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ANALYSIS OF APPLICATIONS OF SOLAR TECHNOLOGY FOR THE TREATMENT OF CHLORINATED ORGANIC WASTE

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ABSTRACT

Recent work has demonstrated that concentrated solar energy can destroy many hazardous chemicals that are of national concern including dioxins, polychlorinated biphenyls (PCBs), and chlorinated solvents. A detailed systems analysis was performed to determine the applicability of solar detoxification to the treatment of chlorinated solvents. This work determined the cost of destruction of trichloroethylene (TCE) a using conventional and a solar-based technology. The cost of solar detoxification and that of the conventional technology were compared for this application. This work provides a basis for choosing an application in which solar energy can be used to its fullest potential to solve a growing national problem.

INTRODUCTION

This century has been characterized by an ever increasing use of resources and, as a result, an ever increasing production of hazardous wastes that accumulate in the air, water, and soil. In recent years, the number of sites considered hazardous under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) has increased sharply from approximately 9,000 in 1980 to more than 27,000 in 1989 (1). Manufacturing facilities continue to release toxic chemicals to the air and water. In 1988, 2.4 billion pounds of toxic chemicals were released to the air in the United States (2). In that same year, 310 million pounds of toxic chemicals were released as water discharges.

Organic wastes constitute a broad range of compounds that are found in soils and groundwater. Many of these substances are currently being produced and released into the environment. The wastes include chlorinated organics such as dioxins, polychlorinated biphenyls (PCBs), trichloroethylene (TCE), perchloroethylene, and methylene chloride. They also include nitrated organics such as trinitrotoluene (TNT) and its derivatives (3,4).

The Solar Industrial Technology Program is looking for industrial and environmental applications such as these for the solar thermal technology. This Department of Energy program is managed by the Solar Energy Research Institute (SERI) with research and development activities at both SERI and Sandia National Laboratory.

In determining a representative application for solar destruction, importance was placed on the quantity of waste that already exists in the environment, the quantity of waste that is currently being released into the environment, and the location of the waste, specifically the occurrence of wastes in the southwestern United States-Colorado, New Mexico, Arizona, Utah, Nevada, and California, the region of highest solar insolation.

Chlorinated organic solvents, as a class, were chosen for this analysis. A search of the National Priority List (NPL) showed that 31% of sites contained these contaminants in the states of Colorado, Wyoming, and Utah. A total of 63% of sites contained these substances in California, Arizona, and Nevada. A search of the Enviromental Protection Agency Toxic Chemical Release Inventory showed that a total of 13,000,000 lbs trichloroethylene, perchloroethylene, and methylene chloride are released annually from manufacturing processes to the atmosphere in Nevada, Utah, Arizona, and California.

Photochemical solar destruction of these types of substances must be based on a photocatalytic or photoinitiated process because these substances do not absorb in the solar spectrum. Photocatalytic and photoinitiated destruction are potentially applicable to mixtures and raise the possibility for dramatic reductions in the reaction temperature. These advantages will be discussed later.

A detailed systems analysis was performed to determine the applicability of solar detoxification to the treatment of chlorinated solvents. This work determined the cost of destruction of TCE using conventional and solar-based technologies. The variation of system cost with reaction conditions and waste characteristics was determined for the solar technology and compared to the cost of the conventional treatment technology.

CONVENTIONAL TECHNOLOGIES OF CHOICE

Chlorinated organic solvents are released from manufacturing processes into the atmosphere in the gas phase. In addition,

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processes that remediate soils contaminated with these substances, e.g., vacuum extraction, also produce a gas stream of chlorinated organics in air. Treatment of these gas streams by conventional methods can be affected by two basic methods, solvent recovery and thermal oxidation.

Manufacturers indicated that solvent recovery systems are used when the flow and concentration of the organics are relatively high (>2000 scfm, >0.0005 by volume) and when the stream contains a relatively pure component that can be reused on site. The solvent is recovered using carbon adsorption followed by steam stripping of the carbon and condensation of the steam. Solvent recovery under these conditions is very economical because the value of recovered solvent pays for the process.

