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# **Thermochemical Energy Systems Research**

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## **Solar Energy Research Institute**

A Division of Midwest Research Institute

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## PROJECT SUMMARY

**Project Title:**

Thermochemical Energy Systems Research

**Performing Institution:**

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**Principal Investigator:**

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**Project Objectives:**

To define thermochemical energy systems that are cost-effective for either long distance transport or long duration storage of solar energy.

**Project Status:**

Analysis of a low-temperature, heat-pumped system using the NaOH-H<sub>2</sub>O thermochemical system indicated cost-effectiveness for storing energy relative to a hot oil system with parabolic trough solar collectors for production of 0.101 MPa (0 psig) saturated steam. Work is under way to define a cost-effective thermochemical energy system for storage or transport of high-temperature (300°-500°C) thermal energy. Work

is also under way to identify a potentially cost-effective system for thermochemically reducing CO<sub>2</sub> to CO for open-loop transport of solar energy.

**Plans and Objectives for FY 1984:**

Work on heat-pumped thermochemical energy systems should continue with emphasis on high temperature systems. Experimental research should be performed on the best systems identified to date. Our overall objective is a small-scale validation of the selected systems. The work on thermochemical reduction of CO<sub>2</sub> should be de-emphasized, since it is a very long term problem that will be extremely difficult to solve.

**Major Publications Related to Project:**

Nix, R. G., A Heat-Pumped Thermochemical Energy System, SERI/TP-234-1957, to be presented at 18th Intersociety Energy Conversion Engineering Conference, Orlando, FL, 21-26 August 1983.

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## THERMOCHEMICAL ENERGY SYSTEMS RESEARCH

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## ABSTRACT

This paper describes research at SERI on heat-pumped thermochemical energy systems and thermochemical reduction of  $\text{CO}_2$  to CO for open-loop solar energy transport. Analysis of the  $\text{NaOH-H}_2\text{O}$  heat-pumped system indicated cost-effectiveness relative to a hot oil solar system with parabolic trough receivers for production of 0.101 MPa saturated steam. Current work is on definition of high-temperature heat-pumped systems. Future work should be experimental with an objective of small-scale validation of high-temperature heat-pumped systems. The thermochemical  $\text{CO}_2$  reduction is an extremely difficult and long-range research problem. Costs are unknown but are suspected to be high because of system complexity. The  $\text{CO}_2$  reduction research should be de-emphasized.

## INTRODUCTION

This paper describes an approach to solving two significant problems in solar energy: how to store energy cost-effectively for long periods of time and how to transport energy cost-effectively over significant distances. A constraint is that the quality of the energy must not be significantly degraded by the storage or the transport process. Of the two problems, transporting energy is more important to solar energy development than storage. Past studies (Iannucci et al., 1977; Iannucci and Eicker, 1978) have considered the question of how much storage is enough and have concluded that a hybrid solar-fossil fuel power plant is much more attractive than an autonomous solar plant with many (500-1000) hours of storage. The transport problem becomes important when the siting of a solar plant is considered. The land area required for a collector field to provide energy for a large industrial process heat application may be some miles away from the user, necessitating energy transport.

The most attractive approaches to energy storage and transport are:

- sensible energy processes and
- thermochemical energy processes.

Other approaches, such as latent energy processes and electrical energy processes, are available but do not appear as versatile or attractive.

Sensible energy processes involve heating and cooling a mass with no phase change. For storage, the

mass can be either solid or liquid. Typical storage applications are represented by the molten draw salt work (Sterrett and Scott, 1982). Molten salt loops for energy transport are common in industry, although distances are typically short ( $<0.5$  km). No one has built a molten salt energy transport line as long as would be required by some solar energy applications. The major disadvantage to sensible energy processes is that the mass is hot and requires expensive insulation, while still resulting in efficiency reduction.

Thermochemical energy processes involve the use of chemical bonds to absorb and release energy. With appropriate heat transfer, storage and transport take place at near ambient temperature, which means that insulation requirements and energy losses are relatively small. In effect, thermochemical energy processes involve the manufacture of a synthetic fuel through either open- or closed-loop cycles. For the open loop the chemicals are used irreversibly in an exothermic reaction, whereas for the closed loop they are cycled back to the endothermic reaction for reuse. The major reasons for using thermochemical energy processes are

- potentially high efficiencies and
- high energy densities.

