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SOLAR ENERGY PROGRAM

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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LBL-20202

APPLIED SCIENCE DIVISION ANNUAL REPORT

SOLAR ENERGY PROGRAM

FY 1985

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Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098

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SOLAR ENERGY PROGRAM

INTRODUCTION

During FY 1985, the Solar Energy Program at Lawrence Berkeley Laboratory (LBL) continued to focus on research extending the technology base for a broad range of solar energy applications and to explore new approaches to solar energy conversion.

Passive approaches to heating, cooling, and lighting of buildings are a major research topic. In these technologies, architectural design, construction materials, and natural energy flows between the interior and exterior environment are used to control a building's interior climate and reduce consumption of nonrenewable energy. In FY 1985, LBL examined the application of passive solar technologies to commercial buildings. Projects in both systems development and materials research were carried out.

In commercial buildings, cooling and lighting requirements, including both electric consumption and electric demand, typically dominate energy operating costs. For this reason, research in passive systems development was directed at daylighting and passive cooling. These activities were supported by system simulations and performance monitoring and evaluation.

In daylighting research, two areas of investigation were pursued: developing and refining innovative roof aperture systems and evaluating existing daylighting systems. A facility for measuring illumination levels and light quality of scale models was used in conjunction with detailed building energy analysis simulations to examine the total energy impacts of various roof aperture configurations on office, school, and other buildings. Evaluation of existing daylit buildings includes not only the energy benefits of daylighting but also the functional and aesthetic advantages of daylit spaces. The basis of energy savings in the technology and in occupants' response to it is the focus of the work.

Systems analyses of passive buildings concentrated in three areas: (1) the total energy impacts of advanced aperture materials, (2) energy characterization of passive opportunities in specific building types, and (3) detailed investigation of the energy impact of specific passive technologies. In FY 1985 aperture materials work focused on high insulation clear glazing and the implications of increased access to the solar resource, for both heat and daylight, without significant degradation of the thermal envelope. Energy characterization research studied both office buildings and schools. Detailed systems analysis was done for a variety of applications of thermal mass, to determine its effect on energy use, in particular on cooling and peak demand costs.

Research on advanced aperture materials also continued. This work is intended to identify and develop promising new optical materials for the next generation of high-performance glazings. Research focuses on four technical areas:

(1) Low-conductance, high-transmittance materials, e.g., durable low-emittance glazings and transparent aerogels.
(2) Optical-switching materials, e.g., electrochromic coatings.
(3) Angle-selective transmitting materials.
(4) Materials to enhance daylight utilization in buildings, e.g., light-guide systems.

The research includes technology assessment studies and multiyear research planning; materials synthesis; studies of optical, thermal, chemical, and structural characteristics; stability and durability studies; energy performance studies; and activities to transfer results of our work to appropriate industrial and other private-sector users.

LBL is also engaged in research on the active solar cooling of buildings. Thermodynamic cycles that have the potential for increasing the efficiency of solar-driven absorption air conditioners by at least a factor of 2, compared to the current state of the art, are being studied. The testing phase of the first of these advanced cycle machines, using the double-effect regenerative absorption cycle, was completed during FY 1985. Stable and efficient operation has been achieved, and design performance has essentially been attained. In parallel with the experimental work, simulations and analyses of solar cooling systems have been performed to establish the operating requirements and thermal performance of current and advanced space conditioning systems. This work is helping to determine future research needs for the DOE solar cooling program. Activities in FY 1985 concentrated on the effects of storage options on solar cooling system performance and on

the comparative performance of advanced absorption and desiccant solar cooling systems under the same operating conditions.

A 25-ton-capacity solar absorption air conditioning system had been installed in LBL Building 71 as part of the Solar in Federal Buildings Program. Repeated problems with the newly developed collectors used for this project, start-up and maintenance problems, and then a problem with the chiller, signaled an early end to this demonstration project.

Research continues to explore advanced concepts for using the microstructural properties of materials in conversion, control, and collection of sunlight. The goal is to find and develop solar applications for small-particle suspensions, aggregates, and diffractive structures through a balanced program of experimental and analytical studies. Previous successful solar testing of the Small Particle Heat Exchange Receiver (SPHER) has led to new research efforts to investigate direct radiant heating of particle suspensions for chemical process applications, for thermal energy storage, and for the detoxification of chemical wastes.

In related research, LBL is developing new materials formed from aggregates of small particles (aerogels), both for transparent insulating windows and as intermediate states in the fabrication of ceramic materials with superior properties.

Finally, one of our more basic research projects concerns biological energy conversion techniques, using one of the simplest and most stable biological energy converters known: the pigmented protein bacteriorhodopsin. This project is attempting to elucidate how the molecular structure of this protein uses sunlight to produce an electrical proton current across bacterial and artificial membranes. Such understanding should ultimately suggest ways to produce novel photoelectric cells and solar batteries.

Research is also underway on the bioenergetics of cyanobacteria (blue-green algae) organisms which carry out an O_2 evolving photosynthesis like higher plants, but which also can fix atmospheric N_2 into ammonia. The focus of these studies is to understand mechanisms of photooxidative damage with the objective of improving their efficiency in photosynthetic biomass and ammonia nitrogen production.

Passive Research and Development*

R.C. Kammerud, J.W. Place, M.R. Martin, M. Adegran, H. Akbari, P. Albrand, B. Andersson, F.S. Bauman, C. Benard, P.H. Berdahl, W.L. Carroll, J.P. Coutier, B. Fleury, P. LeConiac, A. Mertol, J.T. Thornton, T. Webster, K. Whitley, and Z. Yilmaz

The amount of conventional fuel used to heat, cool, and light buildings is determined by (1) the interaction of the building with its environment, (2) the thermal gains associated with the activities occurring within the structure, (3) the thermal storage characteristics of the building, and (4) the operating characteristics of the equipment used to convert conventional fuels to end-use energy. Traditionally, the building design process has not adequately accounted for the combined influence of these four factors on building energy consumption. To do so requires that the designer have access to techniques for properly controlling the interactions of the building with the environment and for managing the energy flow within the structure.

Passive heating, cooling, and lighting strategies integrate the energy control and management schemes into the building design. The design parameters are selected so that they enhance and control the coupling of the building to the environment, thereby reducing the requirements for auxiliary heating, cooling, and lighting energy. In this context, the Passive Program at LBL is directed at theoretical and experimental investigations of the energy performance implications of passive design strategies, with emphasis on natural lighting and passive and hybrid cooling of commercial buildings. The specific objectives of the program are the following:

(1) Develop analytic descriptions of the energy processes that occur within a building and between a building and the environment.
(2) Evaluate the effectiveness of passive systems in reducing energy consumption for space heating, space cooling, and lighting.
(3) Develop techniques for integrating effective passive technologies into conventional building systems and structures.
(4) Develop appropriate design tools as a mechanism for transferring newly gained knowledge on passive technologies to segments of the design and building communities.

The strategy used to meet these objectives consists of coordinated experimental and theoretical tasks leading to advanced energy analysis capabilities that can be used in passive system design and evaluation. The emphasis to date has been on improving our understanding of how energy is transferred within passive buildings, how that relates to energy savings exhibited by existing passive buildings, and how future passive systems can be integrated with the structure, mechanical systems, and functional requirements of buildings to improve their energy, functional, and economic performance. Accomplishments and plans in each of these areas are described below.

ACCOMPLISHMENTS DURING FY 1985

Experimental Buildings

Twenty-three passive commercial buildings have been designed and built with DOE support. These are experimental buildings which push the state-of-the-art design; they incorporate advanced conservation features and passive heating, cooling, and lighting strategies. These buildings are being used to examine the effectiveness of state-of-the-art passive strategies in commercial buildings, thereby better defining research needs in heat transfer, modeling, analysis, and design. The information gathered directly from these buildings is also valuable in confirming or providing a basis for modifying the occupancy and energy-related assumptions typically made during the design process.

The passive commercial experimental buildings program has completed the performance evaluation phase, in which studies have been made of: (1) occupancy effects on thermal performance and occupant satisfaction and (2) thermal/energy performance. Data have been collected on the design process and the designs themselves. In addition, performance data have been collected for a 12-month period after occupation; this consists of reports on occupancy schedules and occupant satisfaction as well as energy use data. In some projects, specialized automated monitoring and data acquisition systems have recorded hourly data.

The Passive Commercial Building Extended Analysis Project of the Passive Research and Development Group consists of two projects: (1) analysis of the effect of roof monitors on lighting, heating, and cooling, with special consideration

*This research was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Solar Heat Technologies, Solar Buildings Technology Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

given to lighting control strategies, both manual and automatic; and (2) analysis of the thermal effects resulting from variation in occupancy and occupant interaction with passive systems. In FY 1984, the major effort was to complete the first project and establish the parameters on the second. In FY 1985 the effort was put toward completion of the thermal effects portion of the project and a special supplement to the lighting effects study to evaluate the quality of lighting at one of the buildings.

The roof monitor portion of the study completed in FY 1984[1–3] resulted in unexpectedly high lighting energy savings with daylighting provided by roof apertures and with fully manual control of electric lighting, as shown in Fig. 1. The four bars represent the electricity consumption with manual control, on/off lighting controls, dimming lighting control, and with no daylighting provided (baseline). The difference between each of the first three and the fourth is the energy saved through daylighting. The study has provided considerable information to direct future research in a field which is still in the process of identifying the basic potentials of different daylighting approaches.

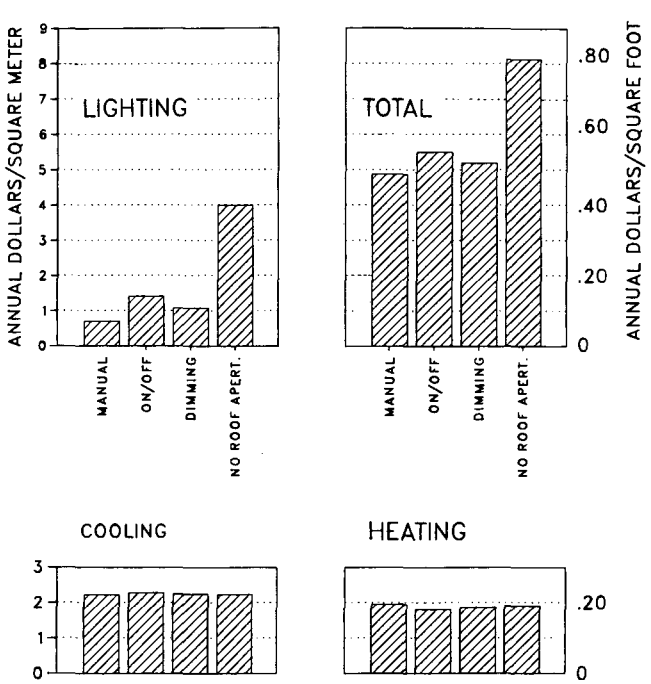

Figure 1. Annual energy costs are shown for the Mt. Airy (North Carolina) Library, broken into lighting, cooling, and heating costs. Dramatic savings could be achieved from daylighting with any of the control strategies tested, but the manual electric lighting control actually used in the building resulted in the greatest savings. (XBL 862-546)

During FY 1985 a supplemental study was completed.[4] The lighting quality in one of the buildings was studied in detail, to determine the effect of different electric lighting and daylighting configurations and combinations and the ability of occupants to read and perform other visual tasks, based on light levels, light distribution, glare, and contrast. Both the task surface and the rest of the visual field were observed. Situations leading to both successful and unsuccessful lighting environments were identified and analyzed.

Thermal analysis of other issues related to occupant comfort, satisfaction, and interaction with passive systems drew on the work of Min Kantrowitz, an LBL subcontractor, for identification of important occupant-related issues. Four areas were evaluated: (1) thermal mass: sensitivity of energy use and comfort to mass amount and exposure; (2) thermostat setback: its integration with mass and effect on comfort; (3) acoustics: its impact on energy use and competition for surface area with passive systems; and (4) shading: energy use sensitivity to variations in shading and shade control. The building energy analysis program BLAST† was used to simulate alternatives in each of these areas. Two to four buildings from the experimental program were simulated to provide a range of situations for each topic.

The results of these studies[1,5] indicated a counteractive relationship between thermal mass and thermostat setbacks strong enough to result in recommendations to eliminate setbacks if significant thermal mass is used and to use only modest levels of thermal mass if deep setbacks are planned to limit energy use during unoccupied hours. It was also found that although acoustic treatment in passive commercial buildings has typically been less effective than occupants desired; in each case methods were found to provide effective acoustic treatment with little or no degradation of the energy performance of the building.

Natural Lighting

In FY 1985, energy analyses on a prototypical, single-story office building outfitted with a variety of roof aperture configurations were continued.[6–9] A prototype building configuration for energy analysis of roof apertures in schools was also developed, and analyses begun. The emphasis in the office building studies was on assessing the effect of roof glazing area, orientation, and tilt in moderating the interac-

†BLAST (Building Loads Analysis and System Thermodynamics) is trademarked by the Construction Engineering Research Laboratory, U.S. Department of the Army, Champaign, Illinois.

tion of the building with the solar resource. In order to assess the implications of this moderating process, calculations were made of lighting electricity consumption, cooling electricity consumption, heating fuel consumption, peak electricity demand, and annual energy operating costs for the building in a range of U.S. climates. The following combinations of orientation and tilt have been examined:

- horizontal;
- south-facing vertical;
- south-facing tilted up sixty degrees from horizontal;
- north-facing vertical;
- north-facing tilted up forty-five degrees from horizontal;
- the combination of south-facing vertical and north-facing vertical;
- the combination of east-facing and west-facing, both tilted up sixty degrees from horizontal;
- the combination of southeast-facing and southwest-facing, both vertical;
- the combination of southeast-facing and southwest-facing, both tilted up sixty degrees from horizontal;
- the combination of north-facing, south-facing, east-facing, and west-facing, all vertical; and
- the combination of northeast-facing, northwest-facing, southeast-facing, and southwest-facing, all vertical.

For each of these glazing orientations and tilts, simulations were performed for a range of roof glazing areas between 0% and 10% of the building floor area, except for north-facing vertical glazing, where the weak collection of sunlight indicated the need to examine larger glazing areas.

Figures 2a–2d show the results of some of these simulations for linear roof apertures on the prototypical office building in Atlanta, GA. Typical Meteorological Year (TMY) data were used in these simulations. In Fig. 2a, annual lighting electricity consumption (at the site) is plotted versus the aperture ratio, defined as the ratio of total roof glazing area to building floor area. (The consumption of primary energy by the utility to generate power would be on the order of three to four times higher than consumption at the site, because of generating inefficiencies and electrical network losses.) Four curves are drawn in Fig. 2a, corresponding to roof glazing which is vertical facing south, vertical facing north, vertical facing both south and north (equally divided), and horizontal (skylights). At all aperture ratios, horizontal glazing has the lowest cooling electricity consumption, reflecting the highly effective annual collection of both diffuse skylight and beam sunlight. At all aperture ratios, the north-facing glazing has the highest lighting electricity consumption, reflecting the negligible collection of beam sunlight and the weaker collection of diffuse skylight resulting from the fact that the vertical glazing faces only half the skydome. Lying approximately halfway between the curves for horizontal and north-facing glazings is the curve for south-facing glazing. The relative positions for these curves are explained by the fact that vertical glazing facing south collects substantially more beam sunlight than vertical glazing facing north, but is substantially less effective than horizontal glazing in the annual collection of both diffuse skylight and beam sunlight. If lighting electricity reductions were the only impact of roof apertures, then horizontal would clearly be the preferred glazing orientation. However, the thermal impacts of roof apertures are also important.