Chlorinated organics in streams that have relatively low flow rates and low concentrations (<2000 scfm, <0.0005 by volume) are generally destroyed using thermal oxidation or thermal catalytic oxidation. This is especially true if the stream consists of a mixture of substances that cannot be used on site. These are generally the circumstances associated with remediation sites.

As an example of this type of stream, a report (5) was published that described the remediation by soil vapor extraction of a contaminated soil site in Michigan. The principal contaminant was TCE along with other chlorinated organics. An analysis of conventional alternatives showed that thermal catalytic oxidation was the most cost effective method for treatment of the off gas from the process. Typical stream characteristics were a flow of 1500 scfm and a TCE concentration between 100 to 5000 ppmv. The stream was produced continuously. An analysis was performed to determine the cost of using thermal catalytic oxidation to treat the off gas. Components of the process are presented in Figure 1. Capital costs include the costs of the catalytic oxidizer, heat exchanger, scrubber to remove hydrogen chloride (HCl), and blower. Operation and maintenance (O&M) costs included cost for fuel (natural gas), annual catalyst replacement, labor, and maintenance. The total annual cost for the process was $158,000.

SOLAR TECHNOLOGY OF CHOICE

Advantages of Solar Energy

Using solar energy to provide the thermal energy to the destruction reaction has a number of advantages. Heating with solar energy eliminates the need for fuel for combustion and eliminates unnecessary production of greenhouse gases. Although solar thermal energy is more expensive than that of natural gas on a Btu basis, elimination of the fuel and extra air needed for combustion greatly reduces the molar flow rate, resulting in a smaller reactor for the same waste throughput. The reduction in molar flow rate is shown in Figure 2. Both gas streams are based on 20% excess air. When solar energy is used, additional air is needed for TCE fractions above 0.08 by volume. When natural gas is used, additional air is needed for TCE fractions above 0.005 by volume. This additional excess air results in a larger reactor and therefore higher capital cost for the nonsolar process.

Solar heating also has the potential advantage of more uniform heating within the reactor resulting in a larger effective residence time at temperature for the same size reactor. Although this effect has not been quantified, field tests (6) indicated that 99.9999% destruction and removal efficiency (DRE) of dioxin could be obtained at 960 °C under purely thermal conditions. Conventional incinerator regulations require 1200 °C for this level of DRE; however, this temperature requirement includes a significant safety factor.

Improvements in performance because of the presence of high-energy photons in the solar spectrum have been demonstrated. The presence of these photons results in a greater reaction rate at a given temperature or a comparable reaction rate at a lower temperature. The main advantage of operating at lower temperatures is smaller reactor capital costs. This is because the volumetric flow rate for a given molar flow rate or waste throughput increases linearly with temperature as a result of the ideal gas law. For a given molar flow rate or waste throughput, reduction in the absolute reaction temperature by a factor of 2 results in a reduction in the reaction volume by a factor of 2 while still maintaining the same residence time. This results in significant savings in the capital cost of the hardware.

The presence of high-energy photons also reduces products of incomplete reaction (PIRs). This effect has been documented in laboratory tests (7) and results in a cleaner and more effective process.

