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SOLAR RADIANT HEATING OF GAS-PARTICLE MIXTURES

Final Report, FY 1985 and FY 1986

A.J. Hunt, J. Ayer, P. Hull, F. Miller,
J.E. Noring, and D. Worth

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SOLAR RADIANT HEATING OF GAS-PARTICLE MIXTURES

Final Report (FY 1985 and FY 1986)

By

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FOREWORD

The research and development described in this document was conducted within the U.S. Department of Energy's (DOE) Solar Thermal Technology Program. The goal of the Solar Thermal Technology Program is to advance the engineering and scientific understanding of solar thermal technology, and to establish the technology base from which private industry can develop solar thermal power production options for introduction into the competitive energy market.

Solar thermal technology involves concentrating solar radiation by means of tracking mirrors or lenses onto a receiver where the solar energy is absorbed as heat and converted into electricity or incorporated into products as process heat. The two primary solar thermal technologies, central receivers and distributed receivers, employ various point and line-focus optics to concentrate sunlight. Central receiver systems use fields of heliostats (two-axis tracking mirrors) to focus the sun's radiant energy onto a single tower-mounted receiver. Parabolic dishes up to 17 meters in diameter track the sun in two axes and use mirrors or Fresnel lenses to focus radiant energy onto a receiver. Troughs and bowls are line-focus tracking reflectors that concentrate sunlight onto receiver tubes along their focal lines. Concentrating collector modules can be used alone or in a multi-module system. The concentrated radiant energy absorbed by the solar thermal receiver is transported to the conversion process by a circulating working fluid. Receiver temperatures range from 100°C in low-temperature troughs to over 1500°C in dish and central receiver systems.

The Solar Thermal Technology Program is directing efforts to advance and improve promising system concepts through the research and development of solar thermal materials, components, and subsystems, and the testing and performance evaluation of subsystems and systems. These efforts are carried out through the technical direction of DOE and its network of national laboratories and SERI who work with private industry. Together they have established a comprehensive, goal-directed program to improve performance and provide technically proven options for eventual incorporation into the nation's energy supply.

To be successful in contributing to an adequate national energy supply at reasonable cost, solar thermal energy must eventually be economically competitive with a variety of other energy sources. Components and system-level performance targets have been developed as quantitative program goals. The performance targets are used in planning research and development activities, measuring progress, assessing alternative technology options, and making optimal component

developments. These targets will be vigorously pursued to insure a successful program.

This report summarizes the research conducted in FY 1985-86 on one of the innovative solar energy conversion technologies under consideration by the Solar Thermal Technology Program, namely, the high temperature absorption and chemical conversion of highly concentrated solar energy using a gas-particle mixture. The short-term goal of this multi-year research effort is to develop the technology base needed for the Solar Thermal Technology Program to compare this conversion technology on a sound technical and economic basis with other competitive methods to absorb and convert concentrated solar energy. If this conversion technology is found to be economically attractive, the research results would be very useful to the solar community in the design, construction, and operation of solar plants employing this conversion technology.

EXECUTIVE SUMMARY

Most solar thermal conversion methods rely on a technology that is derived from more than a century of experience with fossil fuel combustion. This technology is relatively mature, but has biased contemporary thinking about heat transfer mechanisms towards convection, conduction and infrared radiation. Concentrated sunlight, however, is an intense source of purely radiant energy, originating from a 5800°K blackbody, that has quite different characteristics from the less intense and longer wavelength radiation emitted by fossil fuel combustion. It is therefore appropriate to develop new solar energy conversion methods that better match the characteristics of solar radiation.

One such method under investigation at Lawrence Berkeley Laboratory relies on the use of ***small particles, dispersed in a gas, to directly absorb concentrated solar radiation.*** In absorbing materials, radiation is converted to heat within distances comparable to the wavelength of light. Therefore, absorbers in the form of dispersed micron-sized particles can collect the solar radiation efficiently. Moreover, small particles present a very large surface area per unit mass; heat and mass transfer, and surface chemical activity, are greatly enhanced.

This report describes the research program at Lawrence Berkeley Laboratory during FY 1985-1986 to investigate a unique solar receiver concept embodying the above principle. In this receiver, a gas-particle mixture directly absorbs concentrated sunlight to drive an endothermic chemical reaction for the production of a useful fuel or chemical. We call this solar receiver STARR, an acronym for *S*olar *T*hermally *A*ctivated *R*adiant *R*eactor. The objective of the research is to understand the optical, thermodynamic, and chemical processes in solar heated particle suspensions through a balanced program of analytical and experimental investigations. This work was built upon previous work in using gas-particle mixtures to heat a gas, which culminated in the successful test of the concept in 1982.

A previous report covering the work in FY 1984 (see reference 1-12) described the results of the first year of investigation of this project. In that year the research program accomplished several important tasks. A survey was performed to identify candidate chemical reactions suitable for the STARR receiver. Candidates were chosen involving thermochemical reactions in gases or reactions between gases and light absorbing solids. A number of suitable reactions were identified and optical, physical, and chemical data were compiled for the compounds involved.

The FY 1984 Report describes optical analysis techniques that were developed to aid in the design and to predict the performance of the STARR receiver. Computer programs using Mie theory were written to calculate the wavelength dependent absorption and scattering. The heat transfer properties of radiatively heated gas particle suspensions were analyzed. A model was developed to calculate the conductive heat transfer between a particle and the surrounding gas for any particle size. The analysis was used to predict two important performance parameters in the STARR receiver: the maximum temperature difference between the particles and gas, and the achievable heating rates.

The research described in this FY 1985-1986 report builds on the prior work and extends the investigation into the areas of chemical processing of gas-particle suspensions. Four types of chemical processing in gas-particle suspensions were identified and candidate reactions identified earlier were classified by type. The four processes were: 1) the particle acts as a heater for a gas phase reaction, 2) the particle is the feed stock, 3) the particles react with the gas, and 4) the particle acts as a catalyst or photoinitiator to promote a reaction in the gas. This classification was chosen to emphasize the differences in reaction mechanisms rather than the end use of the products. Using this approach various classes of reactions were compared and general conclusions drawn about the advantages and problems of each. Sets of technical and economic criteria were developed and used to arrive at a quantitative comparison of candidate reactions. Useful reactions were found in each type but the case in which the particle acts as a catalyst and photoinitiator appeared to be the most attractive of the reactions evaluated to date.

An existing set of computer codes for calculating the chemical thermodynamics was implemented on the LBL computer system and significantly upgraded by the addition of considerable chemical data for reactions of interest in this work. The codes were used to analyze the effects of process conditions on various chemical reactions.

The development of a model to predict the overall gas-particle radiant interaction was initiated. A two-flux model was developed and used to produce insights into the effects of the direction of flow of the heated particle stream with respect to the incoming solar radiation.

The laboratory program continued the investigation of radiant heating of gas-particle mixtures to verify the analytical calculations and to explore radiantly induced chemical reactions. A solar simulator produced intense radiant flux to

heat flowing gas-particle suspensions to high temperatures. It was demonstrated that a large fraction of the particle could be converted from one oxide state to another in the very short residence time in the receiver/reactor. A number of gas and particle reactions were explored. Temperatures of over 800° Celsius were reached and peak fluxes of over 4000 kW/M^2 (4000 suns) were obtained with the solar simulator.

The increased understanding of chemical processes possible in the STARR receiver as a result of this analysis and experimental research has generated information regarding future applications. No insurmountable barriers were encountered during this study that would preclude the eventual success of this innovative receiver concept. The general conclusion is that the advantages of this approach merit its further development.

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1. INTRODUCTION

Concentrated sunlight is a resource with quite different characteristics than conventional energy sources. Solar energy originates from the sun with a black body temperature of 5800° Kelvin and arrives in the form of pure radiant energy. This high temperature means that most of the energy is carried by photons with much shorter wavelengths than is characteristic of conventional thermal energy sources. Existing energy conversion techniques were developed for much cooler (longer wavelength) heat sources where radiation is less important. Thus, traditional methods of heat exchange (e.g., pipes) are not necessarily the best method for converting sunlight to heat or other forms of energy.

To use the solar resource in the most efficient and economic manner, it is important to examine alternative methods for its capture and utilization. This report addresses the issues of the direct absorption of concentrated sunlight by particles and its conversion to useful heat and chemical products. This approach offers significant advantages over current methods of solar conversion.

Studies of innovative solar receiver designs using small particles dispersed in a gas to directly absorb concentrated solar have been underway at Lawrence Berkeley Laboratory since 1976 [1]. The initial research investigated thermal applications wherein the particles were used to heat air to drive a Brayton cycle turbine [2], Solar engines [3], or to provide industrial process heat. These studies culminated in the successful test of the Mark I 30 kW gas receiver at Georgia Tech's Advanced Components Test Facility in 1982 [4-7]. Following the solar testing of SPHER, comparative studies of a number of high temperature gas receiver concepts were performed [8,9] that identified the SPHER approach as a top candidate for certain central receiver applications. Alternative concepts using carbon particle absorbers without windows are currently being pursued by private industry in the United States [10]. A general research program on radiant heating of microparticles has been initiated in Germany[11].

The more recent focus of the research, and the main topic of this report, is the use of radiantly heated particle suspensions to induce chemical reactions to produce useful fuels and chemicals. We call the receiver based on this principle STARR, an acronym meaning *S*olar *T*hermally *A*ctivated *R*adiant *R*eactor. This report details the investigations during FY 1985 and FY 1986 of the multi-year program to develop the STARR receiver concept. A conceptual design of a central receiver based on the STARR concept is given in Figure 1.

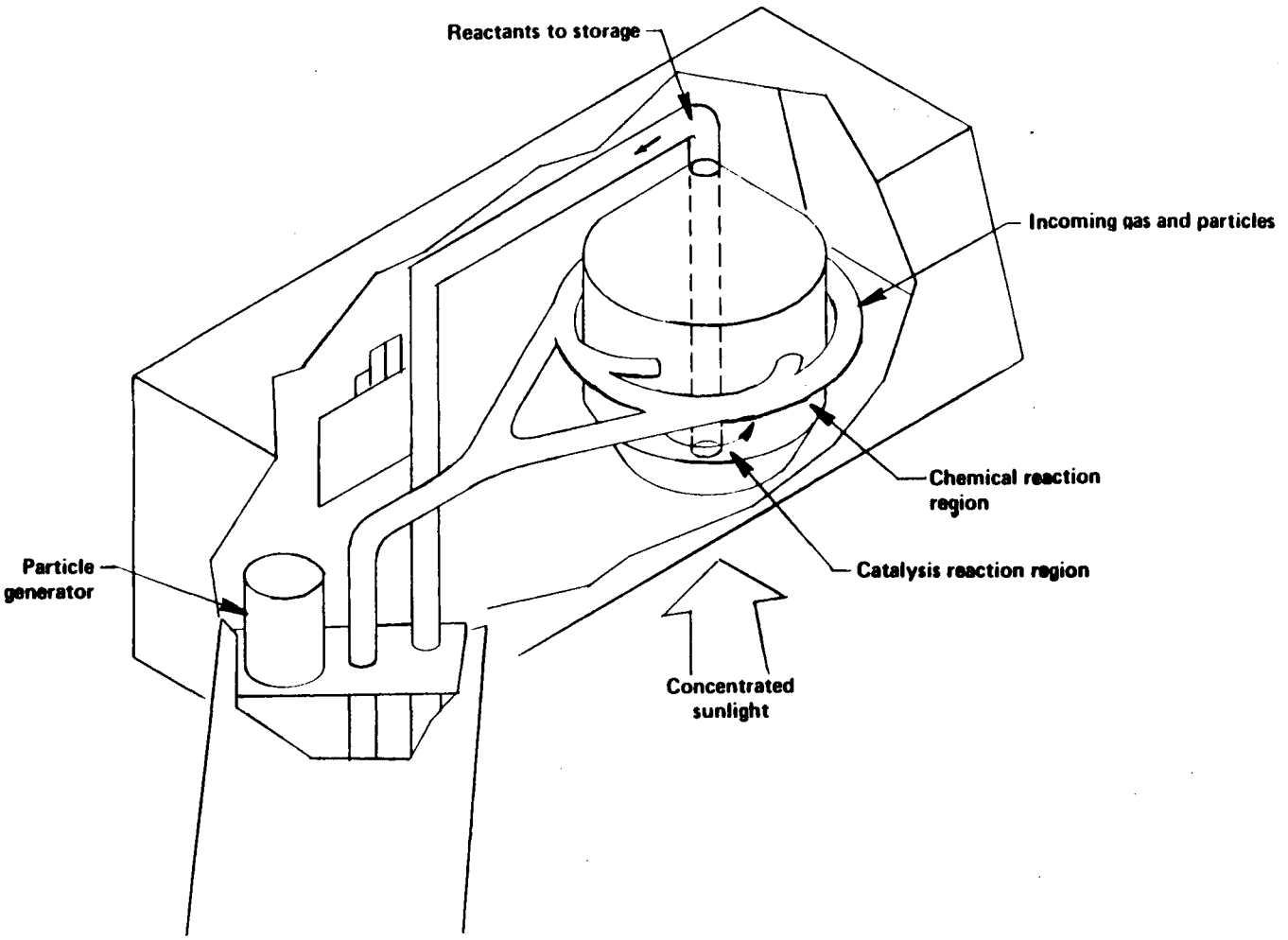

Figure 1. Conceptual Design of a STARR central receiver. (XBL 875-2217)

In order to design and test a STARR receiver it was first necessary to obtain a sound understanding of the basic principles and to establish a firm technological base in the use of small particle absorbers. Such a base did not exist prior to this program. Thus, this investigation was concerned with gaining an understanding of the optical, heat transfer, and chemical processes underlying the STARR receiver concept. Understanding, in a utilitarian sense, the complex and highly intertwined nature of these processes provides the tools necessary to conceptually design a STARR receiver and the balance of plant for performance and cost evaluation purposes.

In FY 1984, we made substantial progress in developing the STARR receiver technology [12]. A survey of candidate chemical reactions was performed. Analytical models of optical and heat transfer interactions in gas-particle

mixtures were developed and improved, most notably an analytical expression to predict the conductive heat transfer between a particle of arbitrary size and the surrounding gas [13]. Experimental studies with entrained particles were carried out using a xenon arc lamp to simulate concentrated solar radiation. Reference [12] (hereafter referred to as the FY 1984 Report) details these accomplishments.

During FY 1985 our research into STARR receiver technology was divided into three primary areas: (1) assessment of technical and economic potential of candidate chemical reactions, (2) analytic studies of thermochemical properties of candidate reactions and development of an integrated model of gas-particle mixtures in STARR receivers, and (3) experimental studies. The accomplishments in each of these areas will be discussed in the following sections.

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2. CHEMICAL PROCESSING BY DIRECT SOLAR IRRADIATION

2.1 Introduction

This chapter summarizes the work accomplished on the study of candidate chemical processes for solar radiant processing. The first section contains a description of the considerations and criteria used for screening candidate chemical processes. The second section describes the four categories of radiant processes considered in this study, and candidate chemical reactions within each category. The last section discusses and ranks the categories.

Direct solar radiant heating of gas-particle mixtures for the production of useful fuels and chemicals is an innovative approach to solar energy conversion. In turn, new approaches to industrial chemical processing are possible with the STARR receiver concept because the combination of high radiant fluxes and high temperatures offers a unique and unexplored environment for initiating chemical reactions [1]. However, we must understand the various physical processes underlying the STARR receiver, including optical, thermal, and chemical effects [2]. The design of such a receiver is a complex iterative procedure since these physical processes are highly interrelated.