SERI has been active in thermochemical energy research for approximately  $3\frac{1}{2}$  years. During this period, open- and closed-loop systems have been studied for both storage and transport (Nix and Bergeron, forthcoming; Nix, 1983). Results indicate that for transport distances exceeding 60 km and storage times exceeding 250 hours some thermochemical energy systems are more cost-effective than molten draw salt sensible energy systems. For storage times and transport distances less than these values, the molten draw salt system is more cost-effective by a small margin (less than a factor of 2). For favorable conditions some thermochemical energy systems are cost-effective compared to fossil-fuel systems using high-priced natural gas or residual oil. The major factors determining the cost-effectiveness of thermochemical energy systems are the investment and the efficiency. The FY 1983 program is aimed at improving cost-effectiveness by reducing investment and increasing efficiency. The program elements are

- heat-pumped thermochemical energy systems and
- $\text{CO}_2$  reduction for open-loop energy transport.

HEAT-PUMPED THERMOCHEMICAL ENERGY SYSTEMS

A thermochemical heat pump is a set of coupled chemical reactions that have the effect of using high-temperature energy to increase the temperature of a large amount of low-temperature energy to a usable intermediate temperature. Various configurations can be proposed for thermochemical heat pumps; one of the more general schemes is shown in Figure 1, as proposed by Fujii et al. (1977). Here, three chemical reactions (or physical processes) are coupled by heat and mass flows. Solar energy ( $Q_{solar}$ ) is absorbed in the high-temperature reaction at temperature  $T_3$ . Low-temperature heat ( $Q_{waste}$ ) is absorbed by an endothermic reaction at temperature  $T_1$ . Products from the two endothermic reactions produce heat in an exothermic reaction at temperature  $T_2$ . The first-law thermodynamic efficiency is approximated by:

$$\eta_1 = \frac{\text{useful heat out}}{\text{useful heat in}} > 100\%$$

since the waste heat input was not at a useful temperature, and the heat output is greater than the solar heat input for a well-designed system. Naturally, the second-law thermodynamic efficiency is less than 100%. The major impact of efficiency is reduction of system size, particularly reduction in the number of expensive solar collectors required. This reduces investment and improves cost-effectiveness of thermochemical systems. Note that the storage function is satisfied by accumulating chemicals, and if the chemicals are suitable for either pipeline or mechanical transport, then the transport function is also satisfied.

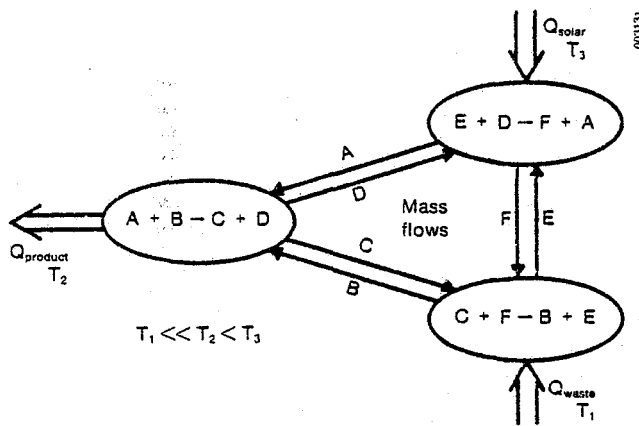
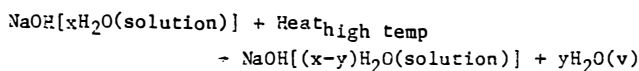
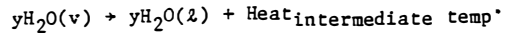


Figure 1. A Generic Heat-Pumped Thermochemical Energy System

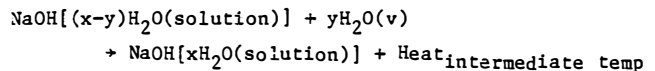
To illustrate the advantages of a heat-pumped thermochemical system, SERI researchers analyzed the NaOH-H<sub>2</sub>O hydration system for the production of saturated steam with solar energy collected by parabolic troughs. The day operation reaction at high temperature is



and



The night operation reaction at intermediate and low temperature is



and



The overall effect is

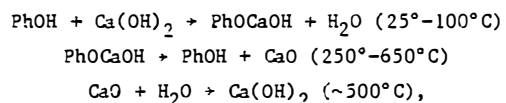
$$\text{Heat}_{\text{high temp}}(\text{day}) + \text{Heat}_{\text{low temp}}(\text{night}) \rightarrow \text{Heat}_{\text{intermediate temp}}(\text{day} + \text{night}),$$

or essentially that the temperature of the waste heat has been increased to a usable intermediate temperature by using some high-temperature solar heat.