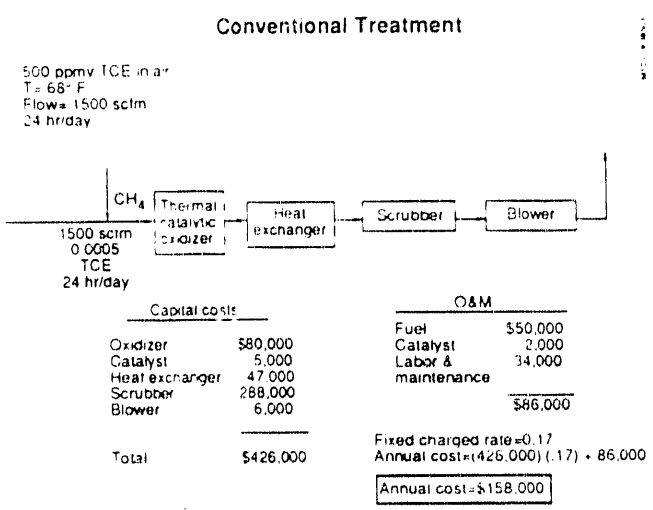

Figure 1. Schematic of waste treatment using thermal catalytic oxidation

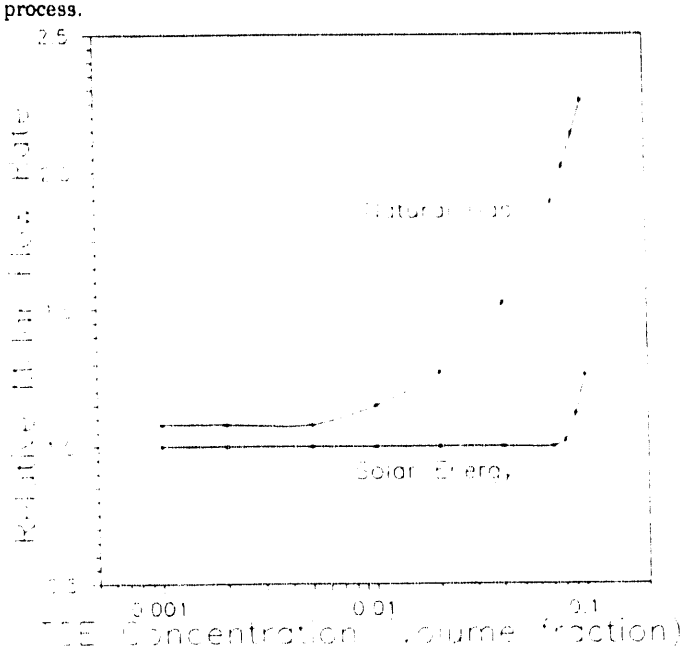

Figure 2. Molar flow rate for 20% excess air: Incinerator using natural gas versus reactor using solar energy

Solar Configuration

A solar configuration was developed to treat the same waste stream as that defined for the conventional technology. A schematic of the configuration is shown in Figure 3. Because the stream is produced continuously, activated carbon is included in the process to serve as a storage buffer for the waste. The waste stream is fed to bed 1 and purified while bed 2 is regenerated

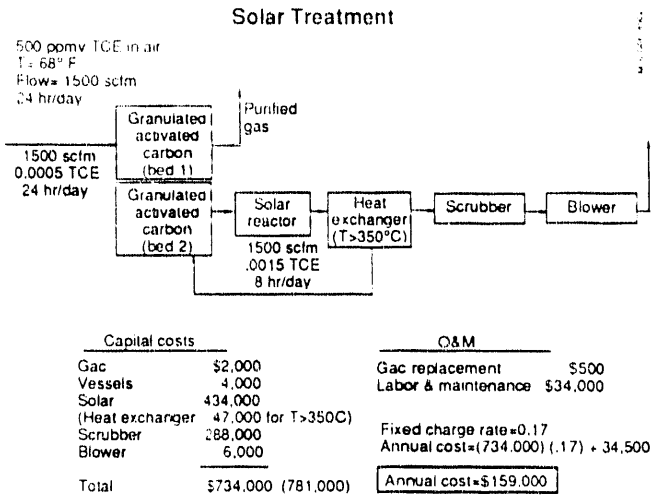

Figure 3. Schematic of solar treatment configuration

using solar energy. Because regeneration only occurs an average of eight hours per day, the average volume fraction of TCE exiting the carbon bed is 0.0015. If TCE is desorbed at a volume fraction greater than 0.0015, the average flow rate to the reactor will be less than 1500 scfm resulting in a smaller reactor and lower capital costs.