The absorptive and scattering properties of individual particles are determined by their complex index of refraction, size, and shape. The amount of energy absorbed by a suspension of particles depends on the characteristics of the incident solar flux and particle density distributions. The ensuing heat transfer between the gas and particles depends on the particle and gas characteristics. The temperatures, residence times, and radiant fluxes that must be achieved vary widely with the chemical process. The choices of entrainment methods, mass loading, and routing of the particle suspensions and mixtures must also be considered. The optics and heat transfer in particle suspensions are intimately connected because the expansion of a heated gas affects the mass loading density of the absorbing particles, which in turn influences the radiant heating. These feedback effects must be understood and properly accounted for in the design of a direct absorption receiver or radiant reactor.

The basic interactions in the direct radiant heating process are similar for a wide range of particle sizes. However, the importance of these interactions varies widely with particle size and mass loading. This study is largely concerned with particles small enough to be entrained in flowing gases, e.g., having diameters of a few hundred micrometers or less. The optimum mass loading of solids per

volume of gas will depend upon the particular application being considered. Low mass loadings are generally appropriate for gas phase reactions wherein the particles act as the radiant heat exchanger. On the other hand, if thermal processing of a feed stock is desired, where the gas simply provides the transport system, higher mass loadings are appropriate. Other cases involving intermediate densities include gas-particle and catalyzed reactions. One goal of this work is to define the range of mass loading for various applications and its effect on the dimensions of the receiver.

2.2 Criteria for Evaluating Chemical Reactions

To establish a basis for proceeding with the development of direct radiant heating processes, a set of technical criteria were established to screen candidate chemical reactions.

1. The process should be technically feasible in terms of the required temperatures, reaction rates, heat and mass transfer coefficients and absorbing characteristics of the particles.

2. The chemical process should make efficient use of sunlight; that is, both first and second law efficiencies should be high. In general, this requires high temperatures, photochemical processes, or both. High temperatures, however, entail higher receiver losses, which must be considered.

3. Thermal energy flows should be integrated within the overall cycle to minimize the need for extensive heat recovery systems.

4. Because direct radiant heating requires sunlight, the chemical process must be adaptable to diurnal or batch operation.

5. There must be suitable chemical feedstocks and/or absorbing particles. If the feedstock is a solid, it must be available in particle form, or an inexpensive and energy efficient method of producing particles of the required size must be developed.

A set of desirable economic characteristics was also developed to aid in assessing candidate chemical reactions.

1. Cost competitiveness: Fuels or chemicals produced using sunlight must have the potential to compete in the future with products made using conventional energy sources. This may be a difficult criterion to apply because of

the uncertainty in predicting the future cost of conventional energy.

2. The product should be of high value or have widespread use. If the product has strategic value, possible tax incentives can be considered in the economic analysis.

3. The production facilities should be near consumption sites for products having significant transportation costs.

2.3 Radiant Chemical Process Categories and Reactions

There are several ways that chemical processes can be initiated in direct radiant processing of gas-particle suspensions. The particles can act either in passive or active roles as chemical initiators. The design of a radiant receiver/reactor and the ancillary processing steps depend in a critical way on the role of the particles. A characteristic common to all types of direct radiant processing is that the particles must be able to absorb sunlight to effectively couple the radiant energy to the chemical process.

There are four main categories of processes considered here: 1) the particle acts only as a heat exchanger to heat and induce a thermochemical reaction in the gas, 2) the particle is the sole feedstock for a pyrolytic chemical reaction, 3) the particle takes part in a chemical reaction with the suspending gas, and 4) the particle acts as a catalyst to promote a reaction in the gas phase component. In the following discussion these categories are considered in more detail by examining specific reactions. These reactions were chosen from those identified in the survey of chemical reactions as some of the better candidates for use with the STARR receiver.

2.3.1 *Particle as Gas Heater*

In this category the particles absorb sunlight and heat the surrounding gas but are chemically inert to the reactants and products in the receiver. If the particles do undergo chemical change, such as oxidation, the process occurring in the reactor is not affected. The use of small suspended particles solely as a gas heater was convincingly demonstrated by the solar test of the SPHER Mark I receiver in 1982 [3]. In this test, submicron carbon particles were used to heat air to temperatures in excess of 1030 °K. The particles were oxidized to leave a clean high temperature gas stream capable of operating a gas turbine or supplying industrial process heat.

In chemical applications involving the STARR concept, entrained particles can be used to heat a gas to thermal decomposition, or they can heat a mixture of gases to initiate a reaction. In this category, the particles do not undergo a chemical change or act as a catalyst. Examples of this type of reaction include:

(A) $H_2S \rightarrow H_2 + S$

(B) $N_2 + O_2 \rightarrow 2NO$

(C) $2H_2O \rightarrow 2H_2 + O_2$

The first reaction in this list is the thermal decomposition of hydrogen sulfide, H_2S, to produce hydrogen and sulfur. Hydrogen sulfide is a highly toxic waste product of the natural gas and petrochemical industries. Large quantities are produced, on the order of several million metric tons/year [4]. The Claus process is used for disposal, wherein the hydrogen sulfide is catalytically oxidized to water and sulfur. However, hydrogen sulfide can be thermally decomposed at temperatures of 1200 °K to 1800 °K to recover the hydrogen and produce sulfur [4]. Thus H_2, a valuable commodity, can be recovered from a toxic waste stream. The STARR receiver may be used to effect this decomposition by seeding the H_2S gas with small absorbing particles and exposing the suspension to concentrated sunlight. At decomposition temperatures the sulfur is a gas, but when cooled condenses to a liquid. Therefore, in addition to coupling the solar radiant energy to the gas, the particles play a second role by providing condensation sites to facilitate separation of the H_2 gas and sulfur components. This also provides a convenient means to remove the particles from the hydrogen stream. Because the petrochemical industry is the largest user of hydrogen, there is a convenient and ready market for the product.

The last two reactions, direct nitrogen oxidation (B) and direct water splitting (C), require very high temperatures for thermochemical initiation and present difficult processing requirements. However, if methods could be found to carry out either of these reactions practically using solar energy, the economic and social benefits would be enormous. Thermal nitrogen fixation was demonstrated (at low yields) on a commercial scale by the Wisconsin process [5] at about 2200 °K. These temperatures can be reached using particles as the solar absorbers. Additionally, the particles can increase the cooling rate of the gases by improving the radiative coupling to a cold background during quenching. However, low yields and the need for rapid cooling make the practicality of this approach doubtful. On the other hand, if the reaction can be carried out at lower temperatures, where the back reaction is slow, the requirements for fast

quenching can be relaxed. This approach for the fixation of nitrogen is discussed further under the particle as a catalyst section.

Useful yields of hydrogen from the direct thermochemical splitting of water require temperatures in excess of 2300 °K [6]. These temperatures can probably be reached in a STARR receiver using refractory particles such as iron oxide as the absorber. However, the product gases must be separated at this high temperature to avoid the extremely rapid recombination that would occur on cooling if they were not separated. This presents difficult material and processing requirements although the process was demonstrated by performing the reaction and quenching within liquid water. Other approaches to water splitting cycles utilizing two or more steps are discussed later.

Another important reaction in this category is the thermal detoxification of hazardous chemical wastes. Vapors of a toxic material containing small entrained particles may be passed through the STARR reactor and heated to decomposition. Toxic chemicals such as PCB's require high temperatures for destruction under isothermal conditions. The decomposition of dichlorobenzene at 1200 °K was demonstrated in a laboratory STARR experiment at LBL [2]. In this case the particles perform a dual role in that they can be used to radiantly heat the gas and also allow the radiation to pass through the toxic vapors, providing the conditions for photoassisted decomposition. Photoassisted thermal decomposition of another toxic analog was recently demonstrated at the University of Dayton. Heated vapors exposed to simulated sunlight were found to decompose at much lower temperatures than required for purely thermal decomposition. In the case of a particle reactor, the particle forms the site for photoabsorption and also for adsorbed toxic vapors. Using a black particle, much more of the solar spectrum is available because of the broad band absorption than if only vapors are present. Considering the vast quantity of toxic waste now in storage and currently being produced, solar detoxification is a technology worth investigating.

2.3.2 *Particle as Feedstock*

In this category, the particle is heated and undergoes an endothermic decomposition or phase change; the gas acts as a carrier for the reacting particulate material. Radiantly heated particles offer significant advantages. The particles may be heated rapidly to high temperatures to increase yields or decrease reaction temperatures. This may occur for two or more reasons. First, there is evidence that high heating rates can induce a chemical reaction more readily

because certain intermediate phases do not have time to form [7]. The second reason is that in most pyrolysis or decomposition of solids, a chemical reaction takes place requiring a chemical species to diffuse throughout the solid. In bulk materials this process can be slow unless melting takes place. Higher temperatures may be used to speed conventional processes, either to cause melting or to induce larger temperature gradients to speed the heating. However, large temperature gradients result in excess temperatures that may cause undesirable reactions resulting in lower yields. Small particles offer an ideal solution for this application. As mentioned earlier, we have experimently demonstrated that oxygen can easily diffuse throughout radiantly heated particles with the result that most of the particle material is converted quickly. Thus small particles can be decomposed without melting or large temperature gradients, resulting in reduced temperature requirements and residence times.

In radiantly heated particle suspensions, the absorbed energy is distributed in three forms (neglecting thermal losses): the energy difference between the initial and final chemical state of the particles, the sensible heat in the particles, and the sensible heat in the gas. At low particle loading and high temperatures, a significant portion of the energy can reside in the sensible heat of the gas and to recover this heat requires the use of heat exchangers. For this reason, reactions in this category must be examined carefully to assess equipment needs.

A reaction in which particles may be thermally processed by concentrated sunlight is the reduction of a metal oxide for the high temperature step in a water splitting cycle. In general, the reaction is:

$$MO_x \rightarrow MO_{x-y} + {}^{y}/_{2}O_2.$$

This decomposition is followed by the oxidation of the reduced metal compound by water to release hydrogen. An example is the reduction of magnetite to iron monoxide [8]:

$$Fe_3O_4 \rightarrow 3FeO + {}^{1}/_{2}O_2$$

in which hydrogen is released in the subsequent low temperature steam processing reaction:

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2.$$

The high temperature reaction occurs above 2000°K. These temperatures, although high, can be reached by radiant heating of magnetite particles. An

important advantage of this reaction is that hydrogen is released in a separate step and no separation of products is required. This would be an especially promising water splitting reaction if high radiant fluxes photolytically enhance the reduction of magnetite at temperatures below that required for the equilibrium reaction. However, this process has yet to be demonstrated (see Appendix A).

Another application in this category is the processing of phosphate ore to produce elemental phosphorus. This is an extremely attractive possibility from the economic point of view because the existing commercial processes use electric arc furnaces. This intensive use of electricity accounts for over half the cost of elemental phosphorus. The direct substitution of solar heat to replace electrically produced heat eliminates the second law losses associated with the conversion of heat to mechanical and electrical energy. This process enhances the economics of solar thermal energy conversion by a factor or 2 to 3 times over that of solar thermal electric power.

In conventional phosphorus production, the reaction proceeds by heating a charge of phosphate rock, carbon, and silica to approximately 1750 °K in an arc furnace. Upon melting, the reaction produces gaseous P_4, CO, and slag. A solar version of this process using a carbon crucible was demonstrated by Whaley and Yudow at the White Sands Solar Furnace [9]. This process may be adapted for use in the direct radiant reactor. Carbon provides an excellent radiant absorber. Several approaches to adapting this reaction to particle receivers are possible, including utilizing solid-solid reactions, melting point reduction techniques or using a solar kiln [10]. Appendix A contains a report describing the use of a solar kilning process in Togo for processing phosphates.

The decomposition of zinc sulfate as the solar driven part of a multistep thermochemical process for the production of hydrogen is another reaction in which radiantly heated particles can form the feedstock material [11]. In processes involving the decomposition of solids, there must be an ability for the reactants to leave the solid phase. As discussed before, small particles facilitate this transformation. The reaction takes place at 1100-1200 °K and the yield as a function of temperature may show a sensitivity to heating rate of the zinc sulfate [7].

Carbide formation in a reaction between two solid components, carbon and lime, is another example where the particle is a feedstock [12]. The carbide may be processed with water to form acetylene, a very useful starting product for plastics

manufacture. Carbon particles are an excellent absorber for this reaction. Again the nature of the reaction under solar conditions is not well known, and melting may form a critical step in the process.

Drying and calcining operations may be carried out in direct flux reactors. Cement making and the calcining of lime are two high temperature processes that may be adapted to direct radiant processing. In slag forming processes, either a melting bed or micromelting techniques must be used to provide conditions for the chemical reaction to take place. In applications where large particles are favored and the reaction proceeds quickly, falling particle receivers studied by SNLL may provide the best solution [13].

In processing applications where a significant portion of the sensible heat would reside in the carrier gas, a different technique may be useful. The carrier gas may be nearly eliminated - that is, have the reaction occur at a low pressure. This may be useful in cases in which the particles evolve gas from the reaction (such as the evolution of oxygen from a metal oxide). The evolved gas can provide a method of removing the processed particles from the reactor.

2.3.3 *Particle-Gas Reaction*

In this category, the particle is a feedstock that reacts with the entraining gas. The large surface area presented by the particles provides ideal conditions for solid-gas reactions. In addition, the short distances that molecules must move to penetrate or leave the volume of the particle eliminates most of the limitations inherent in traditional solid-gas reactions. In micron sized particles we experimentally demonstrated that over 75% of the particle mass could be reacted in short residence times in the STARR receiver.

We consider four types of reactions. The first entails reacting some form of carbon with steam to produce carbon monoxide, hydrogen, and other products. A prime example of this reaction is the gasification of coal. This was demonstrated in fixed-bed direct absorption solar reactors by a number of investigators [14-16]. While the technical feasibility of solar coal gasification has been demonstrated, a head-to-head competition with a commodity as inexpensive as coal makes the economics of the process difficult. This is mitigated somewhat by the fact that solar heating eliminates the need to burn part of the coal with pure oxygen to obtain heat for high value gas. This eliminates the cost of the oxygen plant, a significant advantage.

The need to process significant quantities of carbon containing solids imposes significant material handling requirements on an entrained particle reactor. A positive aspect of this handling process is that when crushed coal is exposed to concentrated sunlight, rapid heating of the water in very fine pores in the coal breaks it into fine particles [17]. Another positive aspect is that carbon particles are excellent absorbers. However, the best application for the STARR receiver is probably a more specialized case in which solar energy is not in direct competition with coal.

A second class of reactions is one in which metal oxides react with a gas. One such reaction involving hydrogen is

$$2Fe_3O_4 + H_2O \rightarrow 3Fe_2O_3 + H_2,$$

with the cycle closed by thermal reduction of hematite:

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + 1/2O_2.$$

The first reaction was explored by heating magnetite isothermally in a furnace to temperatures up to 1100 °C and looking for the presence of hematite. No hematite was detected and predictions of thermodynamic calculations indicated that only small concentrations of hydrogen would be present in equilibrium. In these compounds it is possible that the reaction may be aided by photo-oxidation induced by high radiant fluxes because Fe_3O_4 is a excellent solar absorber and a semiconductor. In a semiconductor, photoinduced electrons and holes may play an important role in reducing water adsorbed on the particle surface (see discussion in 2.3.4).

Another reaction in this category is the production of nitrates and nitric acid from air and water by a novel adaptation of the process developed and demonstrated by Harteck [18]. The Harteck process is as follows: high pressure N_2 and O_2 are reacted exothermally at moderate temperatures (e.g., 700 °K) with a solid metal oxide to form a metal nitrate. The cycle is completed when the nitrate is decomposed at high temperatures and lower pressures to reform the metal oxide and release NO_x. The NO_x is reacted with water to obtain nitric acid. The first reaction proceeds because even though only small amounts of NO_2 are formed in the high pressure reaction it is continually taken up by the metal oxide, thus driving the reaction forward.