In Fig. 2b, annual cooling electricity consumption at the site (fans plus direct expansion cooling unit) is plotted versus aperture ratio. For small aperture ratios, the cooling electricity consumption decrease with increasing aperture ratio, because all the admitted sunlight is being used to displace electric light of higher heat content. In fact, at small aperture ratios (around 1%), the glazing orientations which collect most effectively during the cooling season have the lowest cooling electricity consumption; i.e., horizontal glazing has the lowest cooling electricity consumption and vertical north-facing has the highest. At larger aperture ratios, the order of the curves is reversed, in the sense that the glazing orientations which collect most effectively during the cooling season produce the highest cooling electricity consumption. This result is explained by the fact that at larger aperture ratios, solar gains frequently exceed the illumination requirements of the building. These excess radiation gains create a thermal load which is not offset by reductions in heat from the electric lights. In general, the cooling electricity consumption curves suggest that horizontal is not the preferred orientation for the roof glazing. This is directly counter to the implications of the lighting electricity consumption results.

In Fig. 2c, boiler fuel consumption is plotted as a function of aperture ratio. In general, the curves tend to be fairly flat. Also, the cost per unit of heating fuel energy at the site is substantially lower than the cost per unit electrical energy at the site. Consequently, from an economic point of view, the variations in the boiler fuel consumption with aperture ratio are relatively inconsequential.

In Fig. 2d, annual operating energy cost is plotted as a function of aperture ratio. For small aperture ratios, all the curves decrease with increasing aperture ratio. The rate of decrease of the operating energy cost is largest for the glazings which collect sunlight most effectively. At larger aperture ratios, the cost curve for the horizontal glazing levels off and then starts to increase. This results from the fact that increases in cooling energy consumption and summertime peak demand offset the decrease in lighting electricity consumption. For all the vertical glazings, the costs continue to decrease with increasing aperture ratio up to the full 10%. However, all three curves for vertical glazing are essentially level at a 10% aperture ratio, suggesting that there is little benefit in going to larger ratios for this particular building type, glazing material, and electric lighting control system.

The results can be summarized as follows:

- For small apertures, horizontal glazing yields the greatest cost benefit.
- At larger glazing areas vertical glazing facing south or the combination of vertical glazings facing both south and north yields the greatest cost benefit.
- Vertical glazings facing south or both south and north produce the largest cost benefit per unit of building floor area.
- Horizontal glazing produces the largest cost benefit per unit of installed glazing area.

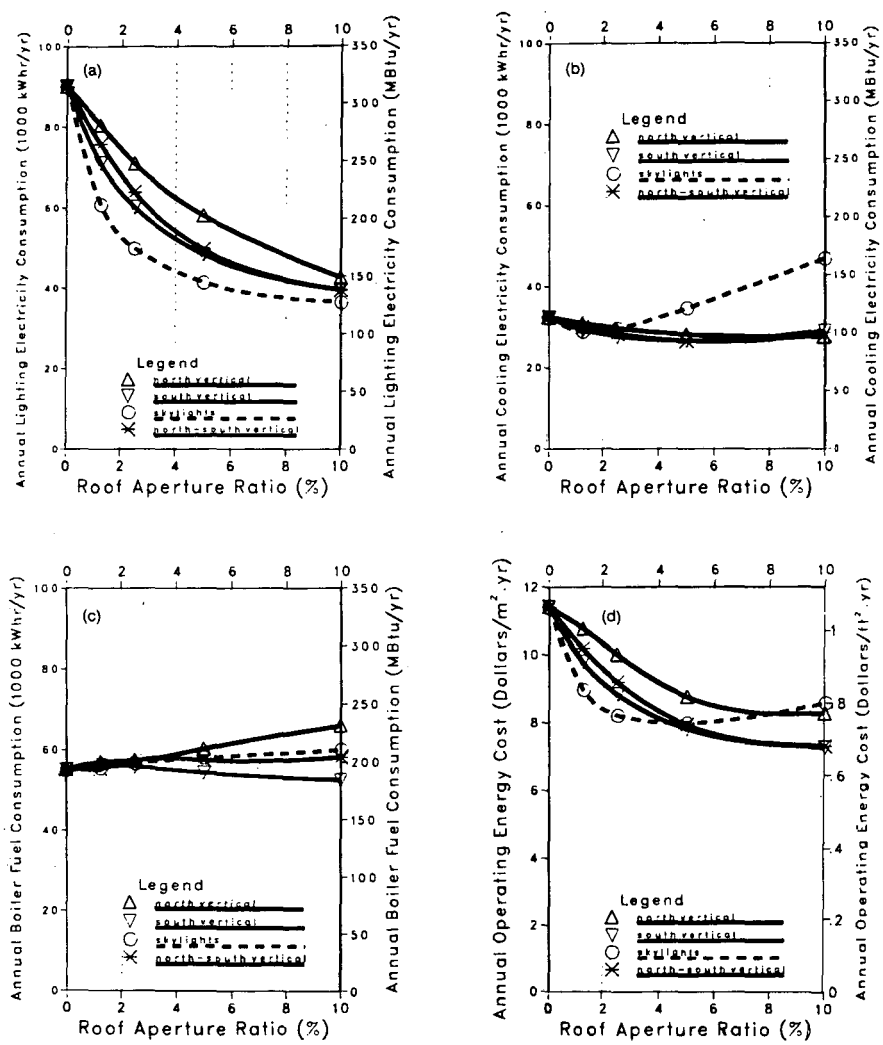

Figure 2. Results of simulations of linear roof apertures on a prototype office building in Atlanta, Georgia, showing the effect of roof aperture ratio on annual energy consumption and cost. Typical Meteorological Year data were used. (a) Lighting electricity consumption; (b) cooling electricity consumption; (c) boiler fuel consumption; and (d) operating energy cost. (XBL 848-3318A)

In general, the results indicate substantial potential benefits from fairly small glazing areas. For example, at a two percent aperture ratio, horizontal glazing produces an energy operating cost savings of about 20 dollars per square foot of glazing.

In addition to the parametric analysis of glazing area, orientation, and tilt, simulations were also performed to determine the sensitivity of the energy and cost predictions to various assumptions in the analysis. Among the factors examined were: thermal comfort conditions in the building, more sophisticated thermal controls of the building, glazing characteristics, obstruction of daylight by snow, dirt accumulation on the glazing, and variation of the internal surface treatments. Of particular significance was the detailed examination of thermal conditions in the prototype building. This study suggested that air temperature alone is not an adequate indicator of thermal comfort in buildings which aggressively utilize environmental resources to reduce energy consumption. In order to deal with nonuniform thermal environments, the Passive Research and Development Group has added a detailed thermal comfort analysis subroutine to BLAST, thereby facilitating a more accurate assessment of the thermal performance of passive buildings.

Design integration was studied in FY 1985. The emphasis in this work was on utilizing the analysis results in a design process examining the integration of the roof apertures with other building systems, such as the building structure, the electric lighting, interior design, the HVAC system, and other passive strategies. Concepts were generated for a variety of roof configurations, both light-weight and thermally massive. A folded-plate, wooden structure was studied in detail (Fig. 3). Structural and economic analyses indicate that there is significant potential for minimizing ceiling and roofing costs by integrating the daylighting apertures with the roofing system.[10] Analysis of integrated roof aperture configurations required the development of specialized measurement equipment. A particularly important development has been the integrating window pyranometer (IWP).[11] Figure 4 shows this instrument applied to a model of the sawtooth configuration in Fig. 3. It is able to measure the solar flux across an *area* of window, rather than just one point, as with other pyranometers. A flux meter of about 4 inches square is placed behind the area of the model to be measured and the back of the material is kept at a constant temperature by continuous flushing with ambient air. As many daylighting configurations are often partially shaded, the integrating effect of this instrument is critical to the analyses.

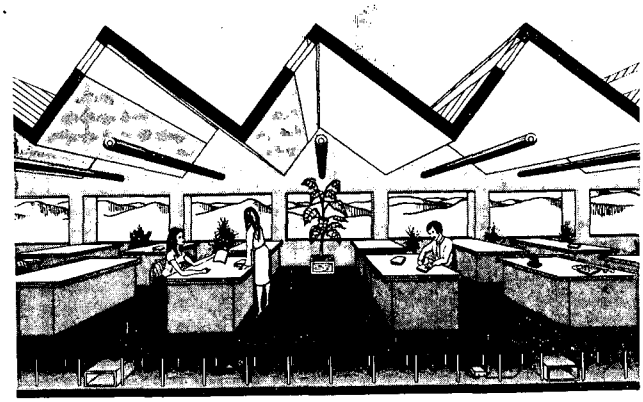

Figure 3. A linear roof aperture system with diffusing glazing tilted toward the south. (XBL 854-1953)

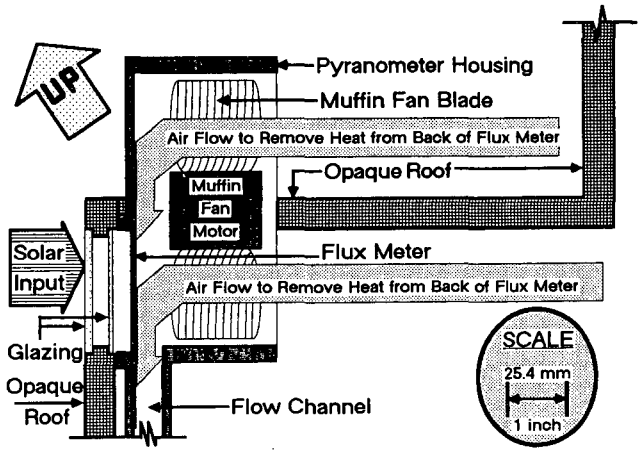

Figure 4. An Integrating Window Pyranometer (IWP) for scale-model measurement of the solar flux over the full glazing area. (XBL 862-547)

Initial efforts at developing design guidelines from both the analytical information resulting from examinations of roof aperture systems and the structural, economic, and design information from the design integration studies were begun in FY 1985.[12]

Residential Thermal Mass

A two-year effort[‡] to explore structural thermal mass on residential heating and cooling loads has been completed. The project had two major phases:

[‡]This research effort has been supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Buildings and Community Systems, Building Systems Division of the U.S. Department of Energy under Oak Ridge National Laboratory Subcontract No. MPO 41X-70373V through Contract No. DE-AC03-76SF00098.

(1) a validation phase, in which simulation predictions were compared with measured data collected by other participants in the program, and (2) a parametric simulation phase, in which predictions of the effects of various thermal mass configurations in models representing realistic buildings were developed and analyzed. Last year's Annual Report described the results from the first phase. The project's second phase consisted of determinating, by simulation, the annual heating and cooling loads for an extensive set of parametric variations of wall thermal mass configurations for a typical residence.[13]

The general approach was to select a prototypical single-family detached residence that had average current practice thermal integrity, design, and use characteristics. The simulated energy performance of this prototypical building in a range of U.S. climates was used as a baseline reference. The baseline configuration was then modified to reflect the incorporation of thermal mass into the exterior walls in varying ways and amounts. The energy performance of these modified configurations was then simulated and compared to the baseline energy performance. Finally, a nonlinear empirical model that represents the energy use results in the data base as a function of wall thermal mass and thermal resistance was developed, and coefficient values for the model were determined by least-squares fits to the data.

All the energy performance simulations for both phases of the project used the building analysis computer program BLAST-3.0. BLAST is a computerized, comprehensive energy analysis simulation tool employing a detailed heat balance solution method with an hourly time increment that correctly accounts for the effects of structural thermal mass on the dynamics of building energy consumption.

The specific house design used for this effort was a 1200 ft^2 three-bedroom residence based on plans developed by the Tennessee Valley Authority (TVA) for a passive solar demonstration project. Choices for layout and materials were taken from detailed blueprints. The design's insulation levels and window thermal integrity were selected to satisfy the requirements of typical building energy performance standards for most U.S. locations. Typical occupant behavior, based on extensive surveys by others, was also assumed. Simulations were conducted for several different climatic conditions. Six cities were chosen to represent the full range of selected climatic parameters representing heating and cooling severity, humidity, and solar gains: Atlanta, Denver, Miami, Minneapolis, Phoenix, and Washington, D.C.

The parametric variations to the house design comprised systematic changes to the values of the thermophysical properties of the exterior walls. The basic wall configuration consisted either of two layers (a low-mass insulating layer and a thermally massive layer with varying thermophysical properties) or of just a massive layer alone. For the two-layer wall, variations also included placement of the insulating layer either external to or internal to the thermally massive layer. Parametric variations were performed separately for the different wall types by combining variations in each of the individual layers. Sufficient intermediate values were used for each parameter to allow the thermal mass and thermal resistance effects to be distinguished. Three hundred and thirteen simulations were performed for each climate, with each simulation yielding annual heating and cooling sensible loads.

The same pattern of load variations was observed for all generic wall types and for all climates, and depends on variations in both the wall thermal resistance and the thermal mass. In general, the data tended to form families of curves: data for one generic wall type in one climate would separate into a series of related curves, where each curve is produced by the data points at various thermal mass levels, for a particular thermal resistance. Several important aspects of behavior were observed in the data:

- For a particular value of wall thermal resistance, increasing the wall thermal mass always reduces both the heating and cooling loads.
- The relative sensitivity of changes to the loads due to incremental changes in the exterior wall's thermal resistance or thermal mass varies widely, and is dependent on the particular values for each, the load type, the wall type, and the climate.
- The relative importance of exterior wall mass for reducing heating loads, as opposed to cooling loads, is strongly dependent on climate.
- For other than massless walls, the loads for different generic wall types with the insulation layer position inverted, but with the same total resistance were different. It was generally true that the loads were lower when the insulation layer was outside the mass layer.

Using a heuristic approach a thermal mass characterization parameter μ for multilayer walls was found:

$$\mu = \sqrt{\sum_{i=1}^{N} t_i \rho_i c_i},$$

where t_i, ρ_i, and c_i are the thickness, density, and

specific heat, respectively, of the ith wall layer. μ is analogous to the thermal resistance of a massless wall.

The general shape of the heating and cooling load variation with μ was the same for the full range of resistances simulated. By trial and error the following analytical form was chosen as the nonlinear regression model:

$$L(\mu,R) = L_\infty(R) + \frac{(L_0(R) - L_\infty(R))}{\sqrt{\tfrac{1}{2}(\cosh(2\sqrt{\pi/24\beta\mu}) + \cos(2\sqrt{\pi/24\beta\mu}))}},$$

where

$$L_0(R) = a_0 + \frac{b_0}{c_0 + R},$$

$$L_\infty(R) = a_\infty + \frac{b_\infty}{c_\infty + R}.$$

Where a_0, b_0, c_0, a_∞, b_∞, c_∞, and β are seven regression coefficients and R is the thermal resistance of the wall. This model was then used in a series of least-square fits to the data. An entire family of data curves including the data for all simulated values of R for a generic wall type can be regressed simultaneously to determine the seven coefficients. The regression procedure was carried out separately for heating and cooling loads, for each of the generic wall types, in each climate.

