MASTER

TITLE: SOLAR HEATING AND COOLING WORKING FLUIDS
RELEASED TO THE ECOSYSTEM

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SUBMITTED TO: Presented at the First Semi-annual
Department of Energy review.
February 16, 1978, Washington, DC

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**SOLAR HEATING AND COOLING WORKING FLUIDS
RELEASED TO THE ECOSYSTEM**

By

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Presented at the First Semi-annual Department of Energy review, "Solar Heating and Cooling of Buildings and the Agricultural and Industrial Process Heat Projects related to Environmental Concerns."

ABSTRACT

Glycols, polyglycols, silicone oils, hydrocarbon oils and various corrosion inhibitors and biocides used in solar heating and cooling systems are tested and evaluated for their potential effects on soils, vegetation, and in regard to potential groundwater contamination.

Experimental tests include measurement of the effects of additions of these substances to soils on soil microbial respiration, above ground vegetation, and on the mobilization of chemicals in soil water, including the test substance and any significant biodegradation products. Experimental work aims at developing the data base necessary to evaluate the environmental acceptability of the wide range of materials used for this purpose, addressing the need for development of disposal practices and the means of mitigating effects on the environment due to accidental releases.

PROJECT OVERVIEW

Objectives

The growth of solar heating and cooling (SHAC) systems for homes and commercial buildings is encouraging the market for a wide range of chemicals for purposes of heat transfer and storage. Our objective is to evaluate the environmental problems and potential impacts which may arise from the release of SHAC working fluids to the ecosystem (Figure 1). Specific issues have been identified in the Environmental Health & Safety Issues and Requirements and apply to the potential toxicity of fluids. Accidental releases to soils are of concern for their effects on soils and plants and as potential groundwater contaminants. In addition to evaluating the potential environmental effects of accidents, there is a need to develop the basis for acceptable disposal practices.

SHAC working fluids are chemically diverse, including a number of glycol/water mixtures, silicone oils, hydrocarbon oils, and various additives. Because of this diversity and due to a lack of fundamental information on the effects of these chemicals in ecosystems, our initial approach is experimental. The experimental work is aimed at obtaining information on the behavior of selected working fluids on soil microbial processes, higher plant life cycles, and mobilization of chemicals in soil water (Figure 2). The results of these investigations will provide the basic information required to evaluate environmental impacts and the means of mitigating these impacts through guidelines for disposal, clean-up of accidents, and other environmentally acceptable practices.

Our project activities are designed to meet specifically identified Environmental Health and Safety Issues and Requirements applied to the EDP for the Solar Heating and Cooling of Buildings. The major issue is that of water quality (WQ), "what constraints should be imposed on the release and disposition of effluents from energy operations that may degrade the quality of ground and

surface waters?" The requirements which are our targets are as follows:

- C.1 Characterize chemical and microbiological transformations of effluents.....
- C.2 Determine the environmental transport mechanism and fate of effluents.....
- D. Determine the effects of effluents and other operational aspects on:
 - D.1 ecological systems
 - D.2 plants and animals
- E.1 Develop environmental decision criteria
- E.2 Develop consensus standards where official standards are nonexistent
- E.3 Develop continuing appraisals of our knowledge concerning the environmental issues and their resolution
- F.3 Develop improved procedures, models, and systems needed for environmental measurements and monitoring and the simulation of environmental phenomena.

Specific to the EDP, our activities are focused on several high priority issues and the respectively identified requirements. Foremost are water quality issues including (3) nitrogen-nitrate in ground water, (4) aromatic hydrocarbons, (5) aliphatic hydrocarbons, (6) pesticides (biocides), (7) sediments (chromate). Other attributes deserve identification, such as (24) antifreezes, (25) eutectic salts, and (33) urban waste.

Projected milestones for this project are developed in the framework of the target EH&S issues and requirements (Figure 3):

- ① Beginning in late FY 77, we carried out literature studies and pilot investigations to develop our approach and plans. Results on a laboratory/field pilot study of ethylene glycol added to soils are reported in this paper.

② By the start of FY 78, we developed a two year study plan including a scoping of working fluids into a generically significant set -- glycols, polyglycols, natural and synthetic hydrocarbons, silicone oils and additives.

③ By the close of FY 78, we will have conducted a broad screening of prototype working fluids, providing the base data necessary for meeting the requirements C.1, C.2, D.1, and D.2. This will include some 10-20 working fluid/additive combinations in one soil type, in the field and the laboratory, over a wide concentration range. We will address toxicity, persistence/recovery, and effects on ground water composition, although much of this work will extend into FY 79.

④ Beginning in FY 79, our attention will focus upon application of experimental data to assessments required according to E.1, E.2, E.3, and F.3. As a means of effective technology transfer, we will coordinate the dissemination of information with the DTO, DCT, DSE, and their contractors in LASL and Sandia who are performing assessment and overview functions. Our results will apply directly, in FY 79, to assessing SHAC system environmental acceptability, developing standards, waste management practices, and other overview requirements.

