_2\text{O}$. However, as yet N_2 and F_2 have not been made to recombine directly without electric spark, despite extensive research.

Each of the above cycles has distinctive problems as regards condensation in distribution lines, heat conduction, toxicity, corrosion and catalyst life. Some of these properties are listed in Table 4. The gas reforming—methanation cycle is the only one of the four that has relatively low toxicity, high thermal conductivity and chemical reducing properties. It suffers from a problem of coke build-up on the dissociation catalyst bed [21]. This

Table 4. Characteristics of gas dissociation working fluids

Feed	Heat (1) dissociation (kcal mole $^{-1}$ feed)	Condensation (2) temperature °C			Thermal conductivity (2) lightest dissociation component (cal cm $^{-1}$ °C $^{-1}$) @300°K	Recombination (4) catalyst	TLV (5) most poisonous component (ppm)	Lethal (5) concentration ~ 1/2 hour (ppm)
		3-3 atm	3-3 atm	3-1 atm				
SO_2	24	80°	60°	52°	0.00064	Pt or V_2O_5	0.3	10-20 ppm unbearable
$\text{H}_2\text{O} + \text{CH}_4$	26	112°	100°	82°	0.00043	H_2	50	6000
COCl_2	26	40°	37°	8°	0.00060	activated charcoal	0.1	25
NF_3	31 (2)	~ -2°	~ -10°	-120°	0.00062	?	0.1	(6)

(1) 457°C data from ref. [3]

(2) Interpolated or extrapolated using data from ref. [10]

(3) From ref. [4] p 4-149

(4) From ref. [2], Vol. 4, pp 447-452; Vol. 10, pp 467-470; Supplement Vol., pp 877-879.

(5) TLV is Threshold Limit Value, formerly maximum allowable concentration per day after day exposure, set by American Conference of Governmental Industrial Hygienists. Data from ref. [10] pp 1129, 524, 1059, 779.

(6) For NF_3 , "concentrations of 50-250 ppm are dangerous, even for brief exposures." from ref. [19] p 822. Emergency exposure limits for both F_2 and NF_3 are 10 ppm for 30 minutes. [20]

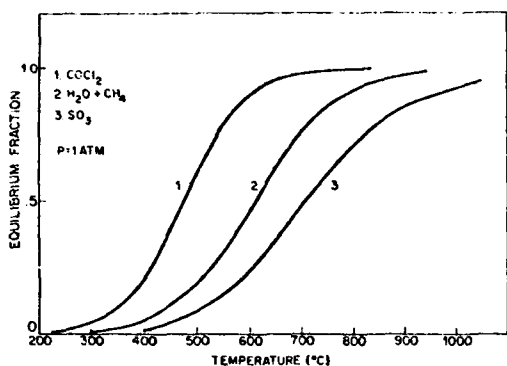


Fig. 5. Comparison of dissociation curves for COCl_2 , $\text{H}_2\text{O} + \text{CH}_4$, and SO_2 as working fluids for a gas dissociation solar power system. The dissociation curve for NF_3 closely matches that of $\text{H}_2\text{O} + \text{CH}_4$. Results are based on JANAF data [1].

difficulty is controlled in industrial practice by use of a 2.5:1 or 3:1 steam to methane ratio. If one accepts the increased pumping load caused by use of excess steam, the gas reforming-methanation cycle is probably the easiest fluid with which initially to work.

For the oxidizing gas feeds, it is essential that bone-dry conditions be maintained in order that corrosion be avoided. Trapping of hydrogen containing vapors in the form of acid salts such as KHSO_4 and KHF_2 appears to be a promising approach for control of gas purity. The toxicity of the circulating gases is an annoying problem. However, the quantities of gas are not as large as handled by industry. Small chemical tank cars hold 12000 gal. of liquid. This corresponds to about 65 tons of SO_2 . The circulation line for 1000 7 m solar furnaces contains about 2.8 metric tons of SO_2 , of which maybe two-thirds could be released into the atmosphere under catastrophic failure. Thus, the area hazard would be only 5 per cent of that of a tank car rupture. The release of phosgene can be a subtle danger since its presence in dangerous concentration is not always noticeable or unpleasant. As used in a Solchem system, phosgene always is mixed with chlorine which provides a warning tag.