In general, the agreement between the model predictions and the data is quite good, both qualitatively and quantitatively. The shapes of the curves are all accurately reproduced, including the complex behavior as a function of R at intermediate and high values of μ. The relative error ranges from a low of about 0.1% to a high of 3.7%, with overall averages of about 1% for both heating and cooling. Figure 5 shows the typical agreement that can be achieved between the BLAST simulation data base and the seven-parameter nonlinear model predictions, using the coefficients derived from the regression procedure. Graphical comparisons for other locations show the same general quality of agreement.

It is expected that the data base, and the model that has been developed to represent it, will ultimately lead to an increased, quantitative understanding of the effect of exterior wall thermal mass on the energy performance of residential buildings.

Climate Analysis

A project was undertaken in FY 1985 to develop an area of research looking into climate issues related to buildings. In the past, such issues have been investigated by building researchers primarily as necessary, but peripheral, undertakings to support the primary research goals of building energy analysis, including some previous climate work done in the solar program.[14] As a result, most of such research has been taken only so far as necessary to achieve the limited requirements of the building research and, being of secondary importance, is seldom published. Therefore, much repetition occurs and communication of results is very limited.

The intention of the project has been to develop a climate research program with two broad goals:

- Create an environment in which climate's relation to buildings is a primary topic of research; and
- Develop, collect, and disseminate information on the climate/building relationship.

During this initial effort, the primary technical task has been a study of the impact of refinements to wind data on energy analysis results.[15] Climate data used for building energy analysis are usually collected at airports or similar unobstructed sites, where there is minimal interference with the instrumentation, and the climate itself is not altered by local

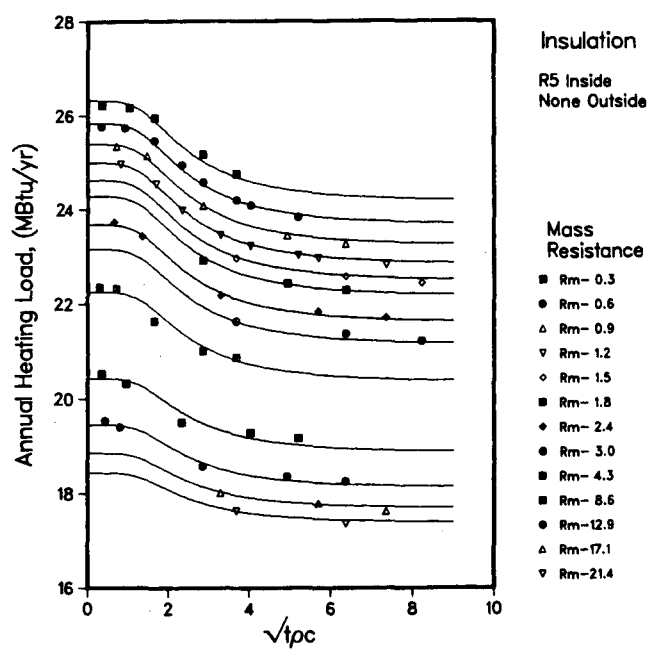

Figure 5. Comparison between BLAST simulation data and empirical model predictions: Atlanta, Heating, Rin=0, Rout=0. (XBL 862-548)

variations in terrain or nearby obstructions. Wind data are usually measured atop a mast, usually standardized now to 25 feet and/or 10 meters, but historically highly variable. Wind speeds around buildings, however, are rarely unobstructed, and the height of the winds of interest is usually much lower than that at which they are measured.

Despite this distinction between measured wind data and that which would better represent wind speeds *near the building*, nowhere in the usual chain of weather data measurement, manipulation, preparation for building analyses, or in the building analysis process itself, is the difference between measured airport data and wind activity around a building corrected.

Alternative algorithms which relate wind speed at different heights and with different obstructions within the same atmospheric wind regime exist. Two well-documented ones were chosen to test the sensitivity of building energy analyses to variations in the description of the wind data used. The first algorithm is part of a method used by Max Sherman and others to identify the actual wind behavior and effects around single-family residences. The second is used by Ed Arens for his program SITECLIMATE, which takes weather station data and adjusts it for use at a specific building site.

Comparisons were made for a standard situation: a one-story residence in a suburban setting in Nashville, with a three-story office building down the street. In all, five simulations were run:

- A constant, high wind (15 mph) superimposed on standard TMY climate data, to set an upper limit
- The base case, using standard TMY climate data
- TMY data with wind speed altered according to the Sherman algorithm
- TMY data with wind speed altered according to the Arens algorithm
- No wind (0 mph) superimposed on the TMY data, to set a lower limit

Each set was run with both DOE-2 and BLAST, in order to identify any program specific anomalies which might occur.

The results can be seen in the two figures showing heating and cooling loads (Fig. 6). In comparison with the base case, overall heating loads are down 19% (Sherman) to 34% (Arens). Cooling loads are up 7% (Sherman) to 17% (Arens). BLAST and DOE-2 show essentially identical effects. To a designer, the more important point might be to identify the total wind impact on his energy use. Starting at the level of no wind, wind adds 20%, 46%, or 81%,

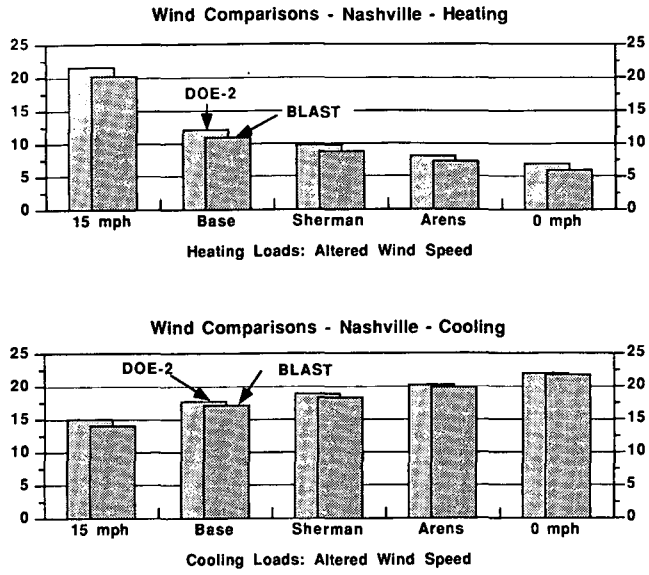

Figure 6. Modifications to wind data to better reflect actual wind conditions in the vicinity of the building can significantly alter the calculated heating and cooling requirements of a residence. (XBL 862-549)

respectively, to the heating load, depending on whether Arens, Sherman, or the base case is used. Likewise, wind lowers the cooling load 8%, 16%, or 21% for the same three cases.

Clearly, the wrong data can provide a false perception of how much energy is being used, and for what purpose. More significantly, those false perceptions can lead to design decisions which are not justified by the actual environment of the building. In new buildings, substantial costs might be incurred in order to solve wind-induced problems which do not warrant them, while more important aspects of the energy environment might be ignored. Likewise, infiltration may be an overemphasized retrofit option, the benefits of which may be considerably less than expected. These results argue strongly for an improved method of determining the actual wind speed in the vicinity of a specific building, and incorporating that into building energy analysis techniques, possibly into the data itself.

PLANNED ACTIVITIES FOR FY 1986

Experimental Buildings

A two-year program to develop a daylighting system evaluation methodology will begin, as part of the Passive Solar Federal Buildings Program. It will provide owners and designers of daylit buildings a method to determine the effectiveness of daylighting

to reduce electric consumption in their buildings. This work will be coordinated with a parallel effort by SERI to develop a methodology for thermal performance of passive buildings.

Natural Lighting

The work which has gone on to date will provide the basis for a set of design guidelines to be developed in FY 1986. These guidelines will cover the use of daylighting in office buildings through the use of roof apertures. The characterization of energy use in daylit commercial buildings will continue with investigations of school and retail buildings.

Climate Analysis

Investigation of climate patterns resulting in peak heating and cooling loads will begin in FY 1986. This work will be a preliminary step in determining the course of research toward better prediction of peak loads and more effective design of mechanical systems.

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Optical Materials Studies*

(This article, except for the section on Aerogels, has been reprinted from the FY 1984 Annual Report.)

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Significant reductions in energy consumed by the building sector will come not only from better building design strategies but also from the development and introduction of new glazing materials. Since the inception of our program in 1976, identification, characterization, and exploratory development of promising new fenestration materials have been major activities. Research on new optical materials and on modifications of existing glazing materials is intended to create a technology base to assist industry with developing the next generation of advanced fenestration systems.

In addition to the research projects described in the following sections, the overall Optical Materials effort at LBL includes development of a multiyear research plan and scientific coordination of related DOE-funded research projects at universities, private sector firms, and other national laboratories. Results of the DOE-supported program are made available to interested parties in the private sector. For example, an annual technical conference and industry forum is held each year in August in conjunction with a meeting of the International Society for Optical Engineering (SPIE). This meeting serves as a forum to review and discuss the direction of the overall DOE program as well as to report on recent technical progress. A joint international effort on glazing optical materials under the auspices of the International Energy Agency is being developed with our participation.

In 1976, when our program began, we identified the development of low-emittance ("low-E") coatings as a major program objective. DOE-supported research activities have helped the fenestration industry to accelerate market introduction of new high-performance window systems incorporating these coatings. Several small firms began offering commercial products in 1982, and in 1984 many of the largest glass and window manufacturers introduced "low-E" products. In the near term, the use of low-E coatings in a conventional double-glazed window provides better thermal performance than triple glazing and makes a lighter and more compact window. In the long term, this coating technology offers the potential to produce transparent windows having heat transfer values as low as those of insulating walls. On an annual basis, such windows should outperform the best-insulated wall, even for a north orientation in a cold climate, since diffuse solar gain will offset some conductive losses. We initiated planning in late 1984 for a Low-E Window Roundtable, to be co-sponsored with the National Fenestration Council. We believe that the positive impact of this DOE-supported effort can serve as a model for the transfer and development of research findings in other optical materials areas.

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GLASS AND PLASTIC SUBSTRATES

Accomplishments During FY 1984

To predict the optical properties of complex window systems incorporating thin-film coatings, the optical properties of the glass and plastic substrates must be accurately known. These properties have not been available in a complete and self-consistent form even for the most common varieties of glass used in windows, hence the need for this measurement effort. This year, we completed work on standard clear glasses, glasses having absorbing additives, and high-purity glasses. Our results are summarized in a paper that includes a complete set of optical constants from the near ultraviolet through the little-studied far infrared for all common window glasses.[1] We also provide some spectrally and directionally averaged bulk properties for calculating solar and thermal radiative heat transfer through windows. Figure 1 shows the real and imaginary components of the complex index of refraction for a clear glass as determined by Kramers-Kronig analysis of reflection measured with a Fourier-transform spectrometer over the near-infrared and infrared spectrum.

Future measurements will be greatly simplified with our new spectrometer, which covers the ultraviolet to the near infrared. In addition to having optics that are far superior to those of our previous instrument, this system features completely automated operation and data collection. The instrument is installed and operating, although not all functions have been tested.

Planned Activities for FY 1985

We will collect, organize, and catalogue our low-emissivity samples. These samples will be com-

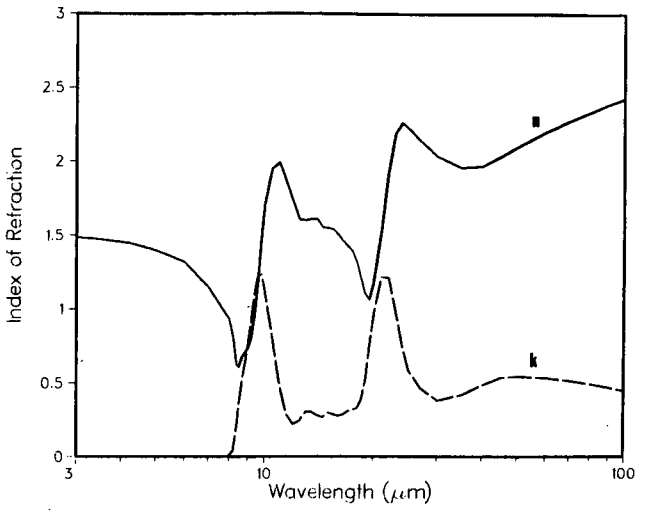

Figure 1. Real (n) and imaginary (k) parts of the complex index of refraction for soda-lime silica glass. (XBL 8412-5271)

pletely characterized as part of our participation in the Low-E Window Roundtable in August 1985. Our spectrometer will be fully functioning.

LOW-CONDUCTANCE, HIGH-TRANSMITTANCE GLAZINGS

An ideal glazing material for residences in cold climates would have good optical clarity, high solar transmittance to admit sunlight in winter, and low thermal conductance to reduce heating costs. Such windows would perform better than insulated walls on an annual basis, even in northern orientations in cold climates. Simulation results for a north-facing window in Madison, Wisconsin are shown in Fig. 2. Windows must have U-value and shading coefficient combinations that place them to the right of the "0" net heat transfer line if they are to provide net energy benefits. Two promising research activities are under way to develop the technical basis for such advanced windows.

LOW-EMITTANCE, GRADIENT-INDEX COATINGS

Accomplishments During FY 1984

Since 1976, we have contributed to the development of window coatings that transmit sunlight but reflect in the thermal infrared, thus suppressing radiative heat transfer. Commercially available coatings based on metal-dielectric multilayer films have satisfactory optical properties but are not sufficiently durable to be used in nonsealed glazings. By producing a film having a continuously varying index of refraction to reduce reflection in the solar spectrum, we could use materials that are inherently more durable but less transparent than the metal films. Our analytical studies suggest that a gradient-index coating could improve solar transmittance by 25% without reducing emittance or durability.

We have begun by studying the titanium oxynitride (TiN_xO_y) system, producing these gradient-index coatings by plasma-assisted chemical vapor deposition (CVD). Better compositional control and durability have been achieved in a limited number of samples deposited by magnetron sputtering. We installed a new sputtering system and completed the first tests for homogeneous coatings. The coatings are being characterized by electron microscopy, Auger electron spectroscopy (AES), and Rutherford

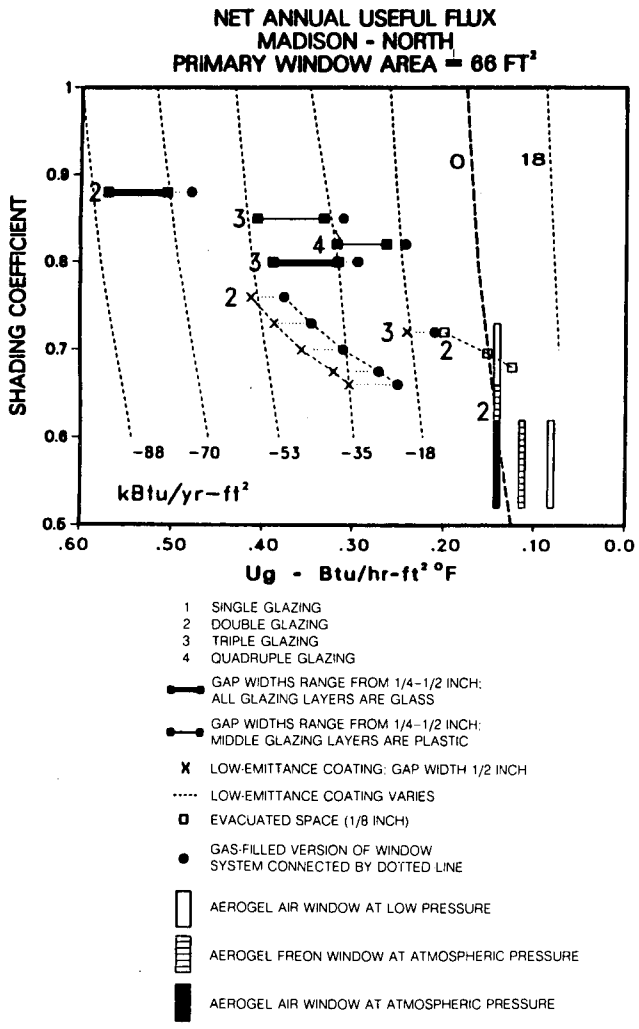

Figure 2. Simulation results for north zone, Madison, Wisconsin. (XBL 856-2870)

backscattering (RBS), in addition to complete optical characterization. RBS has proven particularly valuable in our efforts to remove impurities from the coatings. Figure 3 shows the small amount of chlorine remaining in the coating after adding H_2 to scavenge the bulk of the unwanted Cl in our CVD films.