The reaction may be integrated into the STARR receiver in the following way. Small particles of metal oxide are used in the first (non-solar) reaction because of their high reactivity as discussed before. In fact, the use of small particles may be critical to the success of the Harteck process because the problems of low reaction rates encountered by Harteck. After the particles react to form nitrates in the first step, they are sent to a radiant reactor. There they are radiantly decomposed to release NO_x. The suspension is then separated; the NO_x is scrubbed from the gas phase with water to produce nitric acid, and the particles returned for the high pressure reaction. The thermal processing of the nitrate is an endothermic reaction that takes place at high temperatures (ca. 1000-1500 °K, depending on what nitrate is used). A number of nitrates may be suitable for this reaction. The large and growing world demand for fertilizer, combined with the depletion of energy reserves makes this a very worthwhile process to investigate.

2.3.4 *Particle as Catalyst and or Photoinitiator*

The use of small absorbing particles as sites for reactions of molecules adsorbed from the gas phase is one of the most exciting potential applications of the STARR concept. In this case the particle acts as a solar absorber to supply heat for the reaction and may also act to promote the reactions through non-thermal mechanisms. There are several distinct advantages to this approach. First, small particles in the feed gas provide enormous surface area for reaction. Typically, with very low mass loadings, entrained particles will interact with effectively all the gas molecules in times short compared to the residence time in a radiant reactor. Thus the particles act effectively as entrained chemical reaction sites.

Second, when conventional catalyst materials for endothermic reactions are dispersed in the gas and radiatively heated, the thermal energy to activate the reaction is supplied *directly to the site of the reaction.* This effectively eliminates the problem of supplying heat to the catalyst by conduction through pipe walls and catalyst substrates. This means the catalyst is at the highest temperature so that the reaction proceeds faster than when the catalyst is heated by other means. In some reactions this may be a significant advantage and is therefore a solar beneficial effect.

Third, the chemical reaction may be enhanced by non-thermal effects. In this case, the particles can act to transfer the energy of the solar photons through excited state processes. Examples of this process include the photoinduced

decomposition of HBr on the surface of concentrated silicon particles, [19], or water decomposition on solar illuminated semiconductor electrodes in an aqueous solution [20]. It has been demonstrated in these cases that electron hole pairs are generated by solar photons and act on particle surfaces to supply energy for the reaction. Electron hole pair production within the particle can supply photogenerated charges with extremely high oxidative and reductive ability. Moreover, the charges are produced within the (small) particles and therefore have only to move a short distance to the reaction sites, thus dramatically reducing the recombination probability. This means that more charges will reach the surface to produce more chemical activity. The small size of the particle is also effective in reducing the potential barrier for the charges to reach the surface in semiconducting materials because the Debye screening length is large compared to the particle size. Thus, light can be used via the particles to promote endothermic chemical reactions. Preliminary evidence from high temperature research performed at LBL to study thermochemical storage reactions* indicates substantial enhancement of the *rate* of decomposition of SO_3 in the presence of concentrated sunlight over the rate at the same temperature in an isothermal environment [21]. An analysis of reaction rates relevant to photoassisted catalysis is included in appendix C of this report.

A possible application in this category is nitrogen fixation. The reaction $N_2 + O_2 \rightarrow 2NO$ is catalyzed by Fe_2O_3 which has a bandgap of 2.2 eV (near the peak of the solar spectrum). Normally, high temperatures are required to break the N_2 bonds, but the reaction itself is not favored at high temperatures, thus yield is low. However, if the iron oxide or other metal oxide particles can provide photodecomposition sites to break the N_2 bonds, higher NO yields may be realized at a lower temperatures. It may be difficult to find a good absorber/catalyst particle for this reaction because of the difficulty in breaking the strong N-N bond. Most of the known M-N_2 complexes have absorption bands at energies of 3 ev or higher. Also, the known photochemistry leads to the loss of the N_2 from the metal rather than breaking the N-N bond.

In a similar vein, it may be possible to use a metal oxide particle to enhance the thermal decomposition of water vapor. The facility with which iron can change its oxidation state could be used to react oxygen atoms from the water vapor at the particle surface, thereby performing one step in the water splitting cycle. Appendix B contains a more detailed analysis of the issues involved in the use of

*Supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Storage Technologies, Thermal Storage Program.

iron oxide as a catalyst. Specific mechanisms for this type of reaction can be examined analytically, but an enlightened experimental approach to this type of reaction is probably the best approach.

Another possible reaction involves the processing of methane. Methane may be reacted with N_2 and O_2 to produce ammonia or be reformed to hydrogen and carbon monoxide. Catalysts perform important roles in traditional methods of carrying out these processes. Again the presence of high photon fluxes impinging on the particle surface may act to enhance the rate or lower the temperature for the reaction. However, the economics of the process are dominated by the cost of the methane used to produce the hydrogen for the reaction and hydrogen production from other feedstocks may be the best current approach. (See Appendix B for a more detailed analysis.)

The reaction mentioned earlier studied for thermal storage applications is also included in this category. SO_3 can be thermally decomposed using Fe_2O_3 as a catalyst. In a thermal storage application, the decomposition products, SO_2 and O_2 are stored at near ambient temperatures and later recombined to provide heat at a high temperature. This reaction has one of the higher round trip efficiencies for thermal storage systems. The advantage of using small particles in this reaction is promising and is still under experimental investigation.

2.4 Discussion and Ranking of Reactions

The discussion in the preceding section divided a number of chemical reactions into four groups according to the role the particle plays in the reaction. This classification was chosen to emphasize the differences in the reaction mechanisms rather than the end use of the products. Using this approach it is possible to compare classes of reactions and draw general conclusions about the strengths and weaknesses of each. A comparison of the specific reactions is more difficult because of limited data on reaction mechanisms and lack of experimental information regarding the design of industrial scale direct flux particle reactors. The criteria developed in the third section of this report can be applied in comparing the reactions discussed here. The results of this comparison are displayed in Table I.

The reactions are grouped according to the categories discussed in the preceding section. The solar-driven reactions to be performed in the STARR receiver are indicated in a general way along with the final chemical product if it is a result of a subsequent reaction. The numbers of the columns correspond to the numbers

Table 1.

Type	Reaction	Technical 1	Technical 2	Technical 3	Technical 4	Technical 5	Economic 1	Economic 2	Economic 3	Score	Fraction
Particle as Gas Heater	$H_2S \xrightarrow{\text{carbon}} H_2+S$	G	M	G	M	G	M	M	G	83	$\frac{20}{24}$
	$N_2 + O_2 \xrightarrow{\text{metal oxide absorber}} 2\,NO$	P	P	P	M	G	M	G	M	63	$\frac{15}{24}$
	$H_2O \xrightarrow{\text{metal oxide absorber}} H_2 + \frac{1}{2}\,O_2$	P	M	P	M	G	M	G	U	62	$\frac{13}{21}$
	Waste detoxification	G	M	M	G	M	U	G	M	81	$\frac{17}{21}$
Particle as Feedstock	$ZnSO_4$ Decomposition for H_2	M	M	P	M	M	U	G	U	67	$\frac{12}{18}$
	$Fe_3O_4 \rightarrow 3\,FeO + \frac{1}{2}\,O_2$ for H_2	M	G	P	M	G	M	G	U	76	$\frac{16}{21}$
	Phosphate processing	G	M	M	P	M	G	G	G	79	$\frac{19}{24}$
Particle Gas Reaction	$C + H_2O \rightarrow CO + H_2$	G	M	M	P	M	P	M	M	63	15
	$2Fe_3O_4 + H_2O \rightarrow 3Fe_2O_3 + H_2$	P-G*	M	P	M	G	M	G	U	67-76	$\frac{14-16}{21}$
	$N_2 + O_2$ + metal oxide ; NO_2	U	U	M	M	M	M	G	M	72	$\frac{13}{18}$
Particle as Catalyst	$2H_2O \xrightarrow{\text{metal oxide cat.}} + 2H_2 + O_2$	M	M	M	M	U	M	G	U	72	$\frac{13}{18}$
	$N_2 + O_2 \xrightarrow{\text{metal oxide cat.}} 2NO$	P-G*	P-G*	U	G	U	M	G	M	67-89	$\frac{12-16}{18}$
	$SO_3 \xrightarrow{\text{metal oxide}} SO_2 + \frac{1}{2}\,O_2 \rightarrow$ Heat	G	M	M	G	G	U	M	M	81	$\frac{17}{21}$

of the technical and economic criteria given earlier. The letter entries refer to: G for good, M for medium, P for poor, and U for unknown due to a lack of information. The starred entries indicate that the reaction is assumed to take place by a photolytic process. A numerical rating was assigned to each reaction by assigning the values of 3, 2, and 1 to the good, medium, and poor ratings respectively. Ratings of U were not counted. The score column gives the ranking as a percentage derived from the last column that contains the raw fraction (excluding contributions arising from U ratings). These ratings should be used only as a general indicator and not considered definitive. The ratings were assigned using the present knowledge of the processes involved and assumes equal weight for each of the criteria.

In the first group, where the particle is used as a gas heater, the highest ranking is for the H_2S decomposition. Thermal decomposition of water and thermochemical oxidation of nitrogen suffered because of problems of separation and back reactions at the high temperatures required to initiate the processes. The hydrogen producing reactions for which there was not a dedicated user received a U for the last criterion because of the uncertainty of the proximity of the market. The second highest ranking in this group was received by the detoxification of hazardous chemical wastes. The temperatures are quite suitable for the process and the feedstock is already stored on an indefinite basis.

In the second group, where the particle is a feedstock, phosphate processing ranked highest because of the excellent economics resulting from the replacement of an electric arc furnace by a direct solar thermal process. Because the process considered for phosphate used a solar kiln, not entrained particles, the heat exchanger requirements were less than for the other processes in this category. Producing hydrogen from magnetite has the advantage of evolving the hydrogen in a separate step from the oxygen.

In the category of particle-gas reactions, the first ranked process depended on assumptions regarding photo-induced processes. If photons alter the oxidation state in magnetite in the presence of water, problems with the low yield (see pg. 13) could be overcome and the process ranked highest. If not, the Harteck process ranked highest, although the rating was lower than for other category winners. There is considerable uncertainty in ranking the Harteck process because of the unknown nature of some of the steps.

The last group contains reactions in which the particle acts as a conventional catalyst or photocatalyst. The advantages of performing reactions at lower

temperatures to produce valuable chemicals is reflected by the high possible ranking of photocatalyzed nitrogen fixation. The uncertainty in the possibility of the nitrogen reaction is reflected by the range of the rating. The SO_3 decomposition for thermal storage cycles had the second highest possible ranking in this category.

Useful reactions occur in all of the categories and many are worthwhile pursuing. However, in order to focus the research, it is necessary to concentrate on one of the categories. In three of the categories many of the chemical processes discussed involved the substitution of solar thermal energy in a conventional chemical process. The economics of this substitution can be determined from calculating the anticipated costs for the solar portion of the process and calculating the economic benefits that accrue from the displaced energy costs. However, in the fourth category, where the particle acts as a catalyst, and particularly as a photoinitiator, there is a potential to carry out reactions by nonconventional chemical routes. If a solar driven process can substitute for a conventional process and reduce the energy requirement for the reaction, the benefits of solarizing the process will be improved considerably.

An example of a possible high payoff situation is the oxidation of atmospheric nitrogen. The reaction is not strongly endothermic but with conventional chemical processing, very high temperatures are required (Wisconsin Processes) for its initiation. The economics of the conventional process are driven by the cost of heat recovery because little energy goes into the reaction. If, through the use of a photoinitiated reaction, the oxidation is carried out at lower temperatures, the costs associated with a conventional high temperature heat exchanger are reduced and less energy is required for the reaction. In addition, at lower temperatures the back reactions are reduced and higher yields are possible. If a process like this can be made to work economically, it would have profound effects on the use of solar energy.

From the technical as well as the economic standpoint the category of the particle as a catalyst is the most attractive. The advantages accruing from the use of small particles as entrained chemical reactor sites were discussed earlier. The large surface area and access of the gas to the particle surface provide a natural system to induce reactions. The choice of particle composition and size offer a considerable degree of flexibility in initiating chemical reactions from sunlight. Aside from the basic requirement that the particles be absorbing, additional flexibility may be introduced by exploiting semiconductor properties, doping, and particle composites.

The demonstration of this approach should be exploited to investigate further reactions and to provide a basis for economic evaluation. Once the energetics, kinetics, and yields of a reaction are quantified, the economics of the process may be analyzed through the mechanism of a plant conceptual design.

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3. OPTICAL AND THERMAL ANALYSES

3.1 Introduction

To take advantage of unique thermal and chemical processing opportunities offered by the the STARR approach it is necessary to analyze the optical and thermal properties of particle suspensions. The interaction between concentrated radiant energy and a flowing gas-particle mixture is quite complex. A number of factors influence this interaction, including particle size, material optical properties, spectral nature of sunlight, radiation distribution within the suspension, and temperature-induced gas-particle density changes. To understand these interactions a series of calculations and models were developed and implemented with computer codes to analyze various aspects of the problem. The goal is to incorporate these elements into a more comprehensive model that specifically accounts for the feedback effects between changing gas-particle density and optical properties of the suspension.

The first step in the analysis was to calculate the absorption and scattering from a single particle using Mie scattering theory. These quantities were calculated for all wavelengths and particle sizes to provide input to determine the radiant absorption in an ensemble of particles. The results of this calculation were used to determine the receiver operating parameters. The gas-particle temperature and density distribution must be determined for specific geometries. Finally, to understand the vital role of the chemical reaction on the thermodynamics of the system, the equilibrium and kinetics of the chemical reaction must be understood. The CHEMKIN codes are utilized for this part of the analysis. The radiant analysis is summarized here and treated in more detail in the previous report [1]. The analytical emphasis in the work reported here was on development of a model for flow in a cylindrical tube and chemical equilibrium calculations.

3.2 Optical Properties of Small Particle Suspensions

The Mie theory was used to calculate the single particle absorption and scattering cross sections (Q_{abs} and Q_{sca} respectively,) for the particle sizes found in the suspension and the wavelength range of the incident and emitted radiation. The complex index of refraction of the particle material as a function of wavelength, i.e., $M(\lambda) = n(\lambda)+ik(\lambda)$, must be specified for the Mie calculation. The Mie results are then convolved with the spectrum of the incident solar radiation to determine the propagation of sunlight through an ensemble of particles.

The extinction coefficients are calculated from the scattering cross sections by:

$$\beta(\lambda)_{abs} = \Sigma N_i \, m_i \, Q_{abs,i}(\lambda) A_i \tag{3-1}$$

and

$$\beta(\lambda)_{sca} = \Sigma N_i \, m_i \, Q_{sca,i}(\lambda) A_i \tag{3-2}$$

where N_i is the number of particles per unit volume with mass m_i and cross-sectional area A_i, and $Q_{abs,i}(M,\lambda)$ and $Q_{sca,i}(M,\lambda)$ are the absorption and scattering efficiencies [2]. The intensity of radiation passing through the suspension as a function of traversal distance and wavelength, (neglecting multiple scattering and emission) is given by the exponential:

$$I(\lambda)/I_o = exp\,(-\beta(\lambda)x) \tag{3-2}$$

where x is the distance traversed through the gas-particle mixture, and β is the extinction coefficient, given by the sum of the absorption and scattering coefficients.

Computer codes utilizing the Mie calculation as a subroutine were developed to calculate the absorption of radiant energy propagated through the gas-particle mixture. The broad-band spectral properties of gas-particle suspensions were determined using a computer program called PDISMIE. Figure 2 illustrates the result of these calculations by showing the fraction of light absorbed by various particle suspensions as a function of the product of particle mass loading and propagation distance [3,4]. Data is plotted for magnetite (Fe_3O_4), hematite (Fe_2O_3) and cobalt oxide (Co_3O_4). These calculations were performed for light with the spectral characteristics of the xenon arc lamp used in our experiments. They were also calculated for sunlight. The particles are assumed to have a Gaussian size distribution with the mean particle diameter given for each curve. Note from this figure that the *product* of the particle mass loading and the propagation distance determines the overall absorption of the gas-particle mixture. This is important for STARR receiver design; i.e., the propagation distance is directly related to the receiver size, while the particle mass loading is generally related to the given application. Thus, there is an important coupling between the receiver size and the mass loading that must be considered in STARR receiver design.