Figure 2 shows the system that was analyzed. Evaporation to produce the concentrated NaOH solution can take place in either one or two stages, as shown, to minimize the solar energy input. Hydration of the concentrated solution to produce heat at night can also take place in either one or two stages, as shown, to produce a higher pressure steam. The objective is to deliver 1000 lb/h of saturated steam at either 0.101 MPa (0 psig) or 0.448 MPa (50 psig). The heat-pumped thermochemical system was compared with a conventional hot oil system with parabolic trough solar collectors. Results of the energy calculations, shown in Table 1, indicate that heat pumping can significantly reduce the size of the solar collector field. For example, a single-stage hydration system for production of 0.101 MPa steam requires 55% of the solar energy input that the hot oil system requires.

Cost estimates are under way, but preliminary results indicate that the thermochemical energy system will be more cost-effective than the hot oil system for the production of 0.101 MPa steam, whereas the hot oil system may be slightly more cost-effective for production of 0.448 MPa steam because two hydration stages are required for the heat-pumped system. In addition, thermochemical energy systems can be built in larger sizes with more favorable economics than the hot oil system. The major conclusion of this study is that under the proper circumstances, heat-pumped thermochemical energy systems are cost-effective for solar applications.

However, the real challenge is to identify heat-pumped thermochemical energy systems capable of storage and transport of energy at higher delivery temperatures (300°-500°C). SERI researchers are actively looking for suitable systems. One possible system, based on work reported by Schlosberg and Scouten (1983) is:



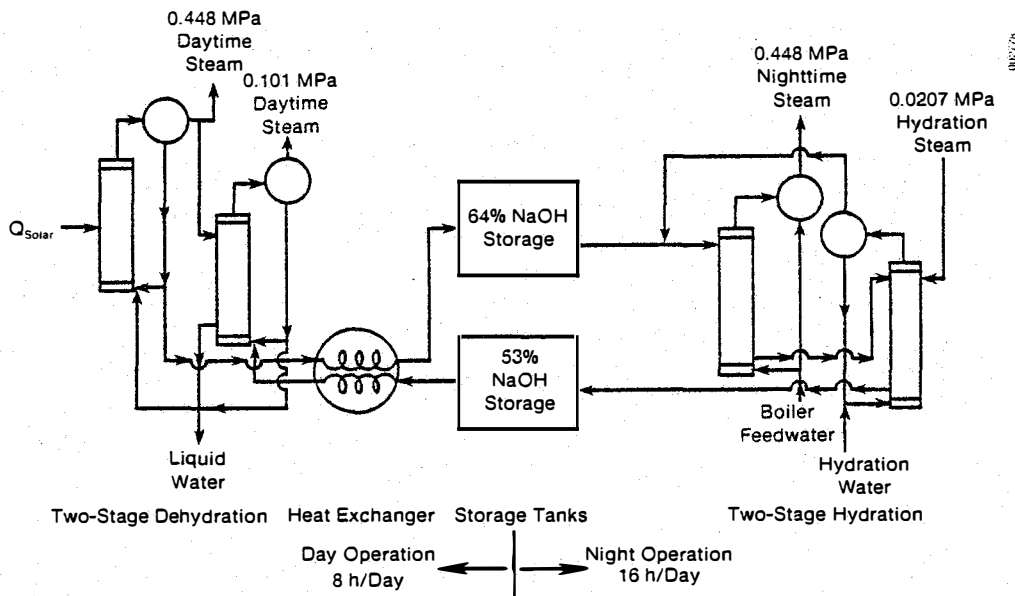


Figure 2. Two-Stage Hydration and Two-Stage Dehydration System for 0.448 MPa Steam

Table 1. Summary of Results

System	Steam Pressure (MPa)	Nominal Steam Rate (kg/h)	Solar Input (GJ/day)	Normalized Collector Field Size
Hot oil	0.101	454	27.9	1.00
Hot oil	0.448	454	28.6	1.03
NaOH-H <sub>2</sub> O (1H, 1D, l) <sup>a</sup>	0.101	454 (2298) <sup>b</sup>	65.7	2.35
NaOH-H <sub>2</sub> O (1H, 2D, l) <sup>a</sup>	0.101	454 (935) <sup>b</sup>	36.6	1.31
NaOH-H <sub>2</sub> O (1H, 1D, v) <sup>a</sup>	0.101	454 (665) <sup>b</sup>	20.3	0.73
NaOH-H <sub>2</sub> O (1H, 2D, v) <sup>a</sup>	0.101	454	15.2	0.55
NaOH-H <sub>2</sub> O (2H, 2D, v) <sup>a</sup>	0.448	454 (432) <sup>c</sup>	32.3	1.16

<sup>a</sup>H designates hydration stages; D designates dehydration stages; l designates liquid hydration water; v designates vapor hydration water.