Planned Activities for FY 1985

We will add reactive gas-handling capabilities to our sputtering system to produce TiN_xO_y films. The process parameters will be varied in an attempt to achieve the optimum optical properties predicted by our analytical models.

AEROGELS

Transparent silica aerogel is being developed at LBL because of its excellent thermal insulation properties for window glazing materials. It is an open cell porous solid containing a very high percentage of voids. Aerogel is transparent rather than translucent because the characteristic pore size is much smaller than the wavelength of light; therefore, it transmits rather than scatters light. A 1-inch-thick aerogel window has an R value of about 7, which can be increased to nearly R-20 by removing 90% of the air from the aerogel. The goals of this research are to improve the optical and thermal properties of aerogel, discover less expensive synthesis methods, develop methods to protect it from the environment, and develop a technology base for production of transparent aerogels.

Aerogel is prepared by mixing a metal alkoxide with water and alcohol along with suitable catalysts.

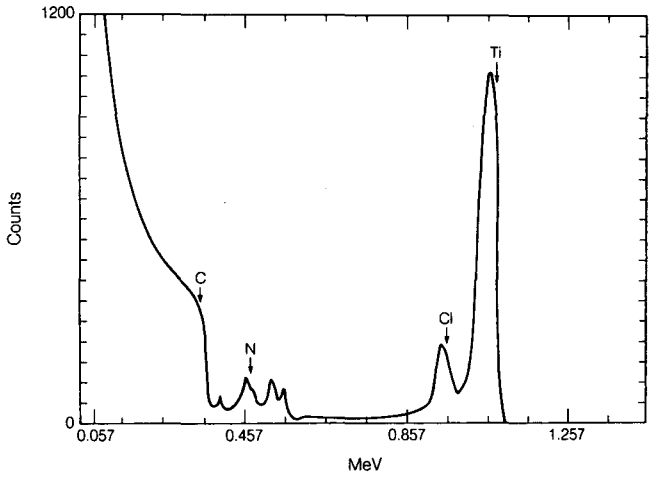

Figure 3. Rutherford backscattering spectrum for titanium oxynitride coating on glossy carbon substrate. (XBL 854-9799)

Water hydrolyzes the alkoxide compound to produce fine solid particles or polymers that link together to form alcogel, a transparent solid containing alcohol. To become useful as an insulator, the alcohol must be removed from the alcogel without damaging the silica matrix through the action of interfacial forces in the very fine pores. These interfacial forces can be eliminated by carrying out the solvent extraction under supercritical conditions. Researchers at LBL have been investigating both the preparation and drying of aerogel.

Accomplishments During FY 1985

Our efforts in 1985 have been concentrated on improving the two critical areas of synthesis of aerogels:

1. hydrolysis and condensation reaction of a less expensive alkoxide TEOS (tetraethylorthosilicate) than the toxic and expensive TMOS (tetramethylorthosilicate) normally used by others;
2. simplification of the drying process of the alcogels to achieve the aerogel without damage to the structure.

In addition, we have developed some unique techniques which allow us to study the microstructure of the gels by transmission electron microscopy and light scattering studies. They are discussed below. Progress in these three areas has significantly enhanced the prospects for large scale industrial preparation of aerogel for windows.

Alcogel Production from Low Toxicity Starting Material

Transparent silica aerogels for Cerenkov counters have been produced by hydrolysis and condensation of TMOS. Since TMOS is a very toxic starting material, the more desirable starting compound, TEOS, was used in the current work. Research in our laboratory led to the successful use of a base to catalyze TEOS.[2–4] Base catalysis of TEOS results in a more suitable material for window material than the acid catalysis method. We have improved the properties of the aerogel by exploring a wide range of process variables using the factorial design method.[2] Light scattering, optical transmission, and electron microscopy data were used to characterize the aerogels produced in our laboratory. Using these techniques we have established that the quality of the improved TEOS aerogels is comparable or better in transparency than those prepared from TMOS. The transmission spectrophotometer results confirming this are given in Fig. 4.

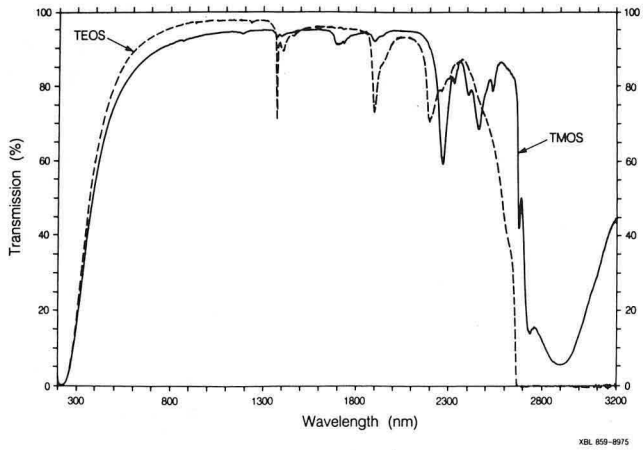

Figure 4. Transmission spectra of a 4-mm-thick sample of base catalyzed TMOS aerogel supercritically dried at 270°C and 110 bars (TMOS) and a 12-mm-thick base catalyzed TEOS aerogel sample supercritically dried by CO_2 but not heated to remove all adsorbed H_2O (TEOS). (XBL 859-8975)

Ambient Temperature Supercritical Drying

Alcogel is a low density open pore material containing a high fraction of voids filled with alcohol. In conventional supercritical drying, the alcohol is removed from the alcogel by slowly releasing the pressure in an autoclave after it has been heated above its critical pressure and temperature. Under these conditions, the interfacial tensions in the alcogel drop to zero. Typical conditions for supercritical drying of alcohol are $\geqslant$ 270°C and 1800 psi. The necessity to cycle pressure vessels to these temperatures makes the drying process expensive and time consuming. We have developed a solvent substitution process[5] in which alcohol is replaced by liquid CO_2, which permits drying of alcogels at $\leqslant$ 40°C and 1200 psi. We have improved the substitution and drying process to minimize shrinkage and damage to the structure. The shrinkage can be controlled to $\leqslant$ 5% of the initial dimensions. The reproducibility of the process is good, and the drying is achieved in less time per batch than the 2–3 days required by the high temperature process. Further efforts are in progress to reduce the shrinkage.

Gel Microstructure

We have developed a variety of sample preparation methods to overcome difficulties in the study of aerogel with electron microscopy.[6] Transmission electron microscope studies using these methods have provided excellent evidence of the physical gelation mechanism. Micrographs show a cross linked chained structure similar to that conceptualized previously by various workers (Fig. 4a). These sample preparation techniques for TEM studies are excellent for studying the microstructural details of gels and aerogels at various stages in the sol-gel process.

We have performed light scattering studies of acid and base catalyzed sol-gel systems. By studying the time evolution of the scattering intensity, we can differentiate gelation mechanisms between the two gels. Information from these experiments is helpful in formulating and controlling the desired properties of complex sol-gel systems.

Planned Activities for FY 1986

In FY 1986 we will explore the substitution of Freon 116 for alcohol to further reduce the supercritical drying conditions to $\leqslant$20°C and 430 psi. If successful, this substitution will lower the processing cost below that of the CO_2 method. Treatment of the gels to render them hydrophobic will be studied to improve the chemical stability of aerogel against weathering and moisture. The adhesion of aerogel to glass plates of the window will be examined to improve the mechanical stability and resiliency of the aerogels.

OPTICAL SWITCHING PROCESSES AND MATERIALS

Optical switching materials or devices can be used for energy-efficient windows and other passive solar applications. An optical shutter provides a large change in optical properties under the influence

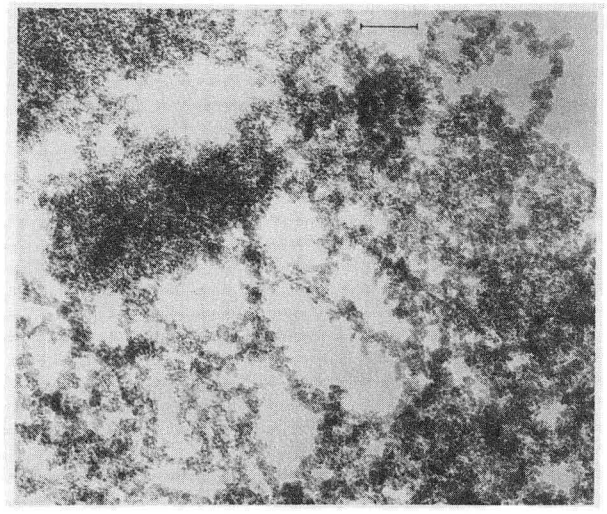

Figure 4a. Transmission electron micrograph of a base catalyzed TMOS aerogel flake after carbon coating. (XBB 859-7482)

of light, heat, an electric field, or their combination. The change can occur as a transformation from a material that is highly solar transmitting to one that reflects over part or all of the solar spectrum (Fig. 5). A less desirable alternative would be a material that switches from highly transmitting to highly absorbing since some of the absorbed energy would enter the building. An optical shutter coating would control the flow of visible light and/or solar heat gain through a building window, thus performing an energy management function. Depending upon design, such a coating could control glare, modulate daylight admittance, and limit solar heat gain to reduce cooling loads, prevent overheating, and improve thermal comfort. Initial results from energy simulation studies of office buildings suggest that the dynamic control attainable with optical shutter coatings provides substantial economic benefits by minimizing cooling and lighting energy use, reducing peak electricity demand, and potentially reducing the chiller and heating, ventilating, and air-conditioning (HVAC) system size.

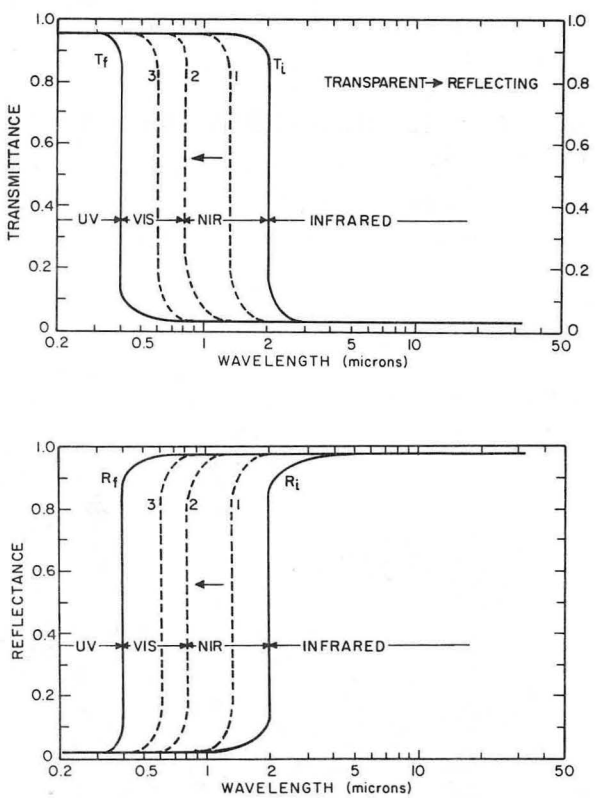

Figure 5. Idealized broadband spectral response for a solar optical shutter. This example ignores the effect of absorption and shows a highly transparent film transforming into a highly reflecting one. Such a shutter can control certain portions of the solar spectrum to provide or restrict both solar heating and lighting. (XBL 828-6452)

We consider materials that possess variable or reversible optical properties as potential candidates for an optical shutter. There are three classes of phenomena that may prove useful:

(1) Chromogenic materials, including electrochromic, photochromic, and thermochromic types.
(2) Physio-optic media, including mesogenic molecules or liquid crystals, and magneto-optic, electro-optic, and mechano-optic or deformable media.
(3) Electrodeposition, including reversible electrodeposition and electrophoresis.

Our research program focuses on electrochromic coatings because they offer the potential for active control (by an applied voltage) in response to building operating requirements and environmental conditions and because there is sufficient experience with optical displays and related applications to suggest that they would be the best candidates for glazing applications. The active control capability will allow the greatest range of potential benefits in terms of reducing cooling loads, providing daylighting savings, controlling peak electricity demand, and reducing HVAC size.

ELECTROCHROMIC DEVICES

Electrochromism is exhibited by many inorganic and organic materials.[7] An electrochromic material undergoes an intense color change when a colored compound is formed from an ion-insertion reaction induced by an instantaneous applied electric field. The reaction might follow:

$$MO_x + yA^+ + ye \rightleftarrows A_yMO_x \quad .$$

There are three categories of electrochromic materials: transition metal oxides, organic compounds, and intercalated materials. The materials that have attracted the most research interest are WO_3, MoO_3, and NiO_x films. With organic electrochromics, coloration of a liquid is achieved by an oxidation-reduction reaction, which may be coupled with a chemical reaction. Intercalated electrochromics are based on graphite and so are not useful for window applications.