⑤ By the close of FY 79, we anticipate that the results of FY 79 will provide a first-order completion of the project to the state where consensus standards and practices can be based upon a thorough technical documentation and evaluation.

⑥ - ⑦ In FY 80, we anticipate that our activity will be focused upon applications of these results to a wide range of problems (Figure 2). Applications work may be in the standard setting areas, environmental impact analyses, or extensions to industrial and large scale solar system's environmental development. New applications of testing systems, transport and effects evaluations, and cross-technology applications will emerge as solar energy systems become an increasingly attractive engineering, economic, and environmentally proven alternative.

TECHNICAL APPROACH AND PROGRESS

Landscapes surrounding SHAC systems are potential sinks for released working fluids and are a basis of concern for environmental effects on soils, vegetation, and groundwater. Landscapes of special concern are those containing high working fluid inventories (as in commercial building complexes or dense solar-housing areas) and particularly in locations in which shallow groundwater is a potable water or irrigation source.

Specific information on the effects and persistence of the wide range of chemical types used as working fluids is fragmentary and inadequate as a basis for evaluating SHAC systems environmental impacts. Thus, techniques are used which will provide a large, reliable data base on effects of working fluids on the ecosystem, and provide an adequate basis for meeting the EDP requirements which have been identified in this report.

Hydrocarbons have been studied extensively as environmental agents, particularly related to petroleum spills.^{3,4} Less information exists on the toxicity, persistence and fate of glycols and silicone oils in natural systems. Glycols are recognized toxic agents, but studies have shown that they may undergo biological degradation by soil microorganisms in a matter of days.⁵ Polydimethylsiloxane (PDMS), a silicone polymer light oil, has been studied for environmental effects

in relation to bulk use as an insulating coolant, replacing PCBs.⁶ PDMS is reported to degrade rapidly in soils, but surface deposited spills killed vegetation in the spill area. PDMS, however, is reported to be of low toxicity in both vertebrates and invertebrates⁷, and the lethal effects on vegetation which were observed in the above study were attributed to the water repellent effects of the silicone - an established effect of hydrocarbon spills. Corrosion inhibitors, bactericides, and fungicides are identified as toxic substances which may compound or dominate the toxic effects of working fluid releases.

Experimental work is developed to produce a systematic and integrated data base which fills the large gaps in information on working fluids and additives released to soils. Experiments are conducted in test systems consisting of intact, undisturbed columns of soil in the field, or brought to the laboratory and maintained as soil microcosms.⁸ These soil columns are treated with varying amounts of working fluids as a surface deposit, and the time courses of several processes are followed. The rate of CO₂ evolution over time from the soil is followed as a measure of the effect of the working fluid on the respiration carried out by soil microflora populations. The relative suppression of soil microflora and the persistence of this effect provides a measure of the relative toxicity of selected working fluids in the ecosystem. Aqueous leachate collected from these soil columns is analyzed for a number of constituents including working fluid and degradation products and soil chemicals including essential nutrients. Field applications are planned to evaluate above-ground effects on selected plant species such as the common lawn grasses, as well as native varieties.

Experimental work began in late 1977 with a study of the effects of varying concentration of ethylene glycol, in glycol/water amendments, on soil microbial activity as indicated by the measured CO₂ evolution rate from soils. The CO₂

evolved from soils contained in closed vessels was measured by back-titrating the CO_2 picked up in a vial of standard NaOH suspended in the vessel for a specific time increment. Laboratory tests and field tests were conducted (incubated, Erlenmeyer flask in the laboratory; PVC pipe driven into the soil in the field), following CO_2 evolution at intervals over several days.

In the laboratory, ethylene glycol/water mixtures of 1, 10, 25, 50, and 100% ethylene glycol (EG) were applied, and the carbon dioxide evolution rates were measured over four time intervals out to 353 hours post application (Figure 4). Soil samples amended with EG at levels below 50% had respiration rates similar to soils amended with water alone. Applications of 50% and 100% levels of EG resulted in a severe initial depression of respiration (2.4 and 1.3 mg CO_2 /day, respectively), compared to the background level of ~20 mg CO_2 /day, and approaching the "blank" value of 0.48 mg CO_2 /day. The time-pattern of carbon dioxide evolution was also interesting and suggests the need to extend the time of the experiments to evaluate the potential for recovery of the system from the applications.

A small, pilot level field study was conducted to compare the laboratory results with the response in the field. Carbon dioxide evolution rates were measured, in situ, in the soils in the vicinity of the LASL Demonstration Solar Heated Mobile Home Facility. In this experiment, plastic tubes (30.5 cm long by 21.6 cm diameter) were driven 20 cm into the ground to isolate an aliquot of undisturbed soil for application with ethylene glycol/water mixtures followed by time-sequenced measurements of respiration rates.