An argument can be made that carbon storage could be used in the thermal catalytic oxidation method to reduce reactor size and cost in that case. However, increasing the concentration of the chlorinated organic in the gas stream is not possible because it results in rapid deactivation of the catalyst.

Documented cases show that soil vapor extraction can work more efficiently when the soil pumping is performed on a intermittent basis (8). This results from the time required for the gas phase organic concentration to come to equilibrium with the organic that is adsorbed to the soil particles. Under these circumstances, a solar configuration could operate on an intermittent basis and would not require activated carbon storage.

Analyses were performed using both trough and dish designs. For temperatures below 300 ^{o}C, a trough configuration was used and the hardware cost included the cost of a catalyst. For temperatures above 300 ^{o}C, a dish configuration was used. The base case (Figure 3) at 300 ^{o}C used a dish configuration.

Size and cost of the carbon, heat exchanger (required for reactor temperatures above 350 ^{o}C), scrubber, and blower were determined in the same manner as those for the conventional thermal oxidation system. A method was developed for determining the size and cost of the solar hardware. Because the exact operating parameters of the solar reactor are not known, the size and cost of the hardware were determined as a function of

1. the fraction of the solar spectrum that is utilized in a photolytic reaction mechanism,

2. the absorptivity of the waste molecules or photocatalyst,

3. the reaction temperature.

A schematic of the analysis method is presented in Figure 4. Waste parameters, fraction of spectrum utilized, and the concentration ratios for the dish and trough are entered. The residence time and total reactor volumes are calculated for the dish and trough systems. The trough aperture width and dish area are entered. The trough/reactor length and capital cost are determined along with the annual operating cost of the system. The reactor size for the dish was determined along with its cost.

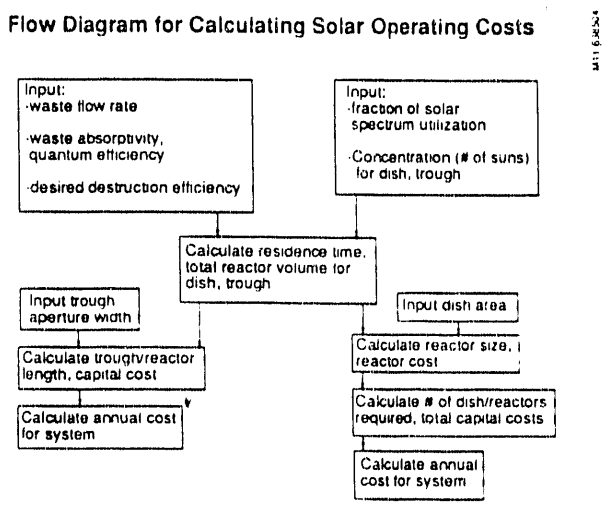

Figure 4. Flow diagram of analysis method

The number of dishes was then determined along with the total capital cost. The annual operating cost is then determined for the dish system.

COST COMPARISON

Many cases were run to determine the variation of annual cost with the operating parameters. The results are presented in Figures 5 through 8. The base case (Figure 3) had the following operating parameters:

1. maximum wavelength utilized = 420 nm (5% of spectrum)

2. absorptivity = 10,000 l/mole/cm

3. reaction temperature = 300 ^{o}C.

Maximum wavelength and absorptivity were based on the absorption spectra of the photoinitiators molecular chlorine and formaldehyde. The reaction temperature of 300 ^{o}C was chosen because this was the lowest temperature at which photointitiated destruction of methylene chloride occurred using molecular chlorine as the initiator. The corrosive properties of molecular chlorine precludes its use in a large-scale process. If another initiator can be found that has a comparable ability to initiate photoreaction but is not corrosive, it will form the basis for a competitive solar process.

In addition, other factors include

1. trough reactor cost = 500 \$/meter (including catalyst)
2. trough cost = 200 \$/meter^2
3. trough aperture = 3 meters
4. dish area = 50 meter^2
5. dish cost = 200 \$/meter^2
6. dish reactor cost = $9725(V_{rctr}/0.20)^{0.6}$ \$

   V_{rctr} = reactor volume in m^3
7. fixed charge rate = 0.17.