A solid-state electrochromic device containing the elements shown in Fig. 6 can be fabricated: a transparent conductor, an electrochromic layer, an electrolyte or fast-ion conductor, a counter electrode, and a second transparent conductor. Many variations on this configuration are possible, although several of the approaches used for small electronic

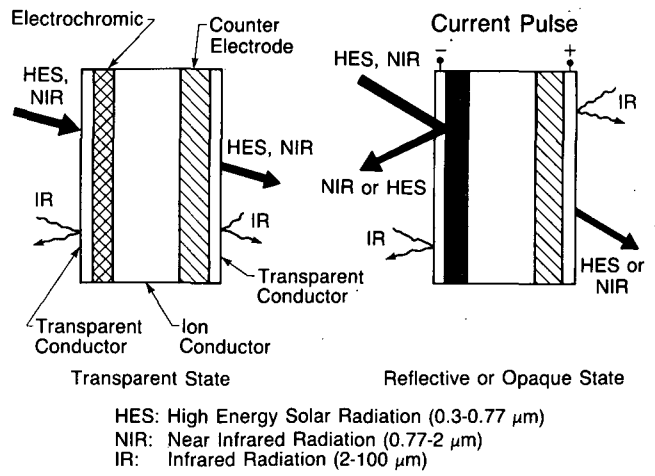

Figure 6. Schematic of an electrochromic optical switch shown in each of two states, transparent and colored. A current pulse causes an ion-based chemical reaction to take place in the electrochromic material (HES, high-energy solar; NIR, near-infrared; IR, infrared). (XBL 842-10105)

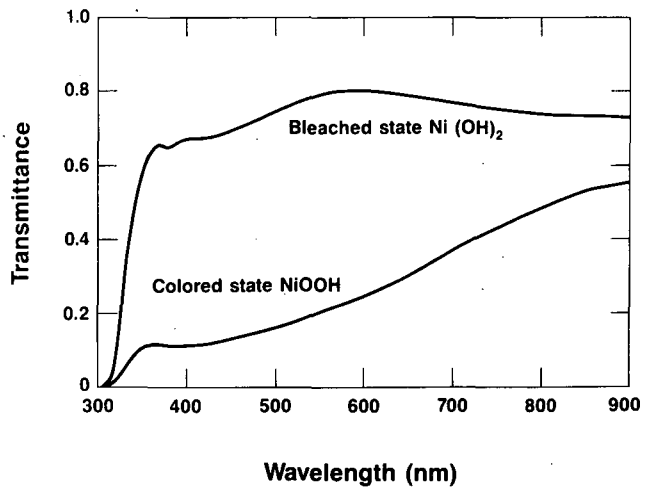

Figure 7. Transmission (near-normal) spectrum for nickel hydroxide in bleached and colored state. Conditions are IM-KOH electrolyte with 1 V applied potential. (XBL 852-6955)

displays cannot be scaled up successfully to the dimensions required for windows.

Accomplishments During FY 1984

Prior to 1984, a technical review of electrochromism revealed many possible materials that could be incorporated into solar glazings.[7] During 1984 our research focused on electrochromism in nickel oxide, which can be switched from transparent to bronze or dark gray, depending on impurities. We performed experiments on oxidized metal films and chemically deposited oxides on indium-tin-oxide coated glass. We obtained a normally transmitting film with solar transmittance (T_s) and visible transmittance (T_v) as follows: T_s (off) = 0.73, T_s (on) = 0.37, and T_v (off) = 0.75, T_v (on) = 0.24. The spectral response is shown in Fig. 7. In an electrochemical cell, 1 volt is required to switch the film. Besides spectrophotometry, voltammetry and Auger electron spectroscopy were performed on this film. These studies will help determine the active species in the electrochromic coloration reaction.

LBL continues to serve as scientific coordinator for the overall DOE-supported switching films program. Associated research was continued in 1984 by EIC Laboratories[8] and the Department of Electrical Engineering at Tufts University.[9] Electrochromic near-infrared reflectance modulation was demonstrated in polycrystalline WO_3 material.[10] Devices based on the configuration in Fig. 6 and with complementary electrochromic electrodes were made. Research by the Solar Energy Research Institute (SERI) has concentrated on devices based on amorphous WO_3 in the configuration: transparent conductor/WO_3/ion conductor/Au or indium-tin-oxide.[11]

Planned Activities for FY 1985

We will complete optical, chemical, and structural studies of electrochromic nickel oxide. We will compare the electrochromic response of sputter-prepared nickel oxide materials to the electrochemically prepared coatings. With our new reactive magnetron sputtering system, we will begin to survey and characterize electrochromism in other candidate materials such as titanium oxide. The objective of this work is to identify and characterize electrochromic materials with performance characteristics that are better than the commonly used WO_3 films.

OTHER SWITCHING FILM MECHANISMS

A number of other materials systems were reviewed to determine their suitability as optical switching materials. We continue to follow development of photochromic and thermochromic materials to determine if any may prove suitable to building applications. We also examined various physio-optic processes (i.e., liquid crystals, magneto-optic and electro-optic materials) as well as processes based on reversible electrodeposition and electrophoresis. Each approach has at least one attractive feature, but in general they appear less promising than the alternatives described above.

Accomplishments During FY 1984

An example of a device studied in FY 1984 is the dynamically light-scattering liquid crystal cell. It transforms from transparent to opaque white under applied potential; no polarizers are required. Its optical properties are T_s (off) = 0.82, T_s (on) = 0.77, T_v (off) = 0.83, T_v (on) = 0.20. Although the response of this device (Fig. 8) is promising as a broadband optical shutter, it suffers from excessive power requirements and lack of uniformity over large areas.

Planned Activities for FY 1985

We will continue to follow these novel approaches for optical switching mechanisms to determine if results in other fields have relevance to aperture requirements. We expect to obtain samples of photochromic plastics to determine their suitability for building applications.

MATERIALS FOR IMPROVED USE OF DAYLIGHT

The intensity and spatial distribution of daylight transmitted through windows and skylights must be controlled in order to reduce electric lighting requirements while maintaining occupant comfort. Conventional solutions rely on architectural elements and interior or exterior devices to control daylight admission and distribution. Greatly improved performance would result from materials or systems that could: (1) transmit maximum daylight with minimal cooling load impact (i.e., reject solar infrared radiation); (2) collect and distribute daylight beyond the perimeter zones in buildings; and (3) provide angular selectivity in accepting and redirecting incident light at the building envelope.

In earlier studies, we evaluated the performance of a variety of devices for daylight acceptance and control on the basis of their reflective and refractive optics. In 1982, we turned our attention to innovative optical materials and devices that showed the potential for replacing more complex mechanical systems. We reviewed the feasibility of approaches such as fiber-optics systems, hollow light guides, holographic coatings, selective-reflectance materials, and various scattering media. One promising approach that uses fluorescent concentrators to collect and redirect daylight is the subject of a patent disclosure.

LIGHT GUIDES

Accomplishments During FY 1984

In 1984, on the basis of the preceding year's review of potential systems for light guides, we focused on two promising areas. We predicted improved performance for hollow reflecting light pipes because of the availability of new low-cost materials of high reflectivity (more than 95%). Figure 9 shows the calculated transmission efficiency of this type of light guide as a function of aspect ratio (length/diameter) for R = 95%. Even for aspect ratios of 50 (e.g., L = 15 m, D = 0.3 m) the transmission has acceptable values at moderate concentration

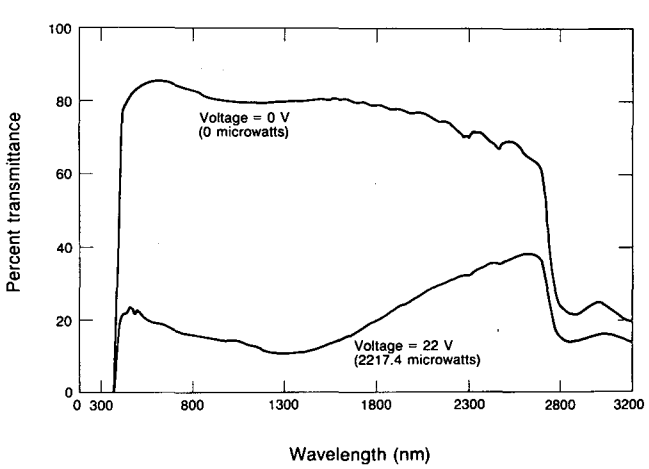

Figure 8. Spectral transmittance (near normal) for a dynamically scattering liquid crystal device. Response includes two glass cover plates and two transparent conductor electrode films. (XBL 852-7033)

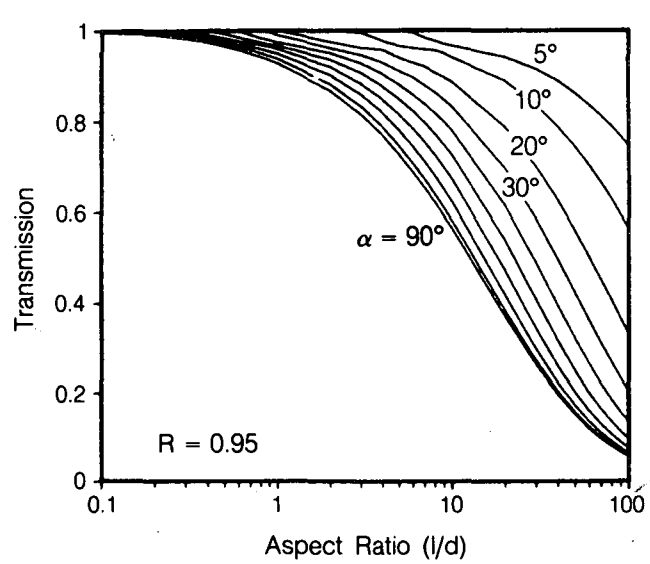

Figure 9. Transmission efficiency of a tubular light guide vs. aspect ratio (length/diameter); α is the half-angle of the concentrated sunlight and R is the inner surface reflectivity. (XBL 854-9798)

angles. We also investigated the performance of plastic optical fibers and evaluated the potential for improvement through further purification of the base polymer.

Planned Activities for FY 1985

We will continue our investigation of hollow reflecting light guides. Available reflecting materials will be completely characterized and the results used in improved analytical models. We will compare these model results with the actual performance of hollow prismatic light guides. Scale models of light guide elements will be tested in our sky simulator.

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Active Solar Cooling*

M. Wahlig, J. Rasson, M. Warren, K. Dao, R. Armer, P. Brothers, and P.L. Chen

The purpose of this project is to make major contributions to the technology base necessary for solar energy to become a viable option for the cooling of buildings. This project has two major tasks: (1) research on improved absorption cycles for high efficiency active solar cooling and heating systems and (2) systems analysis of active solar cooling and heating systems to establish operating requirements, research needs, and thermal performance of current and advanced space conditioning systems.

Absorption Chiller Research

The objective of the research on absorption-cycle chillers is to achieve a significantly higher conversion efficiency than is possible in other approaches to solar cooling and heating of buildings. Being essentially heat pumps, absorption-cycle chillers can be used for heating as well as cooling if the refrigerant fluid does not freeze in the outdoor coil during heating applications. We restrict our fluid choices to those for which this heating option is available.

The absorption-cycle research program consists

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of four phases, each successive phase leading closer to the final machine. The first phase was successfully completed some time ago.[1] By modifying a conventional gas-fired ammonia/water absorption chiller, we demonstrated the capability of our analysis techniques to predict accurately the performance of single-effect (i.e., single-stage) absorption-cycle chillers under operating conditions appropriate for solar-powered cooling.

In the second phase, a completely new solar-driven single-effect chiller was designed, fabricated, and tested, using the experience gained during the first phase. This new ammonia/water chiller had several unique features for recouping thermal and mechanical energy. The second phase was successfully completed[2] in FY 1982.

In the present, third phase, we are investigating the performance improvement obtained by adding a unique second stage to the single-effect chiller tested in the second phase. The concept of the resulting double-effect regenerative cycle (or cycle 2R) has been described previously.[3] Basically, with the addition of the second stage, the overall chiller efficiency increases continuously as a function of the inlet temperature from the solar collectors. This 2R chiller has been designed,[4] fabricated, and assembled; the debugging and testing was started in FY 1983 and was successfully completed in FY 1985.

In the fourth phase, a new concept in refrigeration-absorption cycles—one that should yield a still higher efficiency while requiring less heat-exchanger area, for a potentially lower cost—will be investigated. The basic concept of this single-effect regenerative cycle (which we call cycle 1R) has also been described previously.[5] The probability of successful development of the cycle 1R chiller has been greatly enhanced by our successful experience in developing the cycle 2R chiller.

Systems Analysis

The objectives of the systems analysis activities are: (1) to perform system simulation and analysis of active solar absorption and Rankine cooling/heating systems to establish the operating requirements and thermal performance of current and advanced space conditioning systems; (2) to use the results of these systems and economic analyses to determine future research needs for the solar cooling program and to determine where improvements can and must be made in thermal and electrical performance; and (3) to evaluate by computer simulation the impact of system controls and control strategies on annual energy savings for active solar cooling and heating systems. Previous work has focused on developing cost and performance goals for solar cooling systems.[6,7]

ACCOMPLISHMENTS DURING FY 1985

Absorption Chiller Research

Experimental testing of the 2R chiller was completed in FY 1985. The test results proved that the regenerative process is attainable and stable. Furthermore, the experimental performance results were ±5% of the theoretically predicted results. A full analysis and evaluation of the test results will continue into FY 1986.

Extensive testing of the vapor-driven multistage pump was conducted during FY 1985. The linkage between the drive side and the pump side was redesigned, resulting in improved piston alignment and reduction in friction forces. The pump piston seals were tested to determine the best seal design, i.e., a design that minimizes the leak across the piston with a low, acceptable level of piston friction.

Different seal materials were tested to determine the wear life in a specially designed testing apparatus. The test results showed that all materials tested in ammonia-water solution at room temperature exhibited unacceptable amounts of wear. Additional wear tests will continue as new materials are identified.

Meanwhile, another multistage pump design using an electric motor drive and plastic diaphram pumping elements was completed in FY 1985, as an alternative method of overcoming the seal problems of the vapor-driven pump. This design incorporates a radial configuration for the pistons to reduce the required parasitic power.

Systems Analysis

1. Comparison of Desiccant and Absorption Systems

In FY 1985 analysis was done to compare desiccant and advanced absorption solar cooling systems under comparable conditions.[8] To the extent possible, all cooling systems take advantage of the ability to reject heat directly to the atmosphere. Desiccant systems obtain their cooling effect from evaporative cooling and heat exchange. The advanced cycle desiccant systems have improved heat rejection capabilities. Advanced absorption cooling technology offers the possibility of chillers with thermal COP's of 1.55 or greater at design conditions. When evaporative cooling and heat exchange components

are added to an advanced absorption cooling system, the performance is enhanced further.

System coefficient of performance, system COP, the ratio of cooling effect delivered to heat input to regenerate the device, is calculated under different operating conditions. The heat input can be provided by solar or an auxiliary heat source (natural gas). The system coefficient of performance can be directly compared for different types of systems over the range of outdoor conditions relevant to the particular application.

In the ventilation mode desiccant cooling cycle, the inlet air stream is dried in a desiccant wheel and cooled by heat exchange with the return air stream. The supply air temperature is further reduced by evaporative cooling. The steady state heat and mass transfer of the desiccant wheel is modeled by analogy with heat transfer processes using heat and mass transfer effectivenesses. The cooling effect delivered is the difference between the enthalpy of the room and of the supply air. The thermal energy required to drive the system is the difference between the enthalpy leaving the heat exchanger and that leaving the heat source. Both moisture and heat are rejected from the desiccant wheel. The system thermal coefficient of performance is the ratio of the cooling effect delivered to the heat input required.