The field experiment was conducted in August, with soils relatively wet due to rain fall. EG/water mixtures were applied at rates of 1, 25, and 100% EG and incrementally measured over 0-24, 24-48, and 138-166 hrs. Treatment levels of 1 and 25% did not significantly alter the rate of CO_2 evolution

in the field (see Table 1). Application of 100% EG resulted in cessation of carbon dioxide production, indicating a first-order suppression of microbial activity, perhaps total lethality to microbial populations. These early pilot experiments suggest that laboratory and field observations are reconcilable, a necessary requirement for the testing system.

EXPECTED NEAR-TERM ACCOMPLISHMENTS

To obtain our objective of a systematic characterization and evaluation of the effects of working fluids released to the ecosystem, we have developed the long-range study plan shown in Figure 5. Our experimental program was designed to attain specific goals set forth in the milestones. Because of the large diversity of prototype working fluids, evaluation will initially be conducted on the more common fluids within the chemical types alluded to earlier in this paper.

During FY 78, emphasis will be placed on the laboratory screening procedure of SHAC fluid prototypes. Effects on soil microorganisms will be evaluated over a wide concentration gradient for approximately ten fluid types. Soil water composition will be examined for working fluids and additives not bound in the soil matrix. Mobilization of important nutrients (such as Fe, Ca, K, NO_3 , PO_4) leached from the soil upon addition of working fluids will be determined. Changes in soil chemical parameters, pH and cation exchange capacity, will also be evaluated.

Field studies will be initiated to determine the effects of SHAC working fluids on higher plant life cycles. The field study will be designed so that observations on seedling germination, phenology and plant biomass can be ob-

tained and compared with suitable control plots. The persistence and fate of working fluids and their additives in a natural system will also be examined.

PROBLEM AREAS

Considerable effort in analytical chemistry is required in order to characterize and conduct tests on working fluids. As a number of solar environmental projects are involved in tests on working fluids, the problems of procurement of samples and their analysis are shared to some extent. Discussion of this problem area could consider steps which would minimize duplication of effort, promote analytical quality assurance and standardization, and extend each projects capability.

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Figure 1. SHAC WORKING FLUIDS - Environmentally Acceptable Materials and Practices.

Figure 2. Evaluation of SHAC Working Fluid Impacts on Terrestrial Ecosystems and Pathways to Man.

* Specific milestones (circled) are described in the text.

Figure 3. Project Milestones.

Figure 4. Respiration Rates of Soils Treated with Ethylene Glycol (EG) in laboratory tests.

ECOSYSTEM COMPONENT TO BE STUDIED	GLYCOLS		POLYGLYCOLS	NATURAL HYDROCARBONS			SYNTHETIC HYDROCARBONS	SILICONE OILS	ADDITIVES *				
	Ethylene	Propylene		Aromatic	Naphthenic	Paraffinic		Polydimethylsiloxane	Chromate Salts	Barate Salts	Nitrite Salts	Nitrate Salts	Others
A. Soil Microorganisms 1. CO ₂ Respiration Rate a. Laboratory b. Field	FY78 ←							FY78					
	FY78+79 ←							FY78+79					
B. Soil Studies 1. Nutrient Leaching a. Laboratory b. Field	FY78 ←							FY78		FY78+79			
	FY78+79 ←									FY78+79			
C. Higher Plant Life Cycles 1. Seedling Germination a. Field 2. Biomass a. Field 3. Phenology Studies													
	FY79+80 ←											FY79+80	
	FY79+80 ←											FY79+80	
	FY79+80 ←											FY79+80	
D. Transport of Materials and Residues using Radiotracers and/or Stable Isotope Tracers 1. Migration a. Field Instruments 2. Biodegradation a. Field Instruments													
	FY79+80 ←											FY79+80	
	FY79+80 ←											FY79+80	

* - Additives to be analyzed will vary with the type of fluid

Figure 5. Evaluation Schedule of SHAC Working Fluids.

TABLE 1

Respiration rates of soils
treated with various concentrations
of Ethylene Glycol (EG) and
water in the field

TREATMENT	MEAN CO ₂ EVOLUTION RATE (mg CO ₂ /DAY)		
	<u>0-24 Hrs.</u>	<u>24-48 Hrs.</u>	<u>135-168 Hrs.</u>
1% EG	140(62)	130(48)	202(46)
2.5% EG	150(46)	94(19)	77(13)
100% EG	0(0)	0(0)	2.2(1.7)
100% H ₂ O	62(42)	40(22)	95(36)
CONTROL SOILS	70(30)	22(20)	48(35)

Number in parentheses $\pm$ 1 S. D.