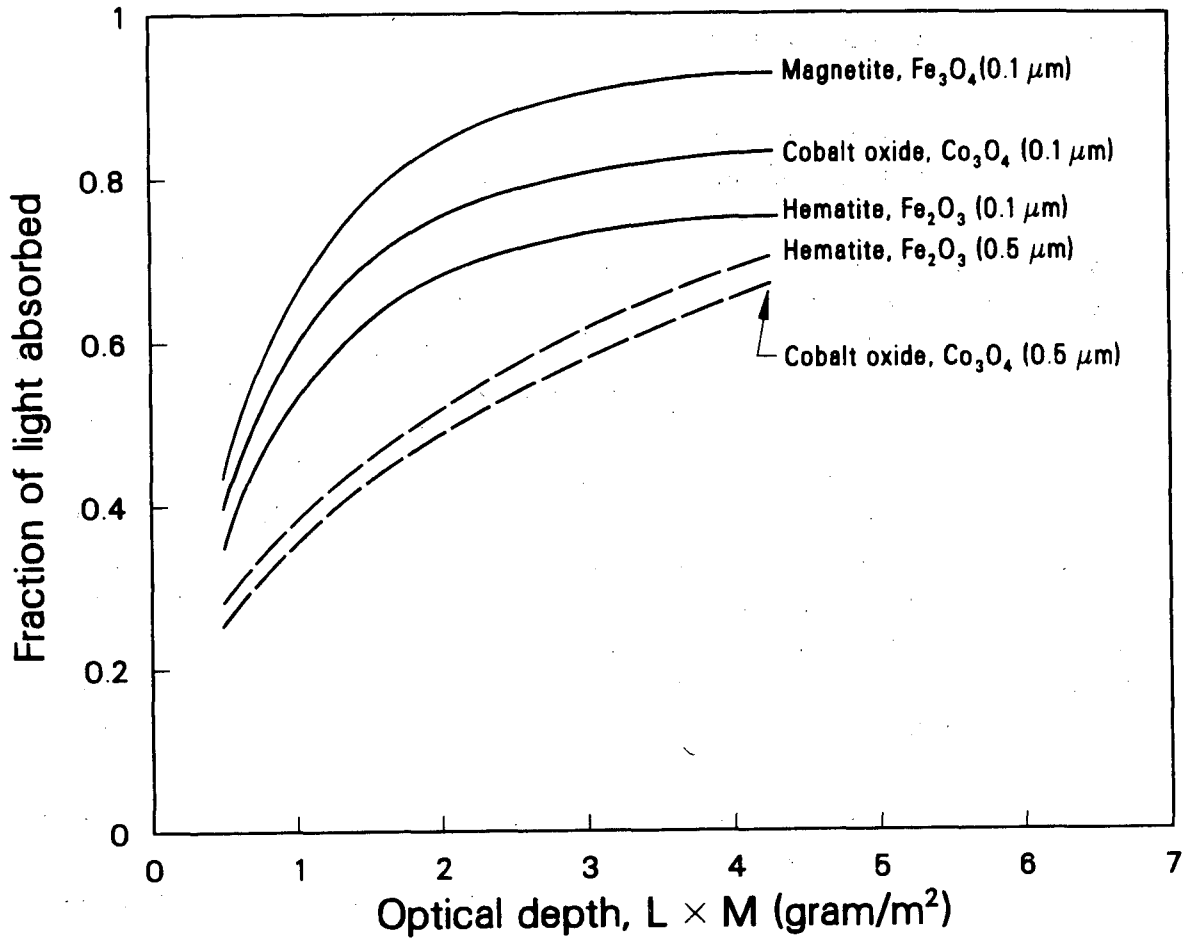

Figure 2. Absorption of various particle suspensions as a function of optical depth. (XCG-7101)

A number of materials (especially metal oxides) with promise as absorbing particles were obtained for study. Not only are the metal oxides generally very good solar absorbers, but several are candidates for reactants in multi-step water splitting cycles. The wavelength-dependent complex indices of refraction of carbon, iron, copper, cobalt, titanium, and manganese oxides were found in the literature and entered in the data files. The computer programs, PDISMIE and PWDISMIE were used to produce plots of the fraction of the total energy absorbed as a function of the product of the mass loading and the path length of the light by a particle suspension of cobalt oxide. Similar graphs were produced for carbon, hematite, and magnetite. Plots were produced for several different mean radii and standard deviations to illustrate the effects of particle size on the absorption characteristics of the particle suspension. As an absorber of solar radiation, the cobalt oxide ranks below carbon and magnetite, but above hematite.

3.3 Heat Transfer Calculations

A new approach to calculating heat transfer rates from particles to gas was formulated in the first phase of this work and was reported earlier [1]. The heat transfer calculation was used to study the effect of particle size, flux density, and gas conditions on the equilibrium temperatures reached by radiantly heated particles. An expression was developed for the heat transfer at intermediate Knudsen numbers (the ratio of molecular mean free path to particle diameter). The expression was developed from a two-zone model in which heat transfer by molecular free flow was assumed to take place within a spherical shell having a thickness equal to the mean free path of the gas molecules. Outside that shell continuum heat transfer was assumed. By matching conditions at the zone boundary an expression of general validity was obtained. This one expression predicts the correct result for both small particles (free molecular heat transfer) and large particles (continuum heat transfer) and provides for the first time an analytical formula at intermediate Knudsen numbers [5]. It was also found to be in good agreement with earlier experimental studies in the field of rarefied gas dynamics.

This expression was used to calculate the differences in temperatures between particles and gas as a function of size and incident flux. It was found that the temperature difference between radiantly heated particles and gas depends strongly on the particle size. An important conclusion was that for submicron particles and flux concentrations typical of solar thermal applications, the temperature difference is very small (e.g., less than one degree Celsius). This simplifies the modeling of thermal properties of suspensions of small particles because they may be regarded as having only one temperature at a given location. The same model was also used to calculate the maximum heating rates for radiantly heated gas-particle mixtures [6,7].

3.4 Integrated Model of Gas-Particle Mixtures

To understand and design a STARR receiver, the gas and particle temperatures, densities, and flows inside the receiver must be determined. To calculate these quantities requires development of a model to predict the effects of solar absorption and heat transfer within gas-particle mixtures, fluid flow, and chemical reactions. Since FY 1984, we have been developing various aspects of such a model that will include most major effects [1,4-7].

In order to calculate actual temperature and flux distributions in a gas particle suspension, a specific geometry must be chosen. Because of its simplicity and its approximation to a more realistic receiver, we chose a cylindrical geometry. A window at one end admits light to heat a gas-particle mixture that flows either away from (co-current) or towards (countercurrent) the light. The situation is diagramed in Figure 3. The equation of radiative transfer was applied to this problem using a gray, two-flux approach [8]. The radiative flux is divided into two components, one in each direction along the axis. An energy equation was developed for this problem assuming constant property slug flow. The equations were nondimensionalized using appropriate quantities and four nondimensional parameters resulted.

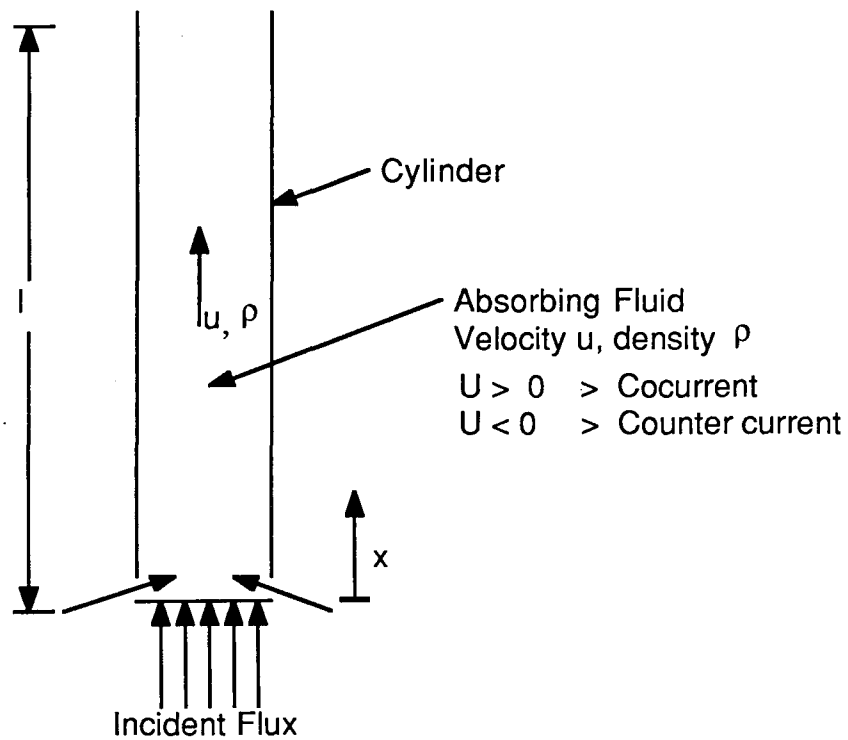

Figure 3. Receiver geometry for the two-flux model. (XBL 871-148)

The energy and radiative transfer equations were solved together to yield temperature and flux distributions for a variety of values of nondimensional parameters. Both diffuse and collimated input were considered.

Two major conclusions were reached from the results. First, countercurrent flow is more efficient (i.e., has a higher output temperature) than the cocurrent flow; the difference depends on the values of the nondimensional parameters, and can be substantial. Physically, this is due to the countercurrent flow having a lower

average temperature along the pipe, and lower losses due to emission and better absorption because the gas does not expand as much. This result would be more pronounced if wall losses were considered. The second conclusion is that while scattering always reduces the efficiency in the diffuse input case (due to back-scatter) it can actually increase the efficiency in the collimated case by giving the beam a longer path length through the mixture, and hence more chance to be absorbed. To better account for wall effects and to provide for temperature and flux distributions in the radial direction, work was initiated to solve a four flux model with the same geometry. The final step will be to include spectral variations.

As an aide to experimental design, a review of methods to measure temperatures in gas-particle flows was undertaken. The results of this review are given in Table II. The table presents the various methods and compares the advantages and disadvantageous of each method along with the appropriate references.

A computer program was written to aid in the analysis of the temperature measurements in the reactor. The calculation simulates the heat fluxes acting on a thermocouple in the reactor. A heat balance is performed on the thermocouple that takes account of its conductive, convective, and radiant heat transfer to the reactor environment. The program allows us to assess the magnitude of the errors arising from the radiant heating of the thermocouple and to more accurately determine the reactor output temperature.

3.5 Chemical Computations

To study possible chemical reactions carried out by STARR, the CHEMKIN computer codes were implemented at LBL. These state-of-the-art thermochemical codes were obtained from Sandia National Laboratories, Livermore. They permit the calculation of chemical kinetics and equilibrium for complex reacting systems including the presence of condensed phase species. The CHEMKIN code is made up of a set of FORTRAN subroutines. Unlike codes developed to solve particular problems, CHEMKIN is more flexible and can be used to model a large range of problems.

Substantial modifications and additions to the CHEMKIN codes were undertaken during this phase of the work to make the codes more useful for our purposes, which are quite different from Sandia's. We acquired thermodynamic data for over 400 species associated with the most promising chemical processes identified

earlier for application to STARR. The CHEMKIN programs were used to analyze a variety of candidated chemical reactions. An example of the results of this program to predict the products of the reaction $CH_4 + CO_2$ is given in Figure 4. The molar contents of the reaction products are plotted as a function of temperature. The data is plotted for a constant pressure of five atmospheres.

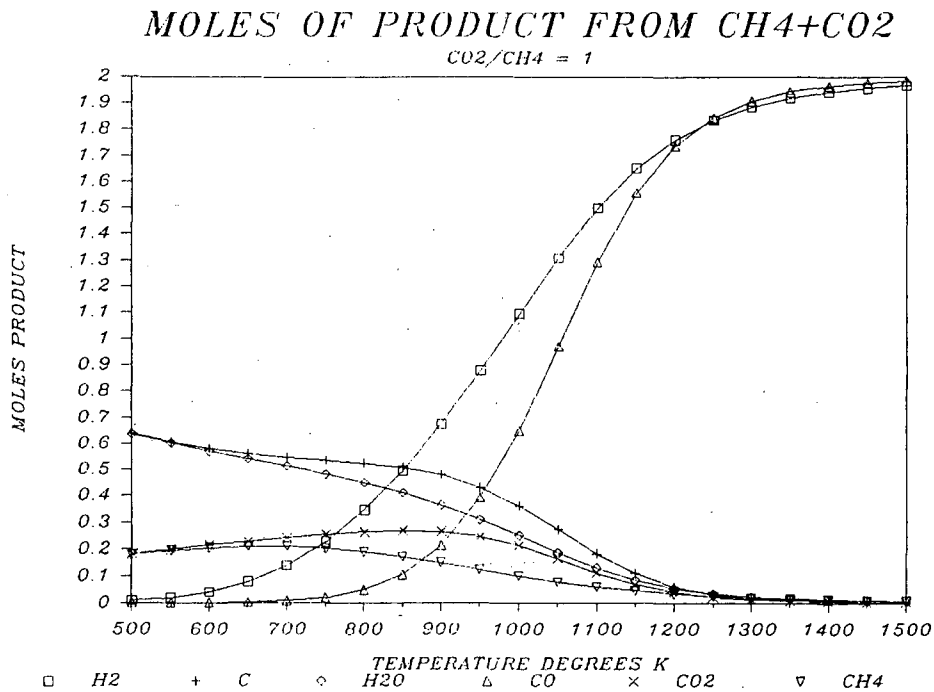

Figure 4. Moles of product for the CO_2 reforming of methane as a function of temperature.(XBL 875-2216)

TABLE II

Temperature Measurement In Gas-Particle Flows

Method	Gas	Part.	Spatial Resolution	Range	Cost/Purchases	Restrictions, Remarks, and Refs.
optical fiber	Yes	No	.25 x .5 mm	500-2000 °C	High, $12,000	Not good below 500 °C yet. Needs to be shielded in radiant environment. Good in oxidizing or reducing env. Subject to frictional heating. [1]
Thermocouples	Yes	No	100 μm bead	0-1300 °C (type K)	low, except micro TCs	Needs to be shielded in radiant env. May not be suitable for some atmospheres. Subject to frictional heating. Aim downstream if possible. [2, 3,4]
1 λ Pyrometer	No	Yes	1 mm^2 beam (?)	?	Filters, PMTs, lens, oscilloscope, laser, off-the-shelf pyrometer	Need to measure scattering and turbidity at the same time. Correction for optically thick. Yields number density at the same time. [5]
Pyrometer (2 or 4 λ)	No	Yes	beam down to 1/4 " (?)	450-1200 °C	Filters, PMTs, lens, oscilloscope	Maybe difficult to apply to low temp. particles. Assumes constant temp. along beam path. Must be careful about CO_2 in system. Must filter light source to eliminate the two wavelengths. [6,7,8,9]
X-Ray Diffraction	No	Yes	?	100-1000 °C	X-Ray tube, detector, shielding	Need 10 sec analysis time unless synchrotron radiation is used. Most involved set up, still needs development. [10]

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4. EXPERIMENTAL STUDIES

4.1 Introduction

Laboratory studies were undertaken to validate the analytic studies of radiantly heated particle suspensions and to explore new ways of inducing chemical reactions with sunlight. Concentrated solar radiation was simulated in the laboratory using a high intensity xenon arc lamp mounted at one focus of an ellipsoidal reflector. The light was focused into the gas-particle suspension passing through the transparent reactor tube. A variety of particles were entrained in gas mixtures and measurements were made of the beam attenuation of the suspensions before and after passing through the reactor. The particles were characterized before and after radiant heating by several techniques.