The dish reactor cost varies as a function of volume to the 0.6 power (9). This is because process vessel costs are proportional to vessel surface area rather than vessel volume.

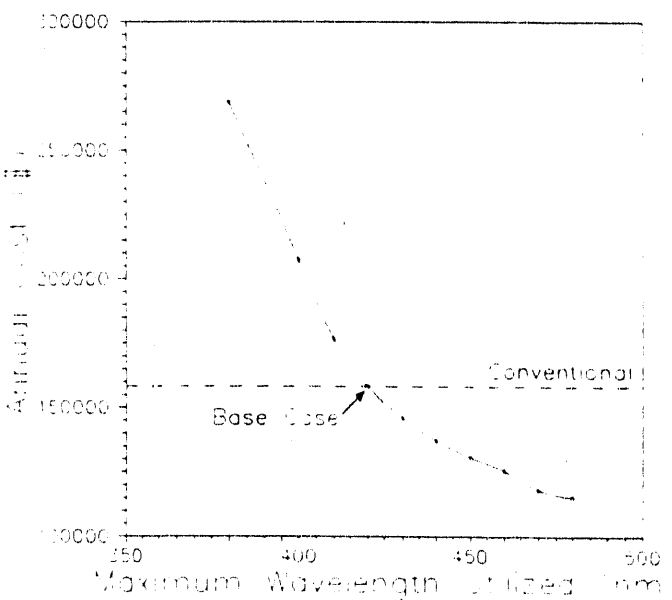

Figure 5. Annual cost versus maximum wavelength utilized

The base case parameters correspond to the costs presented in Figure 3. Figure 5 shows the variation of annual cost with maximum wavelength utilized. It can be seen that the annual cost drops dramatically with an increase in the maximum wavelength utilized. Figure 6 shows the variation of annual cost with absorptivity of the waste or photocatalyst. Again, the annual cost varies dramatically with this parameter.

Annual cost also varies with temperature because of a number of effects. The volumetric flow rate of a gas increases linearly with absolute temperature. This effect causes the reactor volume, and therefore its cost, to increase with increasing temperature. The reaction rate is also temperature dependent. This effect causes the reactor cost to be lowest at temperatures at which the reaction rate is highest.

The variation of annual cost with temperature is shown in Figures 7 and 8. Figure 7 shows the annual cost as a function of