The advanced absorption cooling system is modeled including evaporative cooling, air-to-air heat exchanger, economizer cycle, and an evaporatively cooled condenser as shown in Fig. 1. An air-to-air heat exchanger transfers heat from the outside air stream (1) to the exhaust air stream (7). The cooled inlet air (2) is then mixed with return air from the room (5), based on a ratio of outdoor air, ROA, to determine the conditions of the mixed air

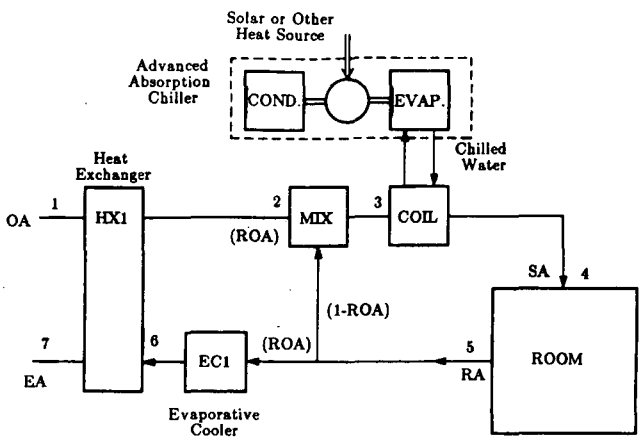

Figure 1. Schematic of a evaporatively cooled-closed cycle advanced-absorption system with evaporative cooling and air-to-air heat exchange. (XBL 864-1521)

(3) to the coil. The coil cools the air to the supply air state (4). The room return state (5) is assumed to be ARI conditions, as in the desiccant case. The room return air is evaporatively cooled (6). The output from the evaporative cooler is used in a sensible heat exchanger to cool the inlet air stream. The warm moist air stream (7) is exhausted. Outdoor air is also evaporatively cooled to cool the chiller condenser.

The thermal energy required to drive the system is determined by the thermal coefficient of performance of the advanced solar-fired absorption chiller operating at a condenser temperature given by the approach to the outdoor wet bulb temperature. For a system with a cooling coil, the system effectiveness, $\eta_{subsystem}$, can be defined as the ratio of the cooling effect delivered to the room to the enthalpy change across the coil. The application of heat exchange and evaporative cooling can greatly increase the system effectiveness, and improves the overall cooling effect delivered per unit of heat required. The chiller is modeled as an absorption chiller that can achieve a certain percentage of Carnot, where the performance depends on the chilled water temperature and condenser conditions. As we are considering the ultimate performance of such systems, we have assumed an efficiency of 0.70 of Carnot for the absorption chillers, consistent with the expected performance of the LBL cycle 1R chiller.

At low outside humidities indirect evaporative cooling can be an effective method of cooling. For this reason simulations were run using the evaporative cooling heat exchange, both with and without a desiccant wheel operating as a total enthalpy exchanger without a heat source for regeneration. Results of this analysis indicate that indirect evaporative cooling using either outdoor or return air is very effective. The use of the desiccant wheel does not improve the performance because moisture is transferred from the exhaust air to the inlet air streams.

Building cooling loads, calculated for a typical 930 m^2 (10,000 ft^2) office building using DOE2, have been analyzed. The hourly systems output file from DOE2 has been combined with the weather file to create a loads file with temperature, humidity, and heating and cooling loads for each of the 8760 hours of annual building operation. The hours of operation and the cooling loads are binned against outdoor temperature and humidity ratio to establish the annual range of operating conditions for the cooling system. By knowing the annual distribution of cooling loads encountered by the system over the year and the system COP over the range of operating con-

ditions, the heat input requirement can be calculated as a measure of annual system performance.

System coefficient of performance and the annual energy performance have been calculated under different operating conditions for open cycle desiccant and advanced absorption systems. The heat input can be provided by solar or an auxiliary heat source (natural gas). The system coefficient of performance can be directly compared for different types of systems over a range of outdoor temperatures and humidities where the bulk of the cooling demand occurs.

Results of analysis show that in Phoenix the seasonal system COP of advanced absorption systems with heat exchange and evaporative cooling is much larger than that of the ventilation mode desiccant system. In Phoenix, 48% of the cooling load occurs at low humidities where the entire cooling load can be met with indirect evaporative cooling. Almost all of the cooling load is Miami occurs at high humidities. In Miami with its greater latent loads, the two systems perform comparably.

The method can be extended to a wide range of desiccant and absorption cooling system configurations and control strategies. Advanced techniques of heat exchange and evaporative cooling that can benefit advanced desiccant systems will give a similar benefit to absorption systems. The ultimate solar application of these technologies will also be determined by other factors, including the coincidence of the solar resource with the cooling demand; the electrical parasitic power required to operate the systems; and the installed system cost. These issues are beyond the scope of this article.

2. Evaluation of Storage Options

Thermal storage is used in solar systems because there is a difference between the time at which energy is available as solar radiation and the time at which energy is required to meet a heating or cooling load. In solar heating systems solar radiation occurs in the daytime, while the greatest heating loads are at night. In solar cooling systems the solar radiation peaks at noon, while cooling loads typically peak around 3 or 4 pm. Storage is needed to bridge the gap between the noon supply of energy and the afternoon demand for cooling.

Different types of thermal storage may be used in a solar cooling system. Energy may be stored as "heat" on the hot side of the chiller, or it may be stored as coolth, on the cold side of the chiller. The storage may be sensible, in which the energy is stored as a change in temperature of the storage medium; or it may be latent, in which the energy is stored as a change in phase of the storage medium.

Computer simulation is used to determine the sensitivity to storage size and type of the annual performance of different storage configuration options.[9] Several issues are addressed: sensitivity of system performance to storage size and to load profile; sensitivity of hot-side sensible storage to storage stratification for both one and two tank systems; performance of hot-side latent storage; and the performance of cold-side storage. The study assumes careful design of solar cooling systems with the sizing of thermal storage based on the interaction between solar radiation and cooling load profiles for specific "design" days.[10] Chiller capacity is also taken into account. The annual performance of solar absorption cooling systems using different storage options is investigated using the simulation program TRNSYS.[11]

The system modeled is shown in Fig. 2. Evacuated tube collectors provide solar heated hot water to the storage device which in turn delivers hot water to the generator. The high performance evacuated tube collectors are modeled with performance data derived from the Sunmaster collector. The collector areas for the baseline system are chosen so that the high-solar fraction system has an annual solar fraction of 80%, and the medium solar fraction system has an annual solar fraction of 40%. The effect of other storage options on system performance is then measured by the change in annual solar fraction with respect to the annual solar fraction of the baseline system. Systems are simulated for an entire year using a 20-minute time step.

For low and medium (40%) solar fraction systems, the chiller is sized to use maximum output of the collectors. The remaining cooling load is provide by an electric backup chiller, as shown in Fig. 2, that operates when the solar system is unable to keep up with the load. For high solar fraction systems, the chiller is sized to meet the peak building load, and natural gas auxiliary backup is assumed.

The performance of systems with different storage options has been compared to the performance of a "state-of-the-art" baseline system that has a stratified hot-side water storage sized for a daily cycle (morning to afternoon).

The storage sizing is sensitive to the load distribution. Storage sizes for baseline systems operating seven days a week are significantly smaller than for comparable heating systems with the same collector areas. For systems which operate to meet 7-day loads with annual solar fractions of about 40%, there is little sensitivity of annual performance to storage size. For systems which have high (80%) annual solar fractions, multiple day storage can be beneficial in climates with variable summer weather. For sys-

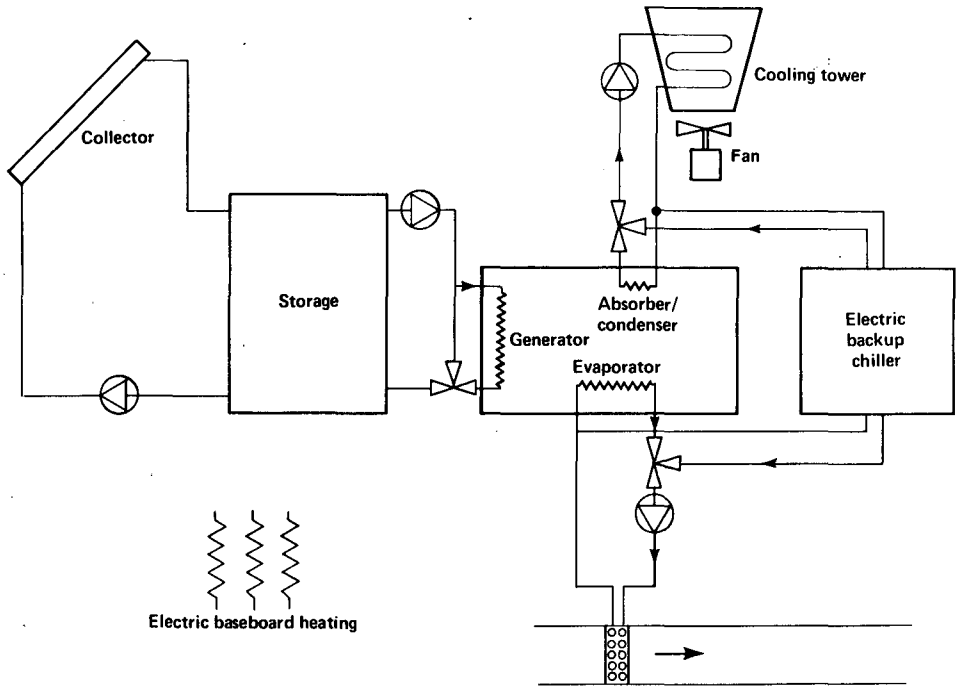

Figure 2. Active solar single-effect absorption cooling system. Medium solar fraction system uses a back-up electric chiller as shown. A high solar fraction system uses the solar chiller thermally fired and sized to meet the load so that no back-up chiller is necessary. (XBL 827-7251)

tems operating to meet 5-day (Monday-Friday) loads, the optimum storage is sized to store energy collected over the weekend. These systems have reduced collector areas (about 5/7) and much larger storage. Annual performance degrades with smaller storage and shows little or no improvement with larger storage.

For a properly sized cooling only system, stratification of hot-side storage has little effect on performance. Only when storage is significantly oversized will stratification play an important role. The use of two storage tanks to force stratification has no practical benefit for a system with high performance collectors.

The hot-side latent energy storage systems perform well when matched to chiller operating temperatures. Their future use depends on the cost of available phase change materials. The use of high temperature phase change materials with appropriate heat transfer fluids could eliminate the need for pressurized water storage for high temperature systems.

The use of cold-side storage by itself lowers the system performance significantly because of later starting times and earlier stopping times (when compared to the baseline system). The use of some hot-side storage can improve solar collection and can reduce the required chiller size, but is unlikely to improve performance above that of the baseline case.

This analysis has been done for today's state-of-the-art absorption technology that has a COP of about 0.7. Development of advanced solar fired absorption chillers gives the potential to achieve a COP of 1.55 at a firing temperature of 115 C (240 F).[5] Such improved chillers would require smaller collector areas to achieve the same amount of cooling rate and smaller hot-side storage volume to achieve the same amount of effective storage. Such systems would require significantly higher operating temperatures that would suggest the usefulness of hot-side latent storage; however, the sizing criteria and the conclusions of the analysis on the comparative advantage of different thermal storage options should remain unchanged.

3. Advanced Solar Cooling System Analysis

In FY 1985, detailed TRNSYS simulations were begun to establish solar cooling system performance using advanced chillers.[12] Both ideal chiller models (based on percentage of Carnot performance) and a performance-map chiller models (based on the characteristics of advanced cycles) were used. The results of the analysis using ideal chillers will be used to set upper bounds for performance and economics

of advanced absorption systems. Work on this analysis is continuing in FY 1986.

4. Advanced Absorption Cycle Analysis

LBL has continued work on modeling of high efficiency absorption chillers for solar cooling based on advanced cycles and working fluids.[13,14] In FY 1985 work on this project continued along three directions: 1) exploration into in-house program development and establishment of the requirements of a dedicated computer program that would model advanced chillers (like the 1R chiller under development at LBL) in sufficient detail to perform the machine design calculations; 2) exploration into the capabilities of packaged chemical process analysis programs, such as ASPEN and ASPEN-PLUS, for use in analysis of advanced-cycle chillers, thereby building on the developments in other industries; and 3) exploration into the capabilities of the analysis program developed by Gershon Grossman of Technion University in Israel for application to advanced-cycle analysis.

The basic computer program structure for the detailed analysis of advanced-absorption chillers was formulated. It consists of a combination of iterative and simultaneous solutions of the governing equations. The method was tested on a simpler single-effect cycle to test the methodology. The nonlinear set of equations was solved using the HYBRID solver from the National Physics Laboratory mathematical analysis package.

A review of chemical process simulation codes (flowsheet simulators) in common usage was also undertaken. Such programs have an extensive development history. ASPEN, Advanced System for Process Engineering, has been extensively developed at MIT under DOE support since 1977. It has been used with limited success in modeling a single-effect heat transformer problem.

Discussions begun in FY 1984 to establish a joint U.S./Israel research project to combine the research strengths of LBL and the TECHNION in the area of modeling, and analysis of advanced absorption cooling systems led to a joint agreement during FY 1985 between the U.S. DOE and the Ministry of Energy and Infrastructure of Israel (MOEI) on Simulation and Analysis of High Efficiency Absorption Systems for Solar Cooling. A project implementation plan was developed by LBL in August 1985.

This joint project allows us to take advantage of the Absorption Heat Pump Simulations and Studies Project that Gershon Grossman of TECHNION did for ORNL, involving the development of a simulation program to evaluate advanced absorption heat pumps for the DOE Conservation Program. The simulation program has been developed and is being tested for simple absorption systems and is being used to simulate absorption chillers under development at Carrier, Phillips, and Trane. The simulation program developed by Grossman at the Technion uses simultaneous solution of nonlinear algebraic equations. It is probable that this program will be capable of modeling closed-cycle absorption machines of moderate complexity. This program could probably also be used to model single-effect open-cycle systems.

Two computer code approaches for modeling advanced-cycle absorption chillers are being pursued. The first constitutes an extension of the Grossman computer code to model absorption-cycle chillers of moderate complexity. The second is the application of ASPEN or ASPEN-PLUS to complex closed-cycle absorption chillers. The TECHNION group will pursue the first approach in FY 1986; the LBL group will pursue the second approach. The Technion group will start developing component and system models for open-cycle cooling systems and will try to model the LBL 2R absorption cycle using slight modifications to their program. LBL will continue developing an iterative-solution model for complex absorption cycles.

PLANNED ACTIVITIES FOR FY 1986

Advanced Chiller Research

Completion of the analysis of the test results and documentation of the 2R chiller program will take place in FY 1986. The 2R chiller design and test results will be published in LBL reports and other scientific publications.

As part of the joint U.S.-Israel (LBL-Technion) project, LBL will continue the development of an analytical computer model capable of calculating performance of high efficiency absorption cycles such as the LBL 2R and 1R cycles and those being developed under DOE/Conservation sponsorship. Subroutines for these absorption-cycle models will be written as necessary, although it is anticipated that existing subroutines written for existing absorption models may be incorporated into these new, broader absorption models with only minor modifications. LBL will also acquire, as needed, available information on properties of working fluids and will share this information with Israeli researchers.

Systems Analysis

Comparative analysis of the performance of advanced absorption and desiccant solar cooling systems will continue during FY 1986. Performance will be calculated on an annual basis over a range of outdoor conditions. Better component models will be incorporated and used for the coil, evaporative coolers, condensers, etc. This effort will be coordinated with SERI researchers to achieve mutually agreed-upon comparative analysis techniques and system configurations. Work will also continue on TRNSYS simulation of advanced absorption cooling systems.

Models for regenerative evaporative cooling will be developed and applied to calculations of the performance of solar cooling systems. Building upon the concept proposed by Ian Maclaine-Cross, we will generate models for this component that can be incorporated into overall cooling systems analyses. These models will then be applied to performance improvement of conventional, absorption, and desiccant cooling systems. We will coordinate with SERI researchers on the model development and its applications.