A variety of radiantly induced chemical reactions were explored with the apparatus. Inorganic oxides were processed at high temperature and radiant fluxes to determine both the oxidation and reduction of entrained particle species. Oxidation of nitrogen and hydrogen production were explored. The chemistry of the carbon dioxide reforming of methane was studied, especially with reference to carbon formation and oxidation. Complementary aspects of these investigations are described in the FY 1984 report and in the following.

4.2 Experimental Set Up

A general diagram of the experimental apparatus is given in Figure 5 and a photograph in Figure 6. In addition to the solar simulator the complete experimental system includes gas supplies, cyclone particle entrainer, baffled optical attenuation tube, fused silica reactor, dichotomous sampler, electronics, and instrumentation to measure temperature and flow. These components are described in the FY 1984 report. Particle composition was monitored off-line using an automatic X-ray diffractometer and gas composition monitored with a gas chromatograph and a chemiluminescent analyzer.

The 2.2 kW xenon arc-image furnace was capable of delivering a peak flux of about 4000 kW/m^2 and a total radiant power to the focus of 520 watts. Several improvements were made on the solar simulator in FY 1985. The most important was that a second tracking axis was added to the calorimeter mount to provide for scanning in both the horizontal directions above the lamp. This provides more precise alignment of the reflector with respect to the lamp in order to obtain higher beam symmetry. However, new beam scans taken in FY 1986

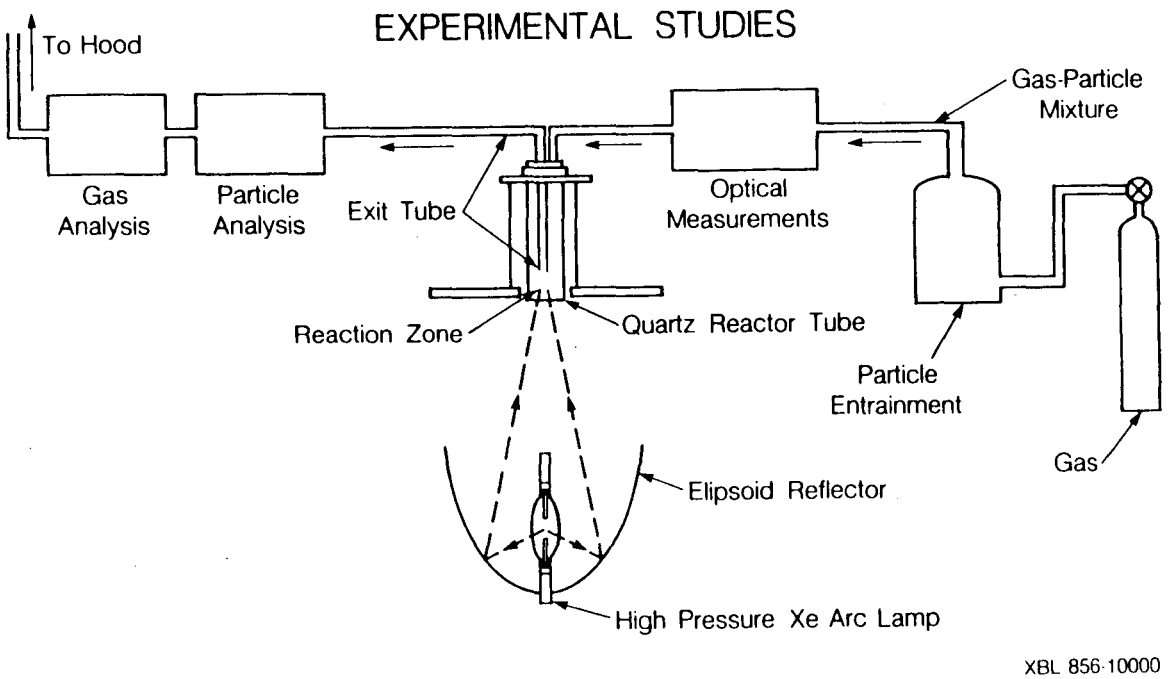

Figure 5. Diagram of flowing radiant reactor experimental set up.

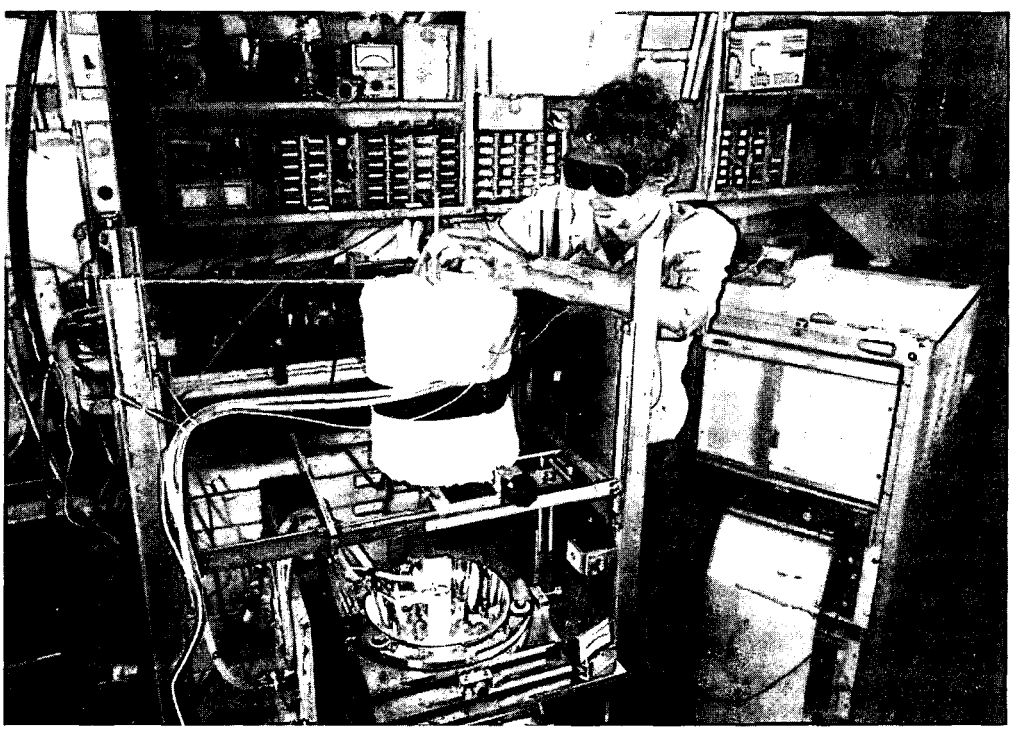

Figure 6. Photograph of the Experimental Apparatus. (CBB 848-5992)

revealed changes. A reduction in beam intensity was observed from the previous measurements. The peak flux was reduced from over 4000 kW/M^2 to $3300kW/M^2$. The cause of the reduction was due to normal aging of the lamp with operating time.

A new reactor insulating jacket was constructed from a two-piece cylinder of Kaiser M-Block wrapped in foil. This new jacket significantly reduces the heat losses. Two experiments were performed to measure the heat loss of the new design and an analysis of the experimental results was initiated. A copy of the state-of-the-art conduction code, HEATING 6 from ORNL was obtained for this purpose.

To determine the gas composition, both before and after it passed through the illuminated reactor, a gas chromatograph and a chemiluminescent analyzer (CLA) were used. The CLA was used in the nitrogen fixation experiments as it detects both NO_x and NO. It is an on line system in which a small amount of gas is pumped first through a filter to remove particles, and then through the analyzer. The gas chromatograph was used to detect CO, CO_2 and CH_4 in the CO_2 reforming experiments. A sample of filtered gas was taken using a syringe and injected into the chromatograph.

A dichotomous sampler was used to obtain particle samples for use with the X-ray diffractometer. The sampler utilized a virtual impactor to separate the output gas-particle mixture into two streams, one containing only the larger particles and the other containing only the smaller particles. The cutoff in the particle diameter depends on the carrier gas. In the case of an air-particle suspension, the cutoff diameter is 5.0 microns. Particles from each stream are collected on a filter. The thickness of the particle coating on each filter is measured by a "beta" gauge, and the mass loading is calculated. The filter is then placed in the X-ray diffractometer to to scan the filter and record the Bragg diffraction pattern. The measured diffraction characteristics are compared by the built-in computer for all materials of interest for identification and quantitative measurement. These instruments make it possible to identify and make a quantitative analysis of the particles both before and after they have passed through the radiant flux. They are valuable experimental tools for determining the chemical composition changes that occur in particles placed in a concentrated flux environment.

4.3 Particle Characterization

Samples of particle materials, including Fe_2O_3, Fe_3O_4, FeO, TiO_2, CdO, Co_3O_4, MnO_2, CuO, Cu_2O, mineral ores, and various types of carbon blacks, were obtained in powder form from the manufacturers. All samples were black or deeply colored fine powders. Thus, they are potentially good absorber materials, and several are particularly important because they have been proposed as reactants in a multi-step water-splitting cycles. Since information about the particle size distribution was not available from the manufacturer, electron microscopy was used to characterize the samples. Electron micrographs were made of particles of cobalt oxide, titanium dioxide, hematite, magnetite, manganese dioxide, beneficiated phosphate ore from Togo, and two copper oxides. A sample of each compound in powder form (as it came from the supplier) was placed in the cyclone shaker to produce an argon/particle suspension. Samples were collected on a quartz-fiber filter from this suspension and a small piece was cut from the filter for viewing with a scanning electron microscope. A micrograph of the phosphate ore is displayed in Figure 7. Particle size distributions for some of the compounds were made from the micrographs.

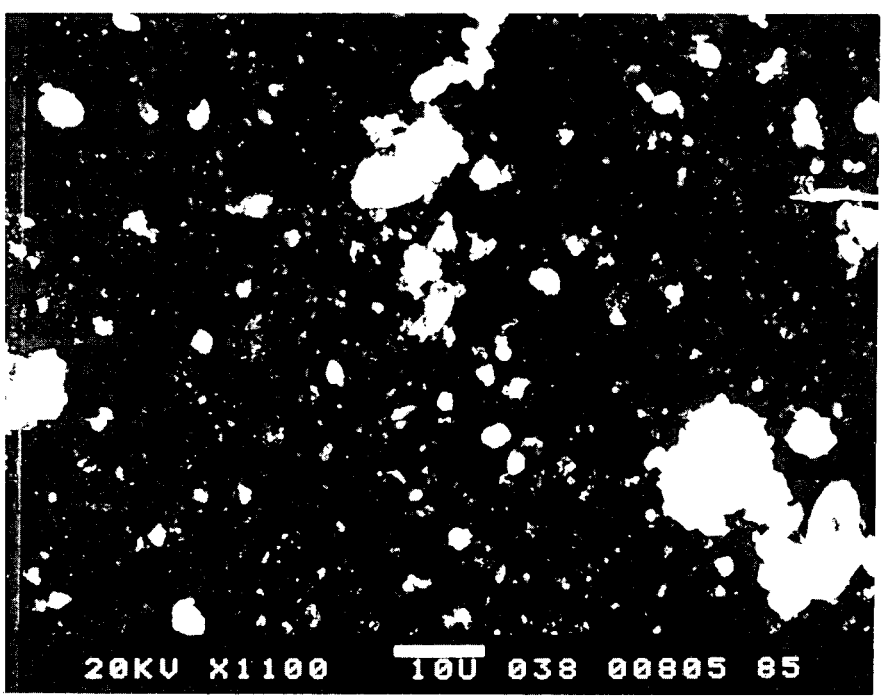

Figure 7. Scanning Electron Micrograph of phosphate ore from Togo. Center bar represents 10 μm. (XBB 863-1734)

A difficulty in calculating the fraction of the energy absorbed by a given particle suspension has been the poor match between the range of wavelengths for which optical data for the materials are known and the spectrum of the light source. In some cases, as much as 20% of the lamp's energy is at wavelengths for which the values of the optical constants are not known. A UV/VIS/NIR spectrophotometer was equipped with an integrating sphere for measuring the diffuse reflectance. It was possible to determine the spectral variation of light absorbed by the particle sample over a range of wavelengths from 185 to 3200 nanometers. Measurements of a hematite sample show trends that are consistent with that predicted from calculations made using the optical data from the literature. This favorable comparison gives some confidence that the absorption measurements from the spectrophotometer will enable us to make reasonable extrapolations for the optical constants of the materials at wavelengths where data is not available.

Two important steps in assessing the suitability of a chemical reaction for the STARR receiver are to evaluate methods of particle production (in addition to particle entrainment), and particle removal from a gas stream. A number of methods were investigated. All the metal oxide particles used in the experiments described in this report were produced by chemical methods. When using chemical preparation methods the particle size is small and can be controlled by controlling the concentration, pH, etc. of the solution. In general, smaller particles are possible with chemical methods than by mechanical grinding and do not require expensive production processes. Particles are produced by chemical methods in vast amounts by a number of industries, so reasonable estimates of production costs are fairly easy to obtain. Methods of recovery and recycling of particles (if necessary) depends strongly on the particular reaction and must be evaluated individually.

A visit to the Particle Technology Laboratory of the University of Minnesota helped to confirm that our research into methods of producing small particles had been adequate as we discovered no methods of particle production we were not aware of. However, much of their research deals with the removal of small particles from gases, and they are an excellent resource in that area. An important part of the visit was to establish lines of communication with a leading particle technology laboratory.

4.4 Reaction Studies

Chemical reactions studied with the experimental apparatus fell into two main areas: 1) chemical conversion of the particle material (particles as a feedstock and particle gas reaction categories, and 2) particle initiated chemical reactions in the gas (particle as heater and particle as catalyst or photoinitiator categories). In most experiments, gas or particle compositions were monitored for experiments to compare samples with no radiant heating and samples that were heated radiantly to temperatures as high as 1300 degrees Kelvin.

The chemical conversion of the particles was studied for inorganic oxides and carbon. The conversion of metal oxides has several applications: it is a key endothermic process in a number of two step water splitting cycles, the reduction of metal oxides is a common and important step in many industrial processes, and changes in oxide states can be used to drive cycles for the production of gaseous compounds, e.g., the Harteck process.

Experiments using carbon were undertaken for several reasons. First, the SPHER Mark I tests revealed that carbon might oxidize at lower temperatures under solar irradiation than isothermal heating with the same temperature history. This may be an example of a radiantly enhanced process that is of interest on basic grounds. Secondly, both the production and oxidation of carbon particles in a radiant environment is of considerable interest to the CO_2 and H_2O reforming of methane and in coal and biomass gasification.

The first experiments described here were undertaken to explore the reduction of the metal oxide in the STARR reactor. The following experiment was carried out for several compounds. A commercially available powder of the oxide was placed in the cyclone shaker and a particle-gas suspension was produced. The suspension was passed through the extinction tube, the reactor vessel, and finally through the dichotomous sampler where particles were collected on filters. The mass loading on each filter was determined by the "beta" gauge and the filter placed in the X-ray diffractometer. Each experiment consisted of pairs of runs with the solar simulator off to collect a sample of the unheated material, and a run with the solar simulator on to to collect the sample after experiencing both heat and concentrated flux. The heating was provided by the arc lamp, no supplementary heating was used. The mass loading was kept low to avoid clogging the filters.

Powders of hematite, magnetite, cobalt oxide (Co_3O_4), copper oxide (CuO), zinc oxide (ZnO), and manganese dioxide (MnO_2) were separately entrained in argon and passed through the reactor. Because of the limited size of the reactor and low particle loading, the particle suspensions were not sufficiently absorbing to reach the maximum theoretically attainable temperatures and the resulting temperatures ranged from 1030°K to 1070°K. Significant reduction of copper oxide (CuO to Cu_2O) was demonstrated by x-ray diffraction measurements. The extent of conversion varied from 14% to 29%. (14% for the fine particles and 28% for the coarse fraction.) Figure 8 gives the x-ray diffractometer measurements of Fe_3O_4 particle samples taken both before and after the solar simulator was turned on. As expected (because of the limited temperatures), hematite, magnetite, zinc oxide, and manganese dioxide did not show reduction. Cobalt oxide did show reduction in a first experiment, but no reduction in a subsequent experiment.