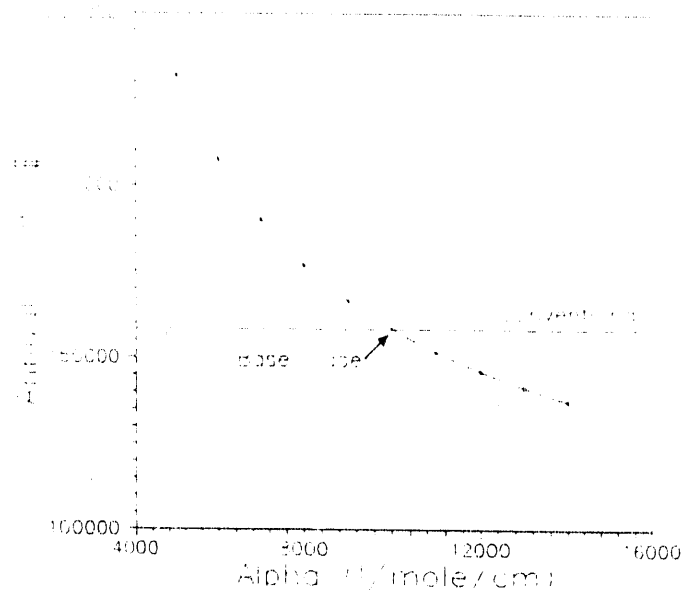

Figure 6. Annual cost versus absorptivity of waste or initiator

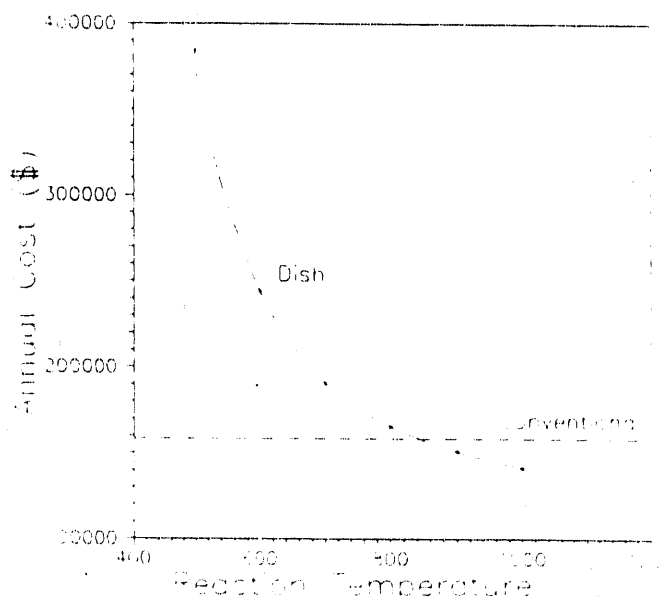

Figure 7. Annual cost versus temperature for a reaction rate that increases with temperature

temperature for a process that has an increasing photolytic reaction rate with temperature. This temperature dependence is typical for pure photolytic reactions and favors operation at high temperatures. Figure 8 shows the annual cost as a function of temperature for a process that has a reaction rate that is relatively constant with temperature. This temperature dependence has been observed in photoinitiated and photocatalytic reactions and favors operation at low temperatures.

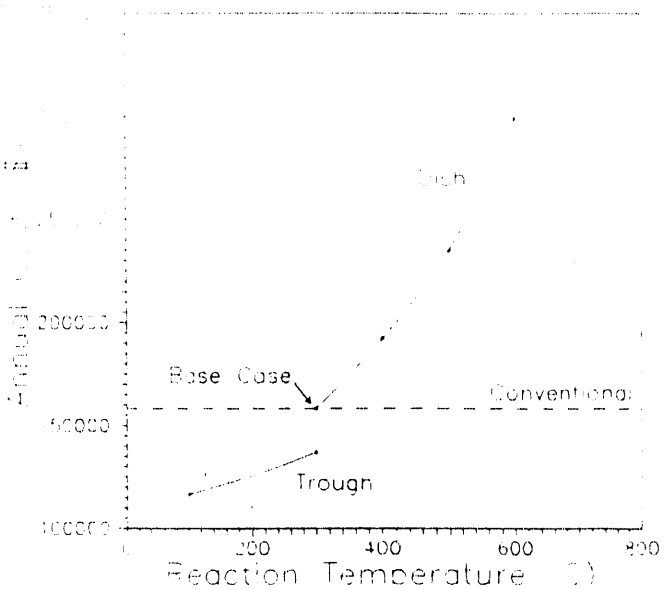

Figure 8. Annual cost versus temperature for a reaction rate that is constant with temperature

CONCLUSIONS

There is a strong market for the treatment and disposal of volatile chlorinated organics in the southwest region of the United States, including both remediation and manufacturing (process) sources. Because large or relatively pure streams of organics can be economically recovered and reused, the best market for volatile chlorinated organics is relatively small waste streams that contain a mixtur of components. The source of these small waste streams may be either remediation sites or manufacturing processes.

The best conventional technology for this market is thermal catalytic oxidation. The strongest advantages of the solar process are reduction in hardware size and cost due to efficient solar radiant heating and photo-enhanced reaction rates. Solar destruction processes can compete with the best conventional alternative if the hardware size and cost can be reduced through efficient utilization of the solar spectrum.

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