The condensation point for fluid in the feed line determines the required operating temperature and insulation requirements of the circulation piping system. For NF_3 and low pressure COCl_2 , uninsulated lines can be employed. For SO_2 and $\text{H}_2\text{O} + \text{CH}_4$, thermal insulation must be employed to prevent heat loss. Condensation at night is a minor problem since the energy required for reevaporation when the blowers are turned on in the morning is a negligible fraction of the energy collected.

ECONOMIC CONSIDERATIONS

The viability of collection of solar energy by the Solchem process depends primarily on the cost of the multiply repeated units of the system, namely the solar collectors with their reactor and integral heat recovery units. The major cost component is expected to be the pointable reflectors which must track the sun. The fact that these collectors point at the sun, however, means that energy per unit area of collector surface is maximized and energy collection can be continued throughout most

of each cloudless day. For example, energy collection with the French solar furnace on good days decreases to roughly 90 per cent of the noon value 4 hr away from noon during summer and 3 hr away from noon in winter [22]. In addition, Solchem promises high overall thermal efficiency. Thus one can afford to pay more per unit area of reflector surface with a Solchem system than with any other solar energy collection concept.

PRISM REFLECTORS

The most likely type of reflection surface to be employed is a metalized plastic or glass mirror. However, on-axis paraboloidal reflectors directed at the sun permit the use of total-reflection multiprism sheets, which we call "Fresnel" reflectors. Such reflectors have a smooth front surface, conforming to the paraboloidal surface of a normal mirror, and a back surface made up of 90° prisms, the apices of which radiate from the optical axis—mirror surface intersection point, as shown in Fig. 6. These reflectors require no metalizing. They do require that the back prisms be accurately 90° , since errors in the prism angle are multiplied by 4 in the angular spread produced in the reflected beam. It is unknown whether the "Fresnel" reflectors will prove ultimately less expensive and more durable than metalized reflectors, but their potential should be examined. (They cannot be used in cylindrical concentrators or tower systems since reflection is achieved only when sun, receiver and prism apices are coplanar.)

USE OF SOLCHEM HEAT FOR CHEMICAL PROCESSING

We have thus far considered the collection of solar energy for the production of electricity. An attractive additional possibility is the collection of solar energy for chemical processing. Depending on system design, Solchem delivers to a central station large quantities of heat in the 400 to 600°C temperature range. Heat at these temperatures is useful in many chemical processes. One process feasible at Solchem temperatures is the distillation of oil from oil shale. Furthermore, it seems possible that Solchem could be engineered to deliver heat at 700°C . In such a case, energization of the production of hydrogen + CO (synthesis gas) from coke plus steam (water gas process) would become possible. In other words, with proper design Solchem energy collection

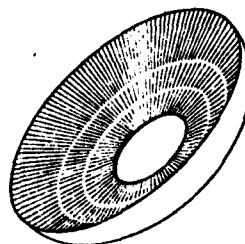


Fig. 6. This figure illustrates the orientation of apex lines as required in a paraboloidal reflector using total reflection. The back surface of the reflector contains right angle prisms which totally reflect incident sunlight after 2 reflections from mutually orthogonal planes.

could impact the recoverability of gaseous and liquid fuels.

SUMMARY AND CONCLUSION

The use of endothermic gas phase reactions appears to make possible efficient, large, scale collection of solar energy in a two step concentration process. The first step involves optical concentration of sunlight by on-axis or off-axis (scoop) paraboloidal reflectors, or by multimirror reflector arrays (tower collectors). At the focus of each solar furnace collector, light is converted to chemical energy by dissociating a gaseous working fluid. The second step involves collection of the gaseous dissociation products from many solar furnaces and their delivery to a central station by means of a closed loop network of pipes in which circulation is driven by externally powered blowers. At the central station, the gas is recombined with emission of heat at a temperature sufficiently high to provide thermal power for dry steam turbo-electric generation or industrial, scale chemical processing. Through the use of heat recovery units on each furnace and at the central station, near ambient temperature circulation lines can be employed. Using the above process in an optimum geographic area, a total of 4350 20 m dia collectors should provide an electrical output of 2400 MWh of electricity per day.