<sup>b</sup>0.101 MPa steam production rate during the day. During the day, excess steam is produced to satisfy the daily water balance.

<sup>c</sup>454 kg/h of 0.448 MPa plus 432 kg/h of 0.101 MPa steam during the day.

where PhOH = phenol. This is an intriguing cycle since it is analogous but superior to the CaO-Ca(OH)<sub>2</sub> cycle studied previously. In that cycle a significant efficiency loss occurred when water condensed at low pressure to produce heat, which was difficult to use. However, in the cycle that has PhOH rather than water as a working fluid, the reject heat is at a much higher temperature (the normal boiling point of phenol is 182°C), making the overall cycle much more attractive. Experimental research is needed to establish magnitudes of energy flows, equilibria, reaction characteristics, materials problems, etc.

CO<sub>2</sub> REDUCTION FOR OPEN-LOOP ENERGY TRANSPORT

SERI researchers are also investigating the thermochemical reduction of CO<sub>2</sub> to CO for open-loop transport of energy as shown in Figure 3. CO<sub>2</sub> would be recovered from flue gas or CO<sub>2</sub>-rich natural gas wells. CO is a medium-Btu (~337 Btu/ft<sup>3</sup>) fuel gas, which would be transported to the user via a one-way pipeline. At the user end, the CO would be combusted to produce very high temperature heat or used as a feedstock for chemical syntheses. The direct reduction of CO<sub>2</sub> to CO is not thermodynamically favored at temperatures attainable with solar energy. Thus, it is necessary to "drive" the reduction by coupling it with other chemical reactions at different temperatures. CO<sub>2</sub> reduction is difficult because the energy state of CO<sub>2</sub> is low and because with a closed thermochemical cycle there is no product other than CO and O<sub>2</sub>. Two methods are used to reduce CO<sub>2</sub> reduction to CO: those that go through elemental carbon and those that do not. Work with oxide systems indicates that one of the best systems using elemental carbon is:

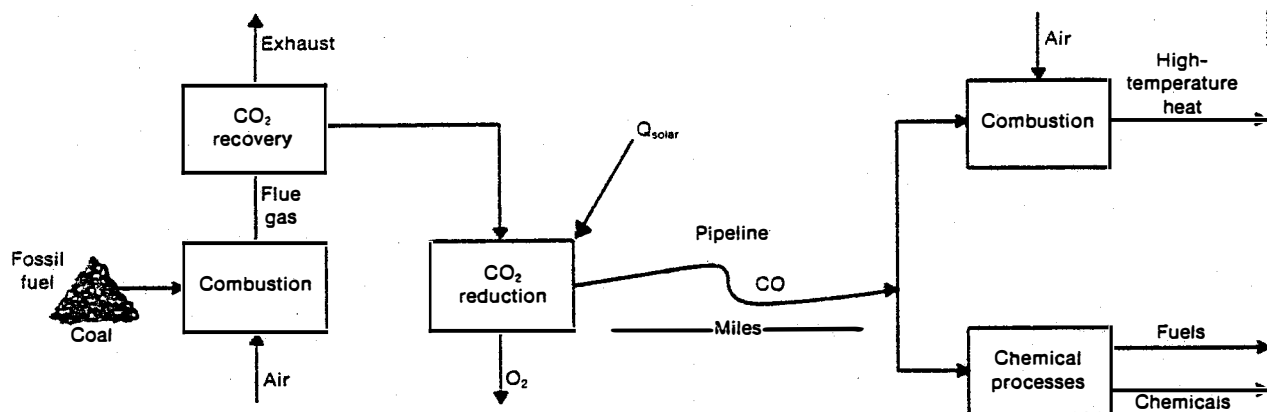
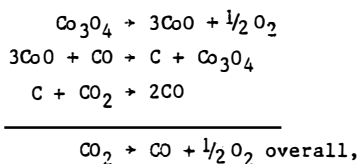
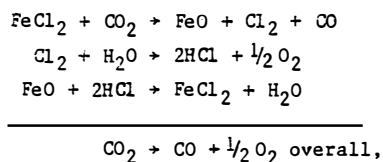