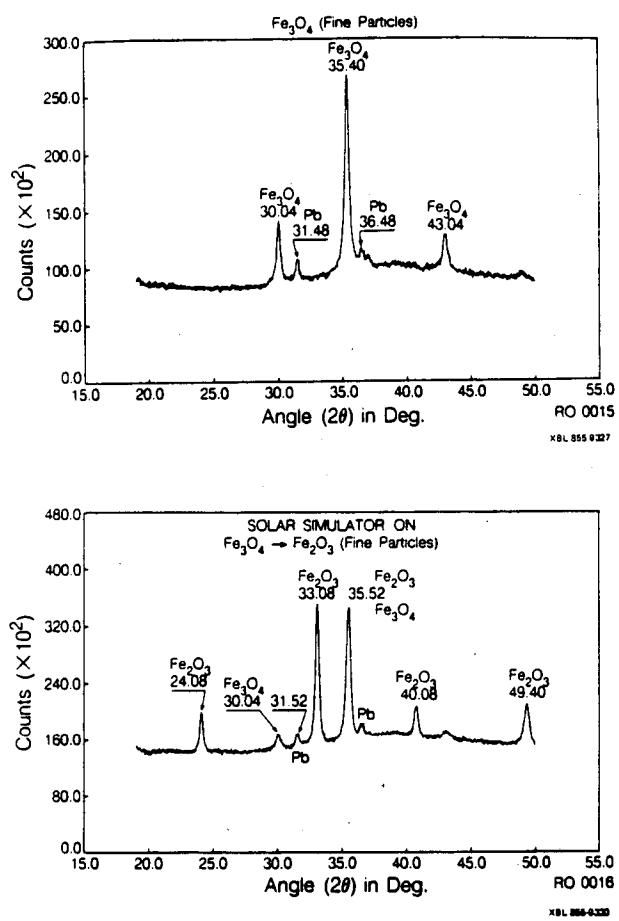

Figure 8. X-ray diffraction data showing particle composition changes. Upper figure is without solar simulator; lower figure is with it on.

The negative result of the attempt to convert hematite to magnetite was used to determine the sensitivity of the system to detect the conversion of hematite to magnetite. A computer generated graph of an x-ray diffractometer scan of a hematite sample of "fine" particles was produced. Using 3 times the standard deviation of the background in the region of 30.09 degrees, the detection limits corresponds to a 12% conversion factor. (The required crystal thickness to produce a Bragg diffraction peak is about 100 nm.) The particles collected on the "fine" filter are smaller than 2500 nm.

An experiment was performed to oxidize powdered magnetite to hematite using air as the entraining gas. An important goal of this experiment was to assess how rapidly oxygen can diffuse into the magnetite particle. The results showed that over 70% of the magnetite particles smaller than 2.5 microns in size were converted to hematite in 6 seconds in the reactor. This demonstrates an important advantage in using micron-sized particles to perform solid gas reactions where diffusion of a gas through the solid is necessary. This also demonstrates that the transport of oxygen through the hematite is not a contributing factor in the failure to reduce the hematite.

Gas processing experiments with the particles acting as heaters and photoinitiators were undertaken to study several reactions identified in Chapter 2. The two main experiments performed were the oxidation of nitrogen and the CO_2 reforming of methane. Nitrogen fixation was pursued to explore photoenhanced reactions at high temperatures for the oxidation of nitrogen. The experiments consisted of seeding an air stream (some experiments utilized water saturated air) with various metal oxide particles and flowing it through the reactor at 800° C. Addition of the particles always resulted in an increase in NO_x, but only for a short time. However, the NO or NO_x concentration did not approach the equilibrium value calculated from the CHEMKIN codes at 800° C. Thus, under the limited experimental conditions achieved, no significant enhancement of the reaction was observed.

The CO_2 reforming of methane is a highly endothermic reaction that is being pursued for thermochemical transport of energy. In particular, as part of the distributed receiver program, SNLA is pursuing research and development on this reaction for solar conversion and transport of energy from individual dish concentrators to a central site. The reaction is reversed at the central site to create heat to operate a heat engine.

In our experiments CO_2 and CH_4 were mixed in a ratio of 4:1 seeded with various metal oxide particles, and passed through the illuminated reactor at 750° C. Gas samples were taken for the gas chromatograph, Unfortunately, column problems in the gas chromatograph prevented a quantitative determination of the results. However, a CO peak was present and a carbon monoxide meter placed near the reactor outlet indicated in excess of 1000 ppm of CO.

Late in the year further experiments were undertaken with methane. These experiments were designed to examine whether carbon formation, usually an unwanted "side effect" in the CO_2 reforming of methane, could be deliberately achieved. If so, this process could be used to form particles *in situ* which could absorb light and thus provide additional heating. Flows of methane and mixtures of methane with Ar, C_2H_2 and CO_2 were heated in a tube furnace and the output stream was monitored for particles using a laser extinction tube. The experiments were run at different flow rates and temperatures. The tube furnace was chosen over the solar simulator because it has a large heated region and the temperature is easier to regulate. The experiments provided three main results. First, the rate of methane decomposition to carbon occurs rapidly above 960° C. The transition from a clear output gas stream to a black stream occurred rapidly. Secondly, minute amounts of C_2H_2 aid the decomposition. This may be due to reactive species released by C_2H_2 breakdown or be due to better heat transfer. Thirdly, CO_2 seemed to have no effect on the CH_4 decomposition as determined by the extinction measurements, but with it was added there was water condensation in the outlet tube indicating other reactions were occurring. Further experiments will be carried out to measure the output gas concentrations.

APPENDIX A

PHOSPHATE PROCESSING IN TOGO USING SOLAR THERMAL ENERGY

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I. Introduction

This report analyzes the feasibility of processing phosphate rock to produce elemental phosphorus using concentrated sunlight. The economic consequence of this process is to increase the value of the phosphate rock by 30 to 40 times (from 3- 4 cents per kg to $1.40 per kg). The effect of this production would be to transfer a portion of the income currently realized from phosphate processing in Europe to Togo by increasing the export value of the product.

The process envisioned uses a number of heliostats to redirect sunlight into a rotary kiln mounted on a tower. It has been demonstrated in France and the United States that extremely high temperatures can be achieved using concentrated sunlight (1). Several thousand of these mirrors have been produced for use in the United States and Europe, and the cost and performance have been evaluated (2). Rotary kilns using sunlight have also been designed and built (3). In 1981 a group from the Institute of Gas Technology successfully demonstrated the production of elemental phosphorus from phosphate using the White Sands Solar Furnace in the USA (4). Similar processes have been demonstrated for other types of chemical production and mineral processing in France and the USA. The feedstocks for the process are phosphate, silica and carbon, all available locally. The presence of carbon guarantees the mixture will be highly absorbing and can effectively capture concentrated sunlight.

Solar processing of phosphate rock represents a unique opportunity to explore the use of renewable energy for industrial processes in Togo. The technical feasibility of directly heating solids and gases to high temperatures using concentrated sunlight has been studied in the author's laboratory for the past 7 years (5). An active research and development program into the processing of fuels and chemicals is currently underway at LBL (6).

The approach is analyzed in the next five sections of this report. The following section provides some background in existing processes and products. Section III reviews current progress in solar thermal processing, presents the industrial requirements, and describes a conceptual solar thermal phosphate processing plant. Following that, the

economics of the plant are estimated. Section V outlines the additional research and development required prior to the final design and construction of the plant. The final section contains a summary of the conclusions and recommendations for the future.

II. Background

Togo is a major exporter of phosphate rock. At the KPEME processing plant near Lome, the phosphate is mined and beneficiated by washing, screening, and centrifugal separation,, and is dried. The plant produces about 10,000 metric tons of phosphate per day in the size range from 25 micrometers to 3 millimeters with a water content of 1.5% or less (7). Docking facilities are located at the plant site for shipment, mainly to Europe. The phosphate is in the form of fluorapatite, containing impurities of silica, iron, aluminum oxides and other minerals.

The value of phosphate increased substantially during the 1970's, took a sharp dip toward the end of that decade and has now resumed a slow rise. Current 1985 prices are in the range of $30 to $42/ton. The value of phosphate can be increased substantially by further processing. The main processing methods are wet acid treatment and smelting in electric furnaces.

In the electric furnace method, a charge of nodulized phosphate rock, silica, and coke is placed in an electrical arc furnace and heated to 1500 °C. Elemental phosphorus is released and condensed under water. The amount of electricity required for this process is substantial — about 14 kWh per kilogram of phosphorus(4). Assuming electric costs of 5 cents/kWh and a phosphorus price of $1.43/kg, the cost of electricity is 50% of the cost of the phosphorus. In 1980 in the United States, about 9% of the phosphate rock was smelted in electric furnaces. The U.S. phosphorus industry in 1979 had earnings of over $500 million.

Phosphate may also be treated with acid to produce a variety of products. Superphosphate is created when phosphate rock is digested with sulfuric acid. If more sulfuric acid is used, phosphoric acid may be produced. If phosphate is acidulated with phosphoric acid, triple superphosphate is produced.

Elemental phosphorus may be oxidized to produce phosphoric acid or converted into numerous anhydrous derivatives. The principle use of elemental phosphorus (45% of the production in the USA) is for the production of industrial phosphates for use in detergents. About 15% is used in foods and beverages, and 10% in metal treating. Phosphorus finds other uses in flame-retardant additives for polymers, liquid fertilizers, lubricating oil additives, matches and pesticides.

III. Solar Processing of Phosphate

Phosphorus is produced by the following chemical reaction that takes place in an electric arc furnace:

$$4Ca_5F(PO_4)_3 + 18SiO_2 + 30C \xrightarrow{heat} 18(CaO.SiO_2.1/9CaF_2) + 30CO + 3P_4$$

where the compounds on the left hand side of the equation are fluorapatite, silica, and coke respectively. The products of the reaction displayed on the right hand side are slag, carbon monoxide, and phosphorus respectively. The feed materials are pelletized to allow for sufficient porosity to allow the gases to evolve, as the furnace is usually deep with large volume. Typically, 10 parts by weight of phosphate to 1.5 parts each of silica and coke are consumed for each part of phosphorus produced. The furnace temperature is raised to between 1450 and 1500 °C to initiate the reaction. The reaction is due to heat alone, and no electrolysis occurs.

Whaley, Yudow, and Schreiber of the Institute of Gas Technology performed a series of experiments in 1981 to demonstrate that the above reaction could be initiated through heating by concentrated sunlight (4). They used a carbon boat illuminated on its side with the horizontal beam from the solar furnace at White Sands, New Mexico. The reactor vessel was stainless steel with a fused silica window and argon as a diluent gas. The off-gases were captured in a series of water bubblers. While the results were quantitative, they unambiguously established that concentrated solar energy could initiate the reaction to release phosphorus.

Recent Progress in Solar Thermal Energy Research

The Solar Thermal Energy Research and Development Program has been a major element of the overall solar energy program in the United States since the early 1970's. It represents a total expenditure in excess of $500 million in research and development. The French have been exploring solar thermal processes for high temperature metallurgy and refractory ore treatment at Odeillo for an even longer period. The work in these and other countries has resulted in the development of several distinct approaches to the utilization of concentrated solar flux. A major eight year development program in the US resulted in the design, construction, and operation of the Solar One solar thermal electric power plant. This plant, located in California, utilizes about 2000 heliostats surrounding a central tower. Each heliostat consists of many smaller mirrors with combined reflective areas of 50 square meters. These heliostats redirect sunlight to a boiler mounted on a central tower. The plant can generate a peak power to 10 megawatts of electricity, and store energy in the form of sensible heat to operate for several hours during cloudy weather or at night. This approach is considered to be at the commercialization stage.

A second thrust of the solar thermal program in the United States has been the exploration of new methods to utilize concentrated sunlight for purposes other than electrical power generation. Concentrated sunlight can be used for the production of process steam for industry, producing very high temperature gas streams, and for the production of fuels and chemicals. It is this last area that is of most interest in the context of this study.

The design, construction, and deployment of heliostats has been one of the major tasks of the solar thermal program and represents one of its most mature elements. The key area of effective utilization of the solar thermal processing of chemicals is the receiver, and device that converts the concentrated solar flux to heat or chemical energy. Lawrence Berkeley Laboratory is a leading research center studying the direct radiant heating of particulate solid matter. In the past seven years the optical, thermal, and chemical properties of radiantly heat particles have been studied, both theoretically and experimentally.

For sunlight to be captured effectively by particulate matter, the particles must be absorbing. For the particles to reach the required temperatures they must have the proper flow conditions and size. To complete the chemical reaction within the given residence time, they must have sufficient surface-to-volume ratios and adequate chemical activity. Under many circumstances, heating particulate matter is most efficiently done using radiant energy. This is most certainly the case for phosphate processing.

Conceptual Design

It is proposed that the solar heating for phosphorus production be carried out by the direct illumination of the mixture by concentrated sunlight in a rotary kiln that faces the heliostats. Figure 1 illustrates the overall conceptual design for a solar powered phosphate processing plant. The largest portion of the plant is composed of heliostats. The heliostats redirect and concentrate sunlight into the rotary kiln located on the tower. Sunlight enters the kiln through a fused silica window as shown in Figure 2. The concentrated sunlight impinges on the mixture and interior of the refractory lined kiln. The charge is premixed and enters through a hopper and screw feed assembly to maintain a positive seal on the chamber. The rotating portion of the kiln is located inside a sealed stainless steel chamber that provides the mounting for the window. As the charge moves towards the lower end of the kiln, it heats and forms slag that is discharged over the lower lip of the kiln. The evolving gases (CO and P_4) leave the chamber and phosphorus is condensed in a tower equipped with water sprays at 45 °C.

Other features of the plant design are indicated in Figure 2. The charge is moved to the reactor by conveyor belts or scoops. The slag leaves the reactor chamber through a trap to prevent evolved gases from escaping. A shaft carries rotary power to the kiln through a sealed bearing in the outer chamber. A portion of the CO_2 is recirculated to provide a gas barrier to prevent vapors from condensing on the window. The flow rate and temperature of the recirculating CO_2 may also be used to control the temperature of the kiln. The plant capacity and size are determined by the number of heliostats, and is open to choice.

Plant Capacity and Size

The optimum size of solar thermal installation has been a matter of much study and some controversy. For this reason, the size for the conceptual plant in this study is large enough to obtain the benefits for the central receiver approach, but much smaller than

the maximum possible size. Various studies and experiments have indicated that sizes less than 0.5 Mw electric (2 to 3 Mw thermal equivalent) have not shown to be economical for electrical power production. A thermal process power of 5 Mw was chosen for the conceptual design. This is above the minimum size, but not so large as to require a very large land area for the heliostats.

Within the limitations of this study it is not possible to perform detailed calculations regarding the optimization of the heliostat field layout, simulated plant performance based on solar data, component efficiencies, or detailed cost studies. Rather, the object is to make a rough assessment of the production capacity and economics of such a plant. If this initial assessment is positive, more detailed studies and further research and development should be undertaken. Reasonable estimates may be made of plant performance based on prior studies, and experience with other solar thermal power facilities.

Once the power level of the plant has been decided, the area required for the heliostats and dimensions of the components of the plant may be determined. The number and size of the heliostats to obtain 5 Mw of thermal power depends on several factors. The most important are the peak intensity of the **direct** radiation from the sun, the reflectivity of the mirrors, and the arrangement of the heliostats.