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Biological Oxidations and Bioenergetic Studies on the Photochemical Conversion of Solar Energy*

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The Membrane Bioenergetics Group is concerned with understanding how membrane structures are involved in biological energy conversion in living systems. To this end, several microorganisms are under investigation.

1) *Halobacterium halobium,* an obligate halophile, synthesizes a unique protein (bacteriorhodopsin), which exists as a two-dimensional crystalline array in the outer membrane, whose sole function is the conversion of light energy to a transmembrane proton gradient. Studies on the isolated bacteriorhodopsin-containing membrane (purple membrane) by chemical modification,[1,2] and tryptic cleavage methods[3] are leading to a determination of amino acid residues involved in the proton translocation process, a stepping stone to elucidating the molecular events in this relatively simple biological pump.

2) Cyanobacteria (blue-green algae) are microorganisms which possess oxygenic photosynthesis similar to that of higher plants, as well as dark respiration similar to that of bacteria, yeast, and mammalian systems. In addition, strains of cyanobacteria, particularly filamentous varieties, are capable of fixing atmospheric nitrogen into ammonia, under aerobic conditions. Another unique feature of organisms of this class is their ability to adapt to extreme environmental conditions (salinity, toxic elements, restricted light regimes). Several lines of investigation using cyanobacteria are under consideration.

The first line of investigation exploits the ability of these organisms to grow under a range of salinities which presents an opportunity to alter the biochemistry of the cell by manipulating environmental conditions. Two organisms, *Synechococcus* 6311, a freshwater cyanobacterium which can grow in up to 0.6M NaCl, and *Agmenellum quadruplicatum,* a marine species which can grow in up to 2M NaCl, were used. The biochemical functions of respiration, photosynthesis, and the directing of photosynthate into osmoticum and cell storage products have been monitored using standard biochemical and novel magnetic resonance techniques (electron paramagnetic and nuclear magnetic resonance spectroscopies).

A second line of investigation deals with use of cyanobacteria as tools for technological and environmental problems. The technological problem involves the use of biological components in the NASA Closed Ecological Life Support Systems (CELSS) program as a regenerative life support subsystems for the revitalizaton of air, waste processing, and for the production of food for long-term space flight. Employment of photosynthetic systems (higher plants, green algae, and cyanobacteria) allows biomass production from relatively simple components which are readily recycled in a CELSS system.

The production of plant material in a closed system presents several problems. A primary consideration is that of the energy requirement for continuous operation, including illumination, temperature control, and various maintenance mechanisms. One way in which the energy demands can be lessened is by modifying the quality of the light used. Illumination of photosynthetic systems with white light (300–700 nm range) is wasteful, since photosynthetic organisms utilize only selected regions of the visible spectrum. Tailoring the emission profile of the light source to match that of the action spectrum of photosynthesis, or to select an "emission band" in a region of maximal absorption by some of the photosynthetic pigments would present an energy saving, especially if the selected "emission band" was in the blue region, when using fluorescent light sources.

A second concern is the probability of nitrogen loss from the closed system by the action of contaminating denitrifying bacteria, which degrade NO_3^- to N_2 gas, which is then lost from the biological system. Denitrification is most likely to occur irrespective of the method of waste processing due to the storage of human waste and non-food biomass (cellulose), which would result in an irreversible loss of fixed nitrogen.

The ability of certain strains of cyanobacteria to counter this loss by fixing atmospheric nitrogen back into ammonia makes them an attractive candidate for the CELSS program.

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The environmental problem is centered on using cyanobacteria for the removal of selenium and toxic compounds that have accumulated in the saline drainage waters on the west side of the San Joaquin Valley. Several species of cyanobacteria have been found with differing capabilities to withstand increased levels of selenate or selenite in the environment. Our research proposes to investigate the effect of selenate and selenite on the growth and metabolism of several species of cyanobacteria, the degree to which selenium compounds are accumulated, the oxidation state of the selenium compounds (species) within the cell, and how the accumulation affects the biology of the organism.

A third line of investigation deals with photooxidative stress, a process experienced by most oxygenic photosynthetic organisms under high light intensities. Chemical intermediates and enzymes involved in protective mechanisms against oxidative damage have been determined. In addition, a novel oximetric method using magnetic resonance techniques has been employed to monitor the intracellular oxygen concentration during photosynthesis/respiration cycles.

3) *Thiobacillus ferrooxidans,* an acidophilic chemolithotroph, utilizes the oxidation of ferrous ions to generate sufficient reductant to fix CO_2 into carbohydrate. Preliminary results have demonstrated a novel component in the electron transport chain of this organism, which may be the site of iron (II) oxidation.

ACCOMPLISHMENTS DURING FY 1985

Bacteriorhodopsin

In the past decade there have been varying reports of the stoichiometry of proton release from purple membrane in suspension and protons pumped after its incorporation into phospholipid vesicles. In an attempt to resolve the range of values observed, we have investigated the H^+/M_{412} ratio, measured in suspensions of purple membranes by the laser flash induced response of pH indicator dyes.[3] We have found this ratio to reflect the aggregation state of the membrane, assessed on the same preparations by quasi-elastic light scattering (QELS).[4] We have also found our measurements of proton release stoichiometry on retinal reconstituted white membrane suspensions to give much higher H^+/M_{412} ratios than the same measurements on purple membrane suspensions.

Using proton release figures for native and trypsin treated membrane preparations, the proton release activity of purple membranes declined from an initial value of 1.5 H^+/M_{412} to a value below 0.5 upon trypsin treatment. Retinal reconstituted white membrane, on the other hand, started with a much higher proton release stoichiometry, close to 4.0 H^+/M_{412}, and even after trypsin treatment it retained most of this activity. In summary, while purple membrane loses two-thirds of its activity, retinal reconstituted white membrane loses less than one-tenth of its activity.

While the absolute H^+/M_{412} figures presented here cannot be directly compared, due to surface charge considerations, the relative figures are most informative. One must remember that, on cleavage of the C-terminal tail by trypsin, the surface loses considerable negative charge, which will in turn increase the amount of deprotonated dye (hydroxycoumarin) in the interface region and so cause an increase in sensitivity of the dye to protons released into this region, decreasing any lowering of H^+/M_{412} stoichiometry upon trypsin treatment. We are confident, however, that our trypsin treatment procedure causes a similar extent of cleavage in both membrane preparations, so this increase in sensitivity should affect each of the samples equally. The fact is that the white membranes showed a much smaller decline in activity than the purple membranes. The reason for this decrease is that native purple membrane consists of a suspension of particles with homogeneous size distribution in a rather narrow range (around 260 nm), and upon trypsin treatment the membranes become extensively aggregated, with a QELS pattern more characteristic of a gel than of a suspension of particles. With the membranes stacked and confined, it is impossible for protons to be released into a region where they can be detected by the dye, or indeed by any other measurement technique. The light flash will still, however, generate M_{412} so that the observed ratio of H^+/M_{412} is apparently lower.

In the case of white membranes there is a quantitatively different effect. In the first place, white membrane patches are smaller (88 nm radius), even before trypsin treatment. Following treatment, they too aggregate, but to a much lesser extent than do purple membranes.

Cyanobacteria

Respiratory electron transport

In addition to oxygen evolving photosynthetic electron transport, cyanobacteria also possess, to a lesser degree, respiratory electron transport components. During the initial exposure of cells to a

saline environment, when photosynthetic electron flux was severely inhibited[5,6] respiratory electron transport was found to increase tenfold, concomitant with a build up of cellular carbohydrate.[6] Using low temperature electron paramagnetic resonance (EPR) spectroscopy to characterize components of the electron transport pathways,[7] Cu^{2+} signals arising from the terminal oxidase[7] were found to increase in salt grown cells,[6] demonstrating that the observed increase in endogenous whole cell respiration was due to elevated levels of the respiratory component (Cytochrome *c* oxidase) rather than an increase in substrate supply or enzyme activity.[6] The elevated respiratory activity, which maintains a transcytoplasmic membrane pH gradient, supplied the driving force for the removal of intracellular Na^+ levels in the high salt environment. Via a Na^+/H^+ antiporter, removal of intracellular Na^+ relieved the inhibition of cellular processes (particularly photosynthesis), which returned to normal levels.[6] However, the respiration rate did not decrease, maintaining the low cellular Na^+.

Effect of C-13 Enrichment on Detectability of Organic Solutes by NMR

This study showed that the detectability of organic solutes by nuclear magnetic resonance (NMR) spectroscopy can be significantly increased by providing cyanobacterial cells with bicarbonate enriched with C-13. Imposing high salinities during growth amplifies the concentration of the intracellular organic solute glucosyl-glycerol, thereby facilitating further its detection. NMR spectra were used to make reasonable quantitative estimates of intracellular solutes if the peaks were well resolved, unambiguously assigned, and if a peak height standard was included. The methodology, in combination with standard cell fractionation and biochemical analysis, permitted us to determine the conditions and time frame of glycogen and osmoregulant interconversion.[9]

The time course of glucosylglycerol accumulation in the light after upshock of the cells (sudden increase in salinity) was comparable to the time course of cell doubling, which is consistent with other studies of carbohydrate accumulation. The diversion of fixed carbon to the synthesis of glucosylglycerol can explain, in part, the marked reduction of cell growth rates observed in cells during the initial period following upshock.[9]

A downshock experiment indicated that depletion of the accumulated glucosylglycerol is very rapid and probably involves the incorporation into glycogen, a strategy that would conserve the cellular fixed carbon pool. However, no evidence for glycogen was observed, either by NMR or conventional chemical analyses.[9]

The upshock data also showed that there is conversion of glycogen to the osmotically active species glucosylglycerol in the light, but not in the dark. This was a surprising observation considering that the cell could fulfill a need for low molecular weight solutes, with a relatively low expenditure of energy. Previously it had been observed that cells of another cyanobacterium (*Synechococcus* 6311) take up salt during hypersaline shock and carry out metabolic processes in the light that enable them to recover from the effects of this high intracellular salinity. Thus, it would appear that the presence of organic "compatible solutes" is not a prerequisite for short-term cell survival either in the light or in the dark. During dark periods, however, these compounds may be required for energy production and different osmoregulatory mechanisms may be employed to compensate for the loss of organic osmoregulants to respiration.

Effects of Selenate Toxicity

The growth rates of laboratory cultures of *Synechococcus* 6311 were determined by measuring increments in cell density over a period of four days. Generation times were calculated during the early logarithmic growth phase. Cultures were subjected to a variety of sulfate and selenate concentrations in Kratz and Myers "C" medium under a light intensity of 50 $\mu Em^{-2}s^{-1}$, at 28°C and bubbled with air supplemented with 1% CO_2.

Near maximum growth rates were obtained with a minimum of 0.1 mM (14 ppm) of Na_2SO_4 in the growth medium. The minimum requirement for sulfate was determined in order to determine the sensitivity of the organism to selenate, since sulfate has been shown to have an antagonistic effect on selenate toxicity. Reproducibility of growth rates was determined using six independent replicates giving a value for the generation (cell doubling) time of 15.58 hours with a standard deviation of 0.50 hours. The reproducibility of the generation time permits a significant interpretation of even small changes in the growth rate.

The generation time (in the presence of 14 ppm and 1000 ppm Na_2SO_4) over a range of Na_2SeO_4 up to 5000 ppm was determined. Cells grown with minimal sulfate (14 ppm) showed sensitivity to selenate at 50 ppm, growth being totally inhibited at 100 ppm selenate. However, increasing the sulfate level to 1000 ppm facilitated cell growth in up to 5000 ppm selenate. Results obtained so far indicate

that it is the selenate/sulfate ratio which determines cell viability and growth, rather than absolute selenate concentration *per se.* When the selenate/sulfate ratio is greater than 1.0, growth inhibition and cell death occurred.

Growth of Cyanobacteria under Selected Light Regimes

Nostoc muscorum, a filamentous hetercystous nitrogen fixing blue-green algae, was grown under blue (400–500 nm) and white (300–700 nm) light at 150 $\mu Em^{-2}s^{-1}$. The cells grow readily under the blue light, even though the cell doubling time (generation time, G) increased by a factor of 2.5. Analysis of photosynthetic O_2 evolution and nitrogenase activity during growth under blue light reveals very little difference from those grown under white light when rates were calculated on a total protein basis. Calculation of rates (particularly photosynthesis) on a total chlorophyll basis revealed an apparent increase in photosynthetic rate. However, this reflected a decrease in total cell chlorophyll, a chromatic adaption to blue light. Analysis of cellular products after a seven-day growth period under blue and white light revealed that little change occurred in soluble sugars, glycogen, or lipids, while total protein decreases only by 10%. A component which does increase is cell wall material.[10]

In conclusion, the nitrogen fixing strain *Nostoc muscorum* is capable of growth under light at the blue end of the visible spectrum. One must evaluate whether the energy saving gained by employing blue photons outweigh the slower growth rate (and hence biomass production). However, if a system employing a continuous culture (kept at a fixed point in the exponential growth phase) for air revitalization, etc., then a slower growth rate may be advantageous, requiring less addition of growth medium to maintain the constant cell density.

Oxidative Damage

Nitrogenase, the enzyme responsible for the biological fixation of atmospheric N_2, is extremely oxygen-sensitive. One of the modes in which cyanobacteria "solved" the problem of N_2-fixation under aerobic conditions was the development of the heterocysts mentioned above. However, as with other nitrogenase containing microorganisms, the mechanisms by which these cells retain an oxygen-free internal environment is not completely understood. In addition, photooxidative damage to cell components occurs under high light, the mechanisms of protection against such damage are important factors in cell viability.

ESR oximetry for the measurement of intracellular O_2. We have recently developed an ESR technique which enables us to measure intracellular O_2 concentrations. We hope to utilize this method to gain a better understanding of the protection mechanisms against the toxic effects of O_2 to nitrogenase.

The technique is based upon the broadening effect dissolved O_2 has on the nitroxide spin-probes ESR signal. Photosynthetically generated oxygen, in a suspension of the cyanobacterim *Agmenellum quadruplicatum,* caused a broadening of the EPR signal by 0.5 G. The effect is even more pronounced when a higher derivative of the spectrum is examined. According to our calculations, this broadening is equivalent to O_2 concentration in the suspension of 2.5 mM.[11] Furthermore, by quenching the extracellular signal, it is possible to examine only the probe inside the cells, and by using the measured degree of broadening to calculate intracellular O_2 concentrations. Studies are presently underway to compare O_2 levels in non-N_2-fixing and some N_2-fixing cyanobacterial cells, as well as to establish the O_2-sensitivity of various photosynthetic activities.

Protective enzyme systems against oxyradical products. The mechanism for removal of inorganic and organic peroxides consists of a highly active ascorbate peroxidase acting in combination with a relatively low intracellular concentration of ascorbate (μmolar level) but which is regenerated by a large (mmolar level) concentration of reduced glutathione. The activities of ascorbate peroxidase observed in *N. muscorum* and *Synechococcus,* with an intracellular concentration of 20 to 100 μM ascorbate, were found to scavenge 60–230 nmoles H_2O_2·mg protein^{-1} min^{-1}. This rate is equivalent to 0.5–2.0 μmoles H_2O_2·mg chl^{-1}min^{-1} which approaches 30% of the photosynthetic electron transport rates and hence appears sufficient to scavenge relatively large amounts of H_2O_2 formed in the cells. The large pool of glutathione in the cells is used partially to regenerate the ascorbate by dehydroascorbate reductase while the steady state level of the glutathione disulphide is low and glutathione is maintained in the reduced form by glutathione reductase activity.[12] That the H_2O_2 removing system involves a cascade of reactions is also supported by studies of catalase. In *N. muscorum* and *Synechococcus* catalase has a very low affinity to H_2O_2 (unpublished results), and therefore is not as effective as ascorbate peroxidase in H_2O_2 removal.