The viability of this approach to the large, scale use of solar energy will be dependent on the capital cost of the collectors, reactors and heat recovery units and on the engineering difficulties encountered in reducing these concepts to practice. It is planned to demonstrate the sunlight-chemical energy conversion process using the solar furnace at the White Sands Thermal Effects Facility. First tests will use a steam-methane working fluid. However, a meaningful effort will require a substantial developmental and experimental program with early emphasis on production of low cost collector units.

Acknowledgement—Information provided by R. G. Taylor and R. N. Hazlett contributed substantially to this paper. The author is particularly indebted to J. J. Nemecek, who has played a creative role in the development and critical evaluation of Solchem concepts.

REFERENCES

1. D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, Second Edition, NSRDS-NBS 37. U.S. Government Printing Office, Washington D.C., 20402 (1971).
2. *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., 10, 821-823. John Wiley and Sons, Inc., New York (1966).
3. *Handbook of Chemistry and Physics*, 48th ed., F-44 and F-2. The Chemical Rubber Co., Cleveland, Ohio (1967-1968).
4. *American Institute of Physics Handbook*, Third Edition, 4-149, 4-154 and 4-159. McGraw-Hill, New York (1972).
5. R. V. Dunkle, Shear fan-heat exchanger. Paper presented at Fourth Australian Institute of Nuclear Science and Engineering Conference (August 1969).
6. W. H. Kohl, *Handbook of Materials and Techniques for Vacuum Devices*, 66. Reinhold Publishing Co., New York (1966).
7. A. F. Hildebrandt, G. M. Haas, W. R. Jenkins and J. P. Colaco, Large scale concentration and conversion of energy. *EOS Trans. Am. Geophys. Un.* 53, 684-692 (1972).
8. E. M. Levin *et al.*, *Phase Diagrams for Ceramists*, compiled by National Bureau of Standards, M. K. Reser, Editor, 384. The American Ceramic Society, Columbus, Ohio (1964).
9. Values for salt components from *American Institute of Physics Handbook*, 1st edn, 4-137 and 4-147. McGraw-Hill, New York (1957).
10. H. J. Emeleus, The phosphorescent combustion of sulphur. *J. Chem. Soc.*, 1942 (1928).
11. C. P. Fenimore and G. W. Jones, Sulfur in the burnt gas of hydrogen-oxygen flames. *J. Phys. Chem.* 69, 3593 (1965).
12. M. F. R. Mulcahy *et al.* Kinetics of interaction of oxygen atoms with sulfur oxides, *Twelfth Symposium (International) on Combustion*, 323. The Combustion Institute, Pittsburgh, Pa. (1968).
13. M. A. Nettleton and R. Stirling, Formation and decomposition of sulfur trioxide in flames and burned gases, *Twelfth Symposium (International) on Combustion*, 635. The Combustion Institute, Pittsburgh, Pa. (1968).
14. V. N. Kondratiev, *Rate Constants of Gas Phase Reactions*, translated by L. J. Holtschdag, edited by R. M. Fristrom. U.S. Department of Commerce Publication COM-72-10014, Washington D.C. (1972).
15. A. C. Gaydon, G. H. Kimbell and H. B. Palmer. A shock-tube study of the Kinetics of decomposition of sulphur dioxide. *Proc. Roy. Soc.* A276, 461 (1963).
16. P. H. Calderbank, Contact-process converter design. *Chem. Eng. Prog.* 49, 585 (1953).
17. *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd edn, 19, 467-470. John Wiley and Sons, Inc., New York (1969).
18. *Handbook of Chemistry and Physics*, 40th edn. The Chemical Rubber Co., Cleveland, Ohio (1958-59).
19. N. Irving Sax, *Dangerous Properties of Industrial Materials*, 3rd edn, 1019. Reinhold Book Corp., New York (1968).
20. *Liquid propellant handling storage and transportation*, CP1A No. 194, 3. Chemical Propellant Information Agency, Silver Spring, Md. (May 1970).
21. M. R. Arnold, D. Atwood, H. M. Baugh and H. D. Smyser, Nickel catalyst for hydrocarbon-steam reaction. *Ind. and Eng. Chem.* 44, 999 (1952).
22. Informal comment by Claude Royere.

Accession For	
NTIS	<input checked="" type="checkbox"/>
GRA&I	<input type="checkbox"/>
ERIC TAB	<input type="checkbox"/>
Unannounced	
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	20 21