Solar data taken in Togo (8) indicate peak intensity for total radiation on a horizontal surface is 800 to 900 watts/sq. meter, but more typical maximums are 600 to 700 watts/sq. meter. The design power for the plant must be based on the peak anticipated maximum thermal input from the heliostats. This will be chosen as 900 watts/sq. meters. However, the average maximum operating power will be about 80% of the design power.

The optical efficiency of the heliostat field is defined by the fraction of total energy delivered to the focus divided by the product of normally incident radiation and the total area of the heliostats. Using a reflectivity of 0.90, a cosine effect of 0.90 (because the mirrors do not directly face the sun, but bisect the angle between the sun and the focus), and a shading, blocking, and circumsolar factor of 0.95, the optical efficiency (product of the foregoing factors) is 0.77.

The heliostat area is determined by dividing the power rating of the plant by the product of the peak incident solar intensity and the optical efficiency.

For the plant under consideration, the area is 7200 square meters or 144 heliostats (assuming an area of 50 m^2 per heliostat). Using a figure of 0.3 for the ratio of heliostat area to land area, and an effective rim angle of 15%, the land area is found to be 24,000 square meters. The heliostat field is aligned north of the tower as an equilateral triangle 236 meters on a side (Figure 3). The tower height is 55 meters. Given the field size, and assumed concentration ratio (750) the diameter of the focal zone will be somewhat less than 3 meters. Thus the kiln opening (and window) should be 3 meters in diameter. Using an aspect ratio for the kiln of 2:1, the kiln would be about 6 meters long.

The process rates may be calculated from the required heat rates and plant power. The heat of reaction is taken to be 25 million Joules/kg of phosphorus produced (4) and we follow Whaley, et al. in assuming that the amount of energy required for sensible heat

and thermal losses is equal to the heat of reaction. The ratio of the plant operating power divided by the energy required per mass to process the product gives the phosphorus production rate. Thus 5M J/sec divided by 50M J/kg yields a phosphorus production rate of 0.1 kg/sec. or 360 kg/hr. The rate of flow of feedstock material is 13 times this rate or 4700 kg/hr.

IV. Economics

The operating revenue from the plant is obtained from total phosphorus production per year. This is dependent upon the solar resource, which must be estimated from the available data of total intensity on a horizontal surface. The integrated energy from tracking collectors is greater than that falling on a horizontal surface because the tracking collector faces the sun, and so has much less of a cosine effect. Preliminary estimates (8) of the total daily average of direct normal radiation in Lome are 6 kWh/day/m^2 or 2200 kWh/year/m^2. The plant production may be approximated by assuming it is operating at full power 6 hours/day (in fact, it would operate a longer time at lower power). On this basis, the phosphorus production is about 800,000 kg/year. The market price (1981) for phosphorus is $1.40/kg yielding gross revenues of (US) $1.1 million/year.

It is difficult to obtain precise figures for the cost of new solar installations, but again a few estimates may be made. Heliostat costs are estimated at $300/$m^2$ at the factory. The heliostat field is the largest single component of the cost at $2.2 million. The tower, receiver, handling facilities are (very roughly) estimated at $1 million, bringing the total plant cost to $3.2 million. Operating and maintenance costs must be included, but no estimates were made. Setting aside the issue of operating costs, the plant would generate sufficient income to reimburse its costs in less than three years. This would normally be considered a good investment.

Several caveats must be noted in this analysis. First, it is a new technology, involving high temperatures and new processes. There must be further research and development work performed on the receiver. The life time of the receiver, in particular the window, is not known. However, the technology for making the windows has been developed by the telescope making industry. Second, shipping and assembly costs for the heliostats have not been included and may be significant.

The cost of the raw materials mainly derives from transportation costs. Because of the high multiple of value added by the processing, the phosphate cost is only about 3% of the value of the phosphorus. Silica is available in the form of sand, which is abundant in Togo. The source of carbon deserves some comment and further investigation. The coastal region of Togo has a very high concentration of coconut palm plantations. The shell of the coconut is one of the best sources for activated charcoal. If the supply is sufficient from copra production or other uses, these could supply the carbon for the process. Alternatively, coke or other sources could be imported, and the cost would still be a small fraction of the value of the phosphorus.*

*See note in proof, page 50.

V. Research and Development Needs

This paper has very briefly set forth the concept and an analysis of a potentially important industrial process. The analysis confirms the initial idea that the economics are favorable, and the process possible. However, there are many unknowns that must be explored before a detailed design effort is warranted. Further work must be carried out in the areas of technical feasibility, economics and establishing a collaborative relationship.

VI. Conclusions and Recommendations

This paper set out to determine whether solar thermal processing of phosphate to make elemental phosphorus made technical and economic sense. The answer, within the limits of this study, is a definite yes. The technology of collecting and concentrating sunlight is relatively well developed. This solar kiln needs further development, but it is well within the spirit of current research and development work underway in the United States. In the section on economics, it was shown that such a plant would pay for itself within three years. Several caveats were noted regarding uncertainties in the development of new technology and realistic cost determinations.

The recommendation of this study is that the technology and economics should be studied more closely through the cooperative research and development programs in both Togo and the United States. It is a reasonable possibility that within five years such a plant may be built and open a new chapter in the industrial use of solar energy.

VII. Acknowledgments

The author takes great pleasure in acknowledging his colleagues in Togo. Profound thanks go to Minister Edoh for his warm support and interest in the project, and his generous help providing logistical support. Sincere thanks go to Professor Gnininvi of the Universite du Benin for his time and efforts in assisting the author. Gratitude is expressed to the CIES for providing funds thorough the Fulbright program, which enabled the author to visit Africa, and in particular, Togo.

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Note added in proof

After completing this paper, the author toured a palm oil plantation near Lome. During this visit it was ascertained that about 20 tons per day of coconut shell residue is produced by this plant. This is sold locally for fuel at about US cent /kg (50FA/kg). The conceptual design plant required about 800 tons per year of carbon. Thus, it appears that this palm oil processing plant could easily supply the required carbon at very low cost. The shells must be heated in the absence of air to produce pure carbon before being used in phosphate processing, but this should not be a difficult or expensive step.

Heliostats and Tower

Specifications

5 MW thermal power
50 m^2 Heliostats
Assumed heat rate 50×10^7 J/kg
Ambient heat of reaction and sensible heat

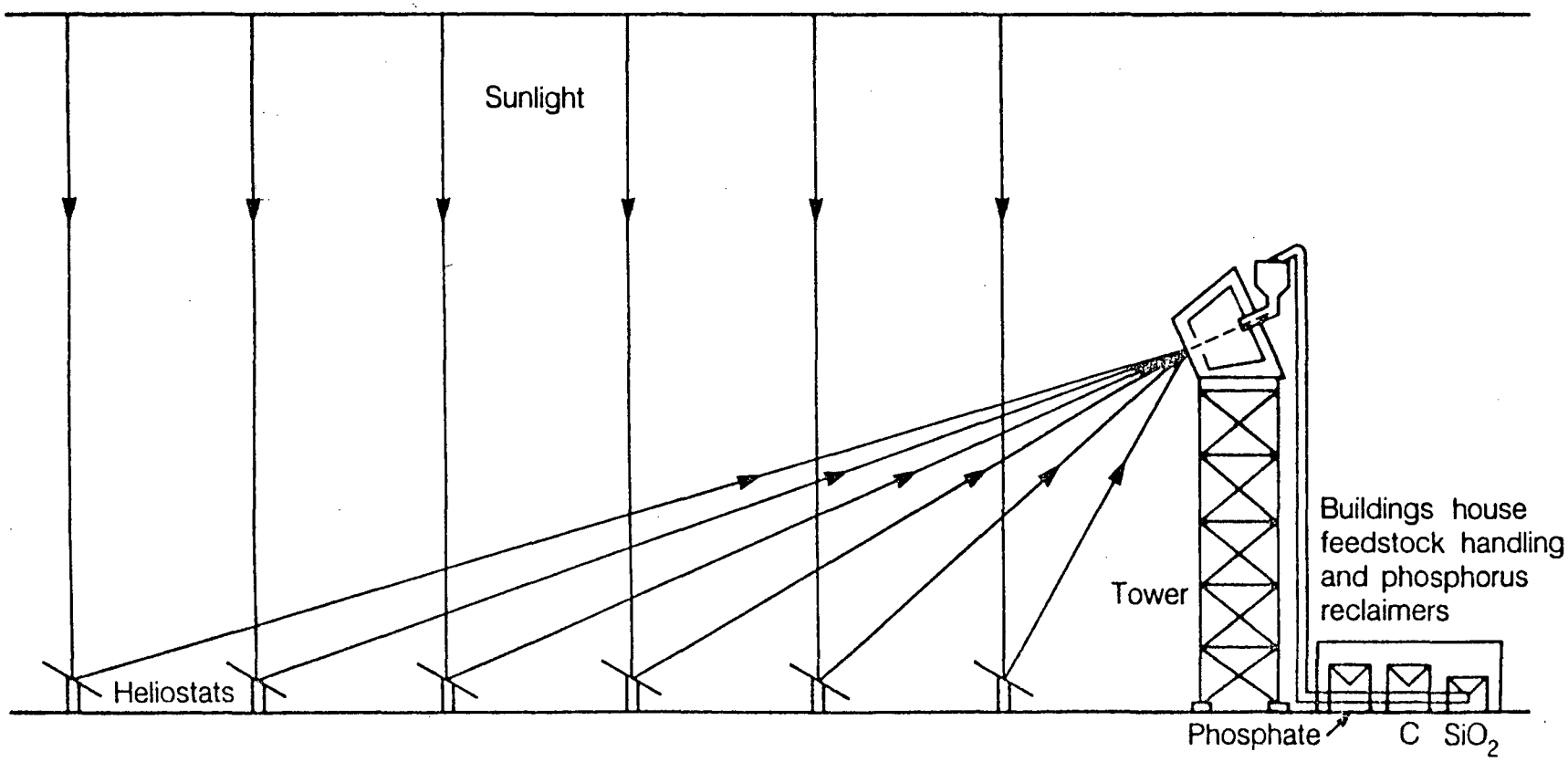
Dimensions

60° Aspect, N or S facing
15° rim angle
30% ground cover
Heliostat field is on equilateral triangle 236 m/side
Tower height = 55 m to center of kiln

Process

360 kg of phosphorus/hr produced
~500 kg/hr of feedstock – (3600 kg/hr)