Figure 3. CO<sub>2</sub> Reduction for Open-Loop Solar Energy Transport



where the maximum temperature is less than 1200 K. Hickman et al. (1974) indicate that Mn oxides work as well as Co oxides with a maximum temperature less than 1250 K. A typical cycle that does not use elemental carbon is



where  $T_{\text{max}}$  is 1300°C. The literature also indicates that  $\text{MnCl}_2$  will work, but that system is patented (Sato and Nakajima, 1975; Sato and Ikezare, 1977). SERI is currently evaluating these systems and others; however, the thermochemical reduction of CO<sub>2</sub> appears to be an extremely difficult problem to solve. Hybrid systems like thermochemical--electrochemical systems may be better. Costs are unknown, but intuition suggests they will be extremely high because of the investment in chemical processing equipment to carry out multiple reactions. Thermochemical CO<sub>2</sub> reduction represents an extremely long-range research problem.

#### PROPOSED FY 1984 WORK

Thermochemical energy systems research has been the subject of intense interest for the last decade, with active research declining to its present low level. Why? Much of the early work was theoretical

and defined the energy potential of thermochemical systems. To achieve this potential, actual chemical systems must be chosen for experimental characterization, research, development, and cost analysis. However, to date no solar energy research projects have included all these elements. On one hand, researchers have tended to choose systems and perform research without the benefit of detailed engineering and cost analyses. On the other, they have tended to perform engineering and cost analyses without the benefit of supporting experimental research. The integrated approach has not been taken. Past studies at SERI have indicated that thermochemical energy systems can be cost-effective for solar applications relative to sensible energy systems. The key point is that not all thermochemical energy systems are cost-effective for a solar application. Certain specific thermochemical systems are cost-effective for a given solar application at a given temperature. The key is to identify and study the proper thermochemical energy systems.

Current research on heat-pumped thermochemical energy systems should continue. These thermochemical energy systems represent a very sound approach to solving the storage and transport problems. Work to date has mainly evaluated the scope and potential of thermochemical energy systems. Work for FY 1984 should emphasize experimental work on the best of the previously studied systems and define the feasibility of innovations to substantially improve the cost-effectiveness of heat-pumped thermochemical energy systems. Because of the difficulty and uncertainty of the thermochemical reduction of CO<sub>2</sub> to CO for cost-effective transport of energy, work on CO<sub>2</sub> reduction should be de-emphasized.

#### References

- Fujii, S., Kameyama, H., Yoshida, K., Kunii, D., "Chemical Reaction Cycles for the Recovery of Low Level Thermal Energy," *J. Chem. Eng. Japan*, Vol. 10, 1977, p. 224.

Hickman, R. G., Krikovian, Q. H., Ramsey, W. J., "Thermochemical Hydrogen Production Research at Lawrence Livermore Laboratory," Proceedings Hydrogen Economy Miami Energy (THEME) Conference, S11-23 [T. Nejat Veziroglu (ed.)], 1974.

Iannucci, J. J., Eicker, P. J., "Central Solar/Fossil Hybrid Electrical Generation: Storage Impacts," presented at American Section of the International Solar Energy Society Meeting, 1978.

Iannucci, J. J., Smith, R. D., Swet, C. J., "Energy Storage Requirements for Autonomous and Hybrid Solar Thermal Electric Power Plants," presented at the International Solar Congress, New Delhi, India, 1977.

Nix, R. G., "Open-Loop Transport of Solar Energy Using Natural Gas Networks," SERI/TP-234-1816, presented at 1983 Annual Meeting of the American Solar Energy Society, Minneapolis, MN, 1983.

Nix, R. G., Bergeron, P. W., Feasibility of Thermochemical Energy Storage and Transport, SERI/TR-234-1655, Golden, CO, Solar Energy Research Institute (forthcoming).

Sato, S., Ikezane, Y., U.S. Patent 4029754 to Japan Atomic Energy Research Institute, Tokyo, Japan, June 1977.

Sato, S., Nakajima, H., J. Nucl Sci Tech. Vol. 12, No. 10, 1975, p. 659.

Schlosberg, R. H., Scouten, C. G., "The Organic Chemistry of Calcium: A New Phenol Separation/Recovery Approach," ACS, Division of Fuel Chemistry, Vol. 28, No. 1, p. 180, 20-25 March 1983, Seattle, WA.

Sterrett, R. H., Scott, O. L., "Analysis and Test Results for a Molten Salt Thermal Energy Storage System," presented at 17th Intersociety Energy Conversion Engineering Conference, Los Angeles, CA, 1982.