Window composition: fused silica
Window diameter: 3 meters



XBL 856-9847

Figure 1. Solar Phosphate Processing Plant

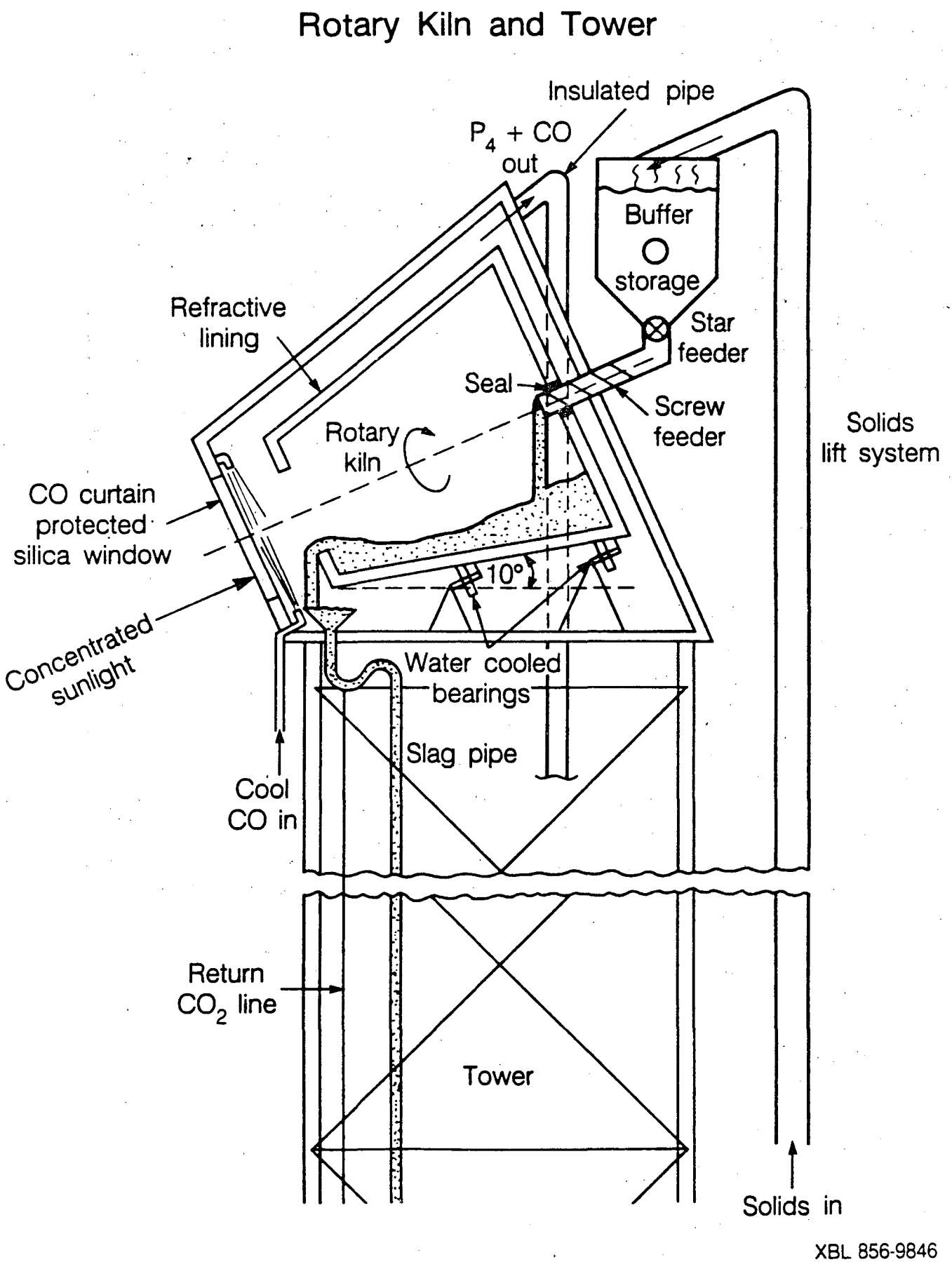


Figure 2. Solar Receiver/Reactor

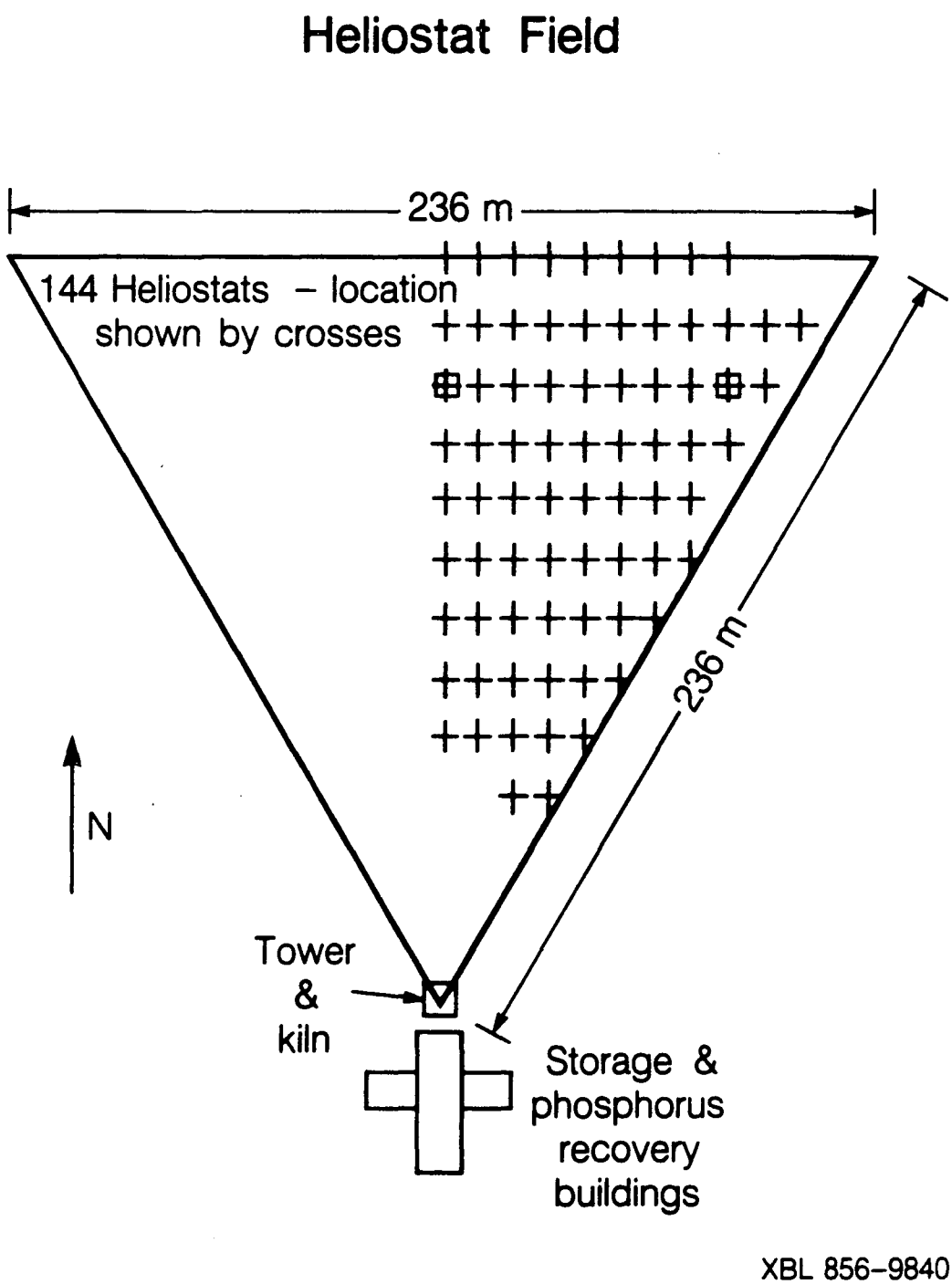


Figure 3. Approximate Heliostat Layout

APPENDIX B

Reactions Catalyzed by Iron Oxides

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There are several reactions that may be catalyzed by iron oxides which are of interest. These include $SO_3 = SO_2 + 1/2\ O_2$, $H_2O = H_2 + 1/2O_2$, $N_2 + O_2 = 2NO$ and $N_2 + 3H_2 = 2NH_3$. The first of these reactions has been discussed in the report: Analysis of Reaction Rates Relevant to Photo-assisted Catalysis. The other reactions will be discussed below.

$H_2O = H_2 + 1/2O_2$. This reaction is most important for producing hydrogen provided a cheap source of energy can be found which will effect this process. The primary source of hydrogen at the present time is methane. Consequently, alternate energy sources must be less expensive. Solar energy is attractive, but the difficulty with the reaction is that it is highly endothermic ($\Delta H^{o}_{298} = -57.80 kcal/mole$) . Thus, the temperature for dissociating water into hydrogen and oxygen ($\Delta G = 0.0$) is over 2,000^{o}C. However, it has been possible to decompose water photochemically in the presence of catalysts[1] and photoelectrochemically using ferric oxide doped with magnesium oxide[2]. These facts suggest that these materials potentially could serve as absorber/catalysts for the photochemical decomposition of water at temperatures significantly lower than those required for the thermal reaction. The requirements for the absorber/catalysts are stringent. They must absorb photons from the solar spectrum; they must evolve oxygen from water under the conditions of irradiation; and they must evolve hydrogen as well.

The chemical properties of the iron oxides indicate that they have some of the features necessary for photocatalysis. Some of the sites are sufficiently oxidizing that they will release oxygen from water; and other sites are sufficiently reducing that they will liberate hydrogen from water. The important thermodynamic relationships are summarized in Table I. At temperatures between 298 K and ca. 1000 K, the reaction between ferrous oxide and water to produce hydrogen is thermodynamically favorable (reaction 1).

$$(1)\quad 3FeO + H_2O_{(g)} = Fe_3O_4 + H_2 \qquad \Delta G_{298} = -11.83\ kcal/mole$$

$$\Delta G_{1000} = +2.01\ kcal/mole$$

Moreover, at ca. 1500 K, Fe_2O_3 decomposes to Fe_3O_4 with an oxygen pressure of 1 atm (reaction 2). However, the difficult step is decomposing

$$(2)\quad Fe_2O_3 = 2/3\ Fe_3O_4 + 1/6\ O_2 \qquad \Delta G_{1500} = 0.00\ kcal/mole$$

magnetite to ferrous oxide. This reaction will produce a vapor pressure of 1 atm of

oxygen only at ca. 2500 K (reaction 3). The decomposition

(3) $Fe_3O_4 = 3FeO + 1/2\ O_2$ $\Delta G_{2500} = -.253\ kcal/mole.$

of Fe_2O_3 to directly give ferrous oxide should give 1 atm of oxygen at ca 2100 K (reaction 4). Providing that the energy of solar photons

(4) $Fe_2O_3 = 2FeO + 1/2\ O_2$ $\Delta G_{2100} = -.215\ kcal/mole.$

(ca. 2.2 eV or 52 kcal) can be efficiently used in photo-decomposing water, there is sufficient energy for that purpose. However, the difficult chemical step is producing appreciable quantities of O_2 from the iron oxides, Fe_2O_3 or more especially, Fe_3O_4. At 1000 K, this reaction is unfavorable by ca. 45 kcal/mole. However, solar photons could provide sufficient energy to decompose Fe_3O_4 since their average energy is ca. 52 kcal. Thus, the practical question is whether or not Fe_3O_4 will decompose in a solar furnace at 1000 K to form O_2 and FeO. In order that the FeO sites be reactive toward water, their mobility should be reasonably high, and the electrical conductivity probably should also be high, since reaction 1 requires electrons to be transferred from the Fe(2+) ions of the lattice to the protons of the adsorbed water molecules. From Samorjai's results[2], doping with another metal oxide such as CaO, MgO, or K_2O may serve this purpose. In fact, $KFe_{11}O_{17}$ is an electronic conductor[3], while the ferrites corresponded to Fe_3O_4 doped with the metal oxides.

Although reduction of Fe_3O_4 to FeO is a necessary condition, it is not sufficient. The next crucial step is the reoxidation of FeO to Fe_3O_4 by water (reaction 1) rather than by O_2 (reverse of reaction 3). This is certainly a reasonable possibility since the oxides should be reasonably good sites for binding water compared with oxygen. The vacancies in photolyzed Fe_3O_4 should also be as mobile as possible in order to provide for fast oxidation/reduction of water, and consequently a high temperature would be desirable. However, the oxidation of FeO by water becomes thermodynamically unfavorable near 1000 K so that too high a temperature is counterproductive. Consequently, it may be necessary to find a compromise temperature for this reaction to take place. 700-1000 K seems to be a reasonable range. The necessary steps outlined above should be investigated experimentally in order to assess the feasibility of using Fe_3O_4 as an absorber/catalyst for the photodecomposition of water.

$N_2 + 3H_2 = 2NH_3$. The Haber process is currently carried out at 450°C and 2000 psi. The catalyst which is used for this reaction is prepared from Fe_3O_4, Al_2O_3, and promoters such as CaO and K_2O by reduction with hydrogen. The active catalyst is metallic iron supported on about 3% Al_2O_3. The mechanism appears to be similar to that described above for SO_2/SO_3 and the decomposition of water. Nitrogen reacts with iron to form a nitride (Fe_2N, Fe_3N, or most likely, Fe_4N). The hydrogen dissolves in iron and reduces the nitride to give ammonia. The catalyst particles are black and 2-6 mm in diameter. The yield of ammonia increases linearly with *decreasing* particle size. This is attributed to enhancing the diffusion rate of NH_3 from Fe. This reaction is thermodynamically more favorable at lower temperatures, with an equilibrium constant of 1

near 25°C. However, high temperatures and catalysts are required to break the very strong N-N bond. If the absorbed N_2 could be cleaved by photons from a solar source, then the reaction might take place at lower temperatures with a more favorable yield and at lower cost. However, the known M-N_2 complexes have absorption bands at 3eV or higher, and the photochemistry that it known leads to loss of N_2 from the metal rather than N-N bond cleavage. the other important point is that the operating cost of the Haber process is primarily due to the price of methane to produce hydrogen used in the reaction. The cost of heating and compressing the gases is also important. On the whole, it doesn't appear that the Haber process would benefit from using solar as an energy source. Production of the hydrogen used for the Haber process would be a more important contribution.

$N_2 + 0_2 = 2NO$. This reaction occurs at high temperatures, and in lightening discharges. The reaction is entropy-driven and would be a reasonable reaction for a solar furnace providing that a suitable absorber/catalyst could be found. The Wisconsin process uses CaO at 2000°K for this reaction. The primary difficulty in photoassisting is the same as described for the Haber process. The MN_2 complexes do not normally absorb photons with energies below 3eV, and when they do, it is the M-N bond that breaks rather than the N-N bond. The properties of N_2 complexes are sufficiently well studied so that it is not easy to guess what type of absorber/catalyst would be useful to try for this reaction.

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3. K.O. Hver, *J. Electrochem. Soc.*, 115, 826 (1968).

Table I

	Reaction	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}	ΔG^o_{1000}
(1)	$Fe + \frac{1}{2} O_2 \rightarrow Fe\,O^a_{0.947}$	-63,461	-16.036	-58,682	-47,420
(2)	$3Fe + 2O_2 \rightarrow Fe_3O_4$	-265,880	-78.404	-242,516	-187,476
(3)	$2Fe + 3/2\,O_2 \rightarrow Fe_2O_3$	-196,500	-65.10	-177,100	-131,399
(4)	$3\,Fe\,O + \frac{1}{2} O_2 \rightarrow Fe_3O_4$	-75,497	-30.30	-66,469	-45,201
(5)	$2/3Fe_3O_4 + 1/6\,O_2 \rightarrow Fe_2O_3$	-19,247	-12.83	-15,423	-6,415
(6)	$H_2O_{(g)} \rightarrow H_{2(g)} + \frac{1}{2} O_{2(g)}$	57,800	10.59	54,644	47,210

APPENDIX C

Analysis of Reaction Rates Relevant to Photo-Assisted Catalysis

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The concept of improving the yields of thermally-produced compounds through photochemistry is an attractive one. Since, by definition, the final mix of reactants and products is kinetically-controlled (non-equilibrium), an analysis of the rates of the relevant reactions is important. The following example should serve to outline the kinetic issues and the relationships between kinetic control and equilibrium conditions.

Consider the thermal reactions of SO_X in the presence of a catalyst.

(1) $SO_3 \underset{k_{-1}}{\overset{k_1}{=}} SO_2 + 1/2O_2 \quad K_{eq} = k_1/k_{-1}$

(2) $A = A^* + \frac{1}{2} O_2$

(3) $A^* + SO_3 = A^*SO_3$

(4) $A^*SO_3 = ASO_2$

(5) $ASO_2 = A + SO_2$

(6) $A + SO_3 = ASO_3$

The dissociation of SO_3 (reaction (1)) is entropy driven and therefore favored at high temperatures. The relevant values of the entropy, enthalpy, and free energy are listed in Table I. If we assume that the values of the entropy and enthalpy are constant with temperature, the equilibrium constant can be calculated as a function of temperature (Table I). A catalyst that enhances the forward and reverse rates of reaction (1) will establish equilibrium between SO_3, SO_2 and O_2 very rapidly. In order to produce yields of SO_2 higher than equilibrium values, two conditions have to be met: the active state(s) of the absorber/catalyst (reaction (2)) must be present in appreciable quantities in order to compete with unactivated absorber/catalyst (reaction (6) vs. reaction (2)). That is, thermalization of the photon energy must be slower than the photo-assisted dissociation of SO_3 (reaction (3)). From this requirement, it would appear that A* must have a reasonably long lifetime. It is possible that some A* which is only electronically excited could exist for a sufficient length of time to bind SO_3. However, a more likely form of A* is the one whose chemical composition is slightly different from its parent A. One possibility would be for reaction (7) to liberate oxygen from A.

(7) $A + h\nu \rightarrow A^* + \frac{1}{2} O_2$

In the present example, where metal oxides such as V_2O_5 and Fe_2O_3 are common catalysts for SO_3 dissociation, loss of O_2 from A to form oxygen-deficient A* is likely.[2] A* would then be re-oxidized by SO_3 (reaction (4)) or by O_2 (reverse of reaction (2)). For discrete molecular species, reaction (7) corresponds to photoreduction accompanied by loss of O_2, followed by re-oxidation by either SO_3 or O_2 (reaction (4) or (2)).

In order that thermal equilibrium *not* be established, at first sight, it would appear that the absorber should *not* be a catalyst for the thermal reaction. However, reaction (4) must take place while SO_3 is bound to the absorber. Consequently, A* (or A) must catalyze the dissociation of absorbed SO_3. In their extensive studies of catalysts for reaction (1) Rocket Research Company[1] concluded that the likely reaction mechanism for the thermolysis of SO_3 corresponds to the reaction sequence: (2) - (5), although they did not assume that the active catalyst was oxygen deficient. Isotopic and kinetic studies of catalyzed oxidations of CO, propylene and other substrates are in accord with this mechanism.[2]

The above requirements establish the optimum conditions for photo-assisted catalysis which are: (1) the absorber should be a catalyst for the reaction, (2) the temperature for the photo-assisted reaction should be significantly lower than the optimum temperature for the thermal reaction. Moreover, the absorber/catalyst should undergo significant photo-dissociation under the proposed conditions of the experiment and the photo-reduced particles should be reconstituted by the substrate under the same conditions. Another way of viewing the system is to think of the photo-dissociation of A as producing the same concentration of A* as is obtained at higher temperatures. That is, the effective temperature could be defined in terms of the ratio, A*/A. This view assumes that the rate of reconstitution of A* is fast at the lower reaction temperature of the photo-assisted reaction.

If this analysis of chemical reactions catalyzed by metal oxides is correct, the absorber/catalysts can be tested for their potential effectiveness by irradiating them in a solar reactor and examining the effluent gases for evolved O_2 (see Table II for the decomposition temperatures for other metal oxide catalysts). The photo-reduced particles could then be treated with the substrate under the same photolytic conditions and then effluent gases examined for products. The other reaction which may have this type of mechanism is the water splitting reaction. It will be more difficult to find an absorber/catalyst that photo-evolves O_2 and is reoxidized by H_2O. However, Fe_2O_3 or Fe_3O_4 or the manganese analogues form reduced oxides which are sufficiently reducing to liberate hydrogen from water. This reaction will be discussed separately.

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Table I

$SO_3 \rightarrow SO_2 + \frac{1}{2} O_2$

$\Delta H^o_{298} = 22.85\ k\ cal/mole\ ;\ \Delta S^o_{298} = 14.36\ e.u.$

ln Keq	Keq	T(K)
-3.46	3.13×10^{-2}	1073
-2.66	6.99×10^{-2}	1123
-1.88	1.53×10^{-1}	1173
-1.19	3.03×10^{-1}	1223
-0.59	5.56×10^{-1}	1273
+0.525	1.69	1378

Table II

Oxide	Decomp Temperature (^oC)	Rel. Activity[1]
Rh_20_3	1100	1.00
Ru0x	108	.76
Pd0	870	.66
$Ti0_2$	164	.36
Nb_20_5	178	.34
Ta_20_5	180	.00
Ni0	199	.27
CoO, Co_20_3, Co_30_4	895, 900-950	.47
CuO	1800	1.00
$Ir0_2$	1100	.95
Fe_20_3	1838	.51
Pt0, $Pt0_2$	550, 450 -> Pt0?	.75

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