Thiobacillus ferrooxidans

Studies on the electron transport chain of this

organism, using low temperature EPR spectroscopy, have revealed a novel component at g = 2.005, which is specifically reduced by Fe(II), and autooxidized specifically in the presence of sulfate ions. This ionic requirement is in agreement with the organism's ionic requirements for the formation of Jarosite deposits. Preliminary work places this novel component on the reduced end of the electron transport chain, and it is a likely candidate for the catalytic center responsible for the direct oxidation of Fe(II) to Fe(III) sulfate complexes. This line of research will be continued in FY 1986.

PLANNED ACTIVITIES FOR FY 1986

Cyanobacteria

Work with cyanobacteria will continue in several areas. The role of respiration, with emphasis on the removal of O_2 to facilitate the protection of the nitrogen fixing enzymes, will continue to be investigated. Components of the respiratory electron transport pathway in addition to the Cu^{2+} containing terminal oxidase will be investigated by EPR spectroscopy. Professor Peschek's group in Vienna, who have isolated outer membrane preparations with high oxidase activity, will make samples available for the determination of the Cu^{2+} containing oxidase and other electron transport components by EPR spectroscopy. The investigation of (photo)oxidative stress in several strains, both unicellular and filamentous will continue, using the standard biochemical and novel ESR oximetric techniques. Inactivation of cellular process by intracellular oxygen will be correlated with the levels of antioxidative enzymes and components within the cell to elucidate protective mechanisms. Two unique cyanobacteria, *Gloeothecae* (a unicellular aerobic nitrogen fixer) and *Gloeobacter* (a unicellular thylakoidless non-nitrogen fixer) will be investigated with respect to their antioxidative, electron transport, and photosynthetic electron transport pathways.

Thiobacillus ferrooxidans

Further characterization of electron transport components of this chemolithotroph will continue, particularly ionic requirements and the nature of the Jarosite deposits formed by the bacterial oxidation of $FeSO_4 \cdot 7H_2O$ at acid pH.

Halobacterium halobium

The role of specific amino acids in the structure and function of bacteriorhodopsin will be assessed by chemical modification, cleavage, and protein reconstitution techniques.

Recently we have been engaged in the selection and further characterization of carboxyl modifications which are region-specific. We propose to use these modifications in conjunction with chemical and proteolytic cleavage techniques to obtain and purify modified fragments of bacteriorhodopsin. Combinations of modified and unmodified fragments will be tested for the ability to reconstitute a native-like protein complex in the presence of the chromophore and native lipids. The products of the reassociation will be analyzed with respect to photocycle kinetics, M_{412} accumulation, light-induced protein release and spectroscopy. Further characterization of the tertiary and quaternary structure will be done by spectrapolarimetry and spectrofluorimetry.

The long-term goal is to develop a method by which the selectivity of amino acid modification can be enhanced by reconstitution of modified with unmodified fragments, so that the amino acids of particular helices can be studied, and the involvement of these residues in protein translocation can be determined.

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LBL Building 71 Solar Cooling Project*

F. Salter

This active solar cooling project is part of the Department of Energy's Solar in Federal Buildings Program. The program is intended to stimulate growth and technical improvements in solar technology through the installation and demonstration of a variety of commercially applicable solar energy systems in buildings owned or occupied by the federal government. The program provides technical and financial assistance through interagency agreements to federal agencies for design, acquisition, construction, and installation of solar heating and cooling equipment projects.

Building 71, which houses the Heavy Ion Linear Accelerator (HILAC), was chosen as the site for this demonstration project. The LBL Plant Engineering Department provides project engineering and contract administration. The LBL Active Solar Research Group provides technical assistance and review of the project.

Overall administration is provided by the San Francisco Operations Office of the Department of Energy (DOE/SAN). DOE/SAN has subcontracted technical management of the project to the Energy Technology Engineering Center (ETEC).

The Solar Cooling System provides substitute capacity for the existing Building 71 chilled water system with a solar-driven chiller installed next to and in parallel with the existing electric chillers. The system consists of roof-mounted collectors; storage tanks; a nominal 25-ton capacity lithium bromide chiller package; and associated pumps, piping, insulation, valves and fittings, controls, and instrumentation. The chiller package was supplied by Arkla Industries, Inc.

Table 1 summarizes the design parameters of the cooling system. The collector array uses Energy Design HP-250 evacuated-tube solar collectors.

ACCOMPLISHMENTS DURING FY 1985

Construction had been delayed for the first seven months of 1984 because of a lack of funds, with work resuming in August 1984. The solar loop was pressurized and 10 solar collectors were found to have leaks. Attempts to field-weld the solar collector stainless steel tubing were unsuccessful, and the entire tubing circuits were replaced with new copper fluid circuits for the damaged solar collectors.

Prior to acceptance tests, the construction subcontractor placed the solar loop in operation in November 1984 and operated the solar chiller for three days in December 1984. The solar loop was left operational until July 1985 when it was shut down by LBL because of excessive leakage from solar collectors and especially from silicone hose connections between solar collectors.

*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Solar Heat Technologies, Solar Buildings Technology Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Table 1. Parameters of LBL Building 71 solar cooling system.

Chiller Capacity	25 tons (nominal)
Chiller COP	0.73
Average Operation	6 hr/day (at 22-ton loading)
Generator Entering-Water Temp.	185°F (adjustable 170°F to 200°F)
Exiting Chilled-Water Temp.	45°F
Entering Condenser-Water Temp.	80°F
Maximum Storage Temp.	250°F
Collector Area	5100 ft^2 (gross area)
Collector Type	evacuated tube (198 collector modules, with 7 tubes per module)
Storage Tank	2500 gallons
Thermal Ballast Tank	500 gallons
Expansion Tank	500 gallons

By January 1985 relatively little work remained to complete the project (aside from leakage problems), yet LBL was unable to expedite the subcontractor construction. Work continued at a very slow pace, especially after the subcontractor filed a $248,000 claim against LBL (claim was primarily against delays and problems associated with solar collector delivery and operation) in February 1985. LBL negotiated with the subcontractor during the spring and summer of 1985, eventually eliminating the claim.

The final inspection was held in September 1985. Acceptance tests were started in early November. The chiller failed during the course of the tests and the solar system was shut down.

LBL has since written to DOE recommending that the solar system be shut down permanently. This is based on the high cost of replacing the Arkla chiller ($48,000; Arkla, now owned by Preway, no longer manufactures or services solar chillers) and on major problems with the solar collectors. The solar collectors have had a high failure rate due to severe crimping at 180° bends within each evacuated tube and at tack welds on spacers between supply and return headers. Additionally, the silicone hose connections between solar collectors extrude beneath the hose clamps causing excessive leakage and need for repeated maintenance. LBL is concerned that all the solar collector stainless steel tubing circuits may eventually fail, possibly at an accelerated rate, especially with the potential for stress corrosion cracking of the stainless steel tubes. Eliminating leakage at solar collector connections would be extremely costly due to the high stagnation temperature (approximately 600°F), resulting thermal expansion, and narrow spacing between solar collectors. LBL is presently corresponding with Energy Design based on the above collector items.

Being a demonstration project, cost effectiveness was not one of the initial project requirements. At this point, the limited economic benefit of the project (savings of conventional fuel costs) makes it very difficult to justify the anticipated additional equipment costs and maintenance costs involved in proceeding to repair and operate the system.

PLANNED ACTIVITIES FOR FY 1986

Assuming that DOE accepts the LBL recommendation to discontinue operation of this system, this project will terminate in early FY 1986. The main outcome of the project has been increased experience with construction rather than with operation of solar cooling systems. Valuable information on use of stainless steel collectors (how not to do it!) will hopefully prevent the problems that surfaced here from re-occurring in future solar cooling and heating systems.

Solar Energy Conversion Using Microstructured Materials: Direct Radiant Heating of Small Particle Suspensions*

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The Solar Advanced Micromaterials Research and Development Group is investigating the use of microstructured materials for the conversion, control, and collection of solar energy. Current research is underway in four areas: (1) direct radiant heating of small-particle suspensions to produce useful fuels and chemicals, (2) radiant heating of small-particle suspensions to initiate reversible chemical reactions for thermal energy storage and regenerative electrochemical cells, (3) production of hydrogen from water, and (4) development of microporous optical materials for insulating windows and ceramics. This article describes research in the first area. Work in the second and third areas is reported in the Thermal Energy Storage section of the Chemical Process R&D Program (LBL-20201). The insulating windows and the ceramics research in the fourth area are described in the "Optical Materials Studies" and the "High Temperature Ceramics Development Using the Sol-Gel Process" articles of this chapter, respectively.

BRIEF HISTORY OF WORK PRIOR TO FY 1985

For the past seven years, we have been actively involved in developing solar thermal energy conversion systems using the principle of direct absorption of concentrated sunlight by a gas-particle mixture.[1-3] Small particles absorb sunlight concentrated by a field of mirrors or a parabolic dish to heat a gas to high temperature for electric power generation or industrial process heat. The concept was demonstrated experimentally by the design, construction, and successful solar test of an air-heating, 30 kW_t SPHER Receiver (SPHER is an acronym meaning *Small Particle Heat Exchange Receiver)* at the Georgia Institute of Technology Advanced Component Test Facility in FY 1982.[4] The solar tests confirmed the predictions that (1) small particles are effective solar absorbers, (2) high gas temperatures can be attained, and (3) the high temperature zone may be isolated from the surrounding walls. In two DOE-sponsored comparative evaluation studies of a number of advanced high temperature gas receivers the SPHER concept ranked first and second.[5,6]

Since FY 1983, we have been investigating the possibility of initiating high temperature chemical reactions by directly illuminating particle suspensions with concentrated sunlight. We call such a receiver STARR, an acronym meaning *Solar Thermally Activated Radiant Reactor,* in order to differentiate it from the strictly gas heating SPHER receiver. In this concept, the particles absorb sunlight to drive a chemical reaction.

In FY 1984, we made substantial progress in developing the STARR receiver technology. A survey of candidate chemical reactions was performed. Analytical models of the 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.[7] Experimental studies with entrained particles were carried out using a xenon arc lamp to simulate concentrated solar radiation. Reference 8 details these accomplishments.

ACCOMPLISHMENTS DURING FY 1985

Our research into STARR receiver technology was divided into four interrelated areas: (1) assessment of technical and economic potential of candidate chemical reactions, (2) calculation of optical properties of gas-particle mixtures for candidate small-particle materials, (3) continued development of an integrated solar thermal and fluid mechanical model of gas-particle mixtures in STARR receivers, and (4) experimental studies. The accomplishments in each of these areas will be discussed separately.

Assessment of Candidate Chemical Reactions

In FY 1984, we identified a large number of chemical reactions as candidates for the STARR receiver. In FY 1985, we evaluated these reactions using a set of technical and economic criteria. The technical criteria included process feasibility, efficient use of sunlight, adaptability to diurnal operation, and the availability of suitable particle materials. Economic criteria included cost competitiveness with similar products made using conventional energy sources, high product value, and plant location (to reduce transport costs for bulk products).

*This work was supported by the Solar Fuels and Chemicals Program managed by the San Francisco Operations Office, under the Assistant Secretary for Conservation and Renewable Energy, through the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the Solar Energy Research Institute.

Each candidate reaction was assigned to one of four categories dependent on the role of the particle in the process reaction:

1. *Particle as Gas Heater.* The particles absorb sunlight and heat the surrounding gas but do not participate in the process reaction.
2. *Particle as Feedstock.* The particle is the reactant for the process reaction; the gas acts solely as a carrier for the reacting solid material.
3. *Particle-Gas Reaction.* The particle undergoes a chemical reaction with the entrainment gas.
4. *Particle as Reaction Catalyst.* This is similar to the first category above except that the absorbing particle also acts as a catalyst or photocatalyst. Photocatalysis of high temperature reactions is an exciting and surprisingly little studied area that offers the potential of developing solar unique processes, that is, processes driven with solar energy that cannot be economically duplicated using conventional energy sources.

Chemical reactions worthy of further study were identified in each category. In gas heating applications, the thermal decomposition of hydrogen sulfide (H_2S) to hydrogen and sulfur ranked highest. It only requires 1/7 the energy per mole to produce hydrogen from H_2S as it does from water. In addition, H_2S is very plentiful and is an undesired byproduct of the natural gas and petrochemical industry. The absorbing particle may be carbon or a metal oxide.

Three reactions stand out in the category of the particle as feedstock. At present, elemental phosphorus is produced in electric arc furnaces by reacting phosphate ore with carbon and silica. The direct replacement of electrically derived heat by solar thermal heat produces an extremely attractive economic benefit. This may be accomplished by pelletizing the premixed feedstock and heating it to a high temperature with concentrated sunlight to initiate a reaction to release elemental phosphorus. Another interesting application of solar solids processing is provided by the Harteck process.[9] In the first step of this cycle, high pressure air is reacted with metal oxide particles to form a metal nitrate (the use of small particles may substantially enhance this reaction). In the second step, solar heat is used to decompose the metal nitrate particles to form NO_x and recover the metal oxide. The NO_x is then scrubbed with water to form nitric acid, an industrially important chemical. The net effect of this cycle is to fix atmospheric nitrogen with sunlight. The third reaction can be used in a thermochemical process to produce hydrogen and oxygen from water. In this reaction, magnetite (Fe_3O_4) particles are reduced by decomposition at high temperature to form FeO and release oxygen. In the second step of this thermochemical water splitting cycle, the FeO particles are oxidized to magnetite by low temperature steam to release hydrogen from water.

In the particle-gas reaction category, another type of water splitting reaction was identified in which both steps are solar driven. This involves the reaction of magnetite with water to form hematite (Fe_2O_3) and hydrogen. Since this reaction has a slightly positive free energy change it cannot occur spontaneously. However, magnetite is an excellent solar absorber which, under high radiant fluxes, may photo-reduce water adsorbed on its surface. The cycle is completed by the high temperature decomposition of hematite to reform magnetite.

In the particle as catalyst category, two reactions stand out. The photocatalyzed oxidation of nitrogen in air at moderately high temperatures (e.g., 1700 K) is a possibility. In the Wisconsin process (partly commercialized in the 1950's), temperatures in excess of 2500 K are required to thermally oxidize nitrogen, followed by a requirement for rapid quenching to temperatures below 1700 K to prevent decomposition of the nitric oxide. Driving this reaction photocatalytically at a temperature below 2000 K would overcome both of these stringent requirements. In another reaction, SO_3 decomposition forms the basis of several solar energy conversion processes, including multistep thermochemical hydrogen production and storage or transport cycles in which SO_2 and O_2 are recombined to produce heat. Iron oxides are used to catalyze SO_3 decomposition, and photocatalysis may play an important role in enhancing the dissociation.

In summary, several good candidates for STARR receiver application were identified. Among these candidates, we believe that the moderate temperature photo-oxidation of nitrogen in air, if it can be effected, would have the highest payoff for two reasons. First, the product, fixed nitrogen for fertilizers, is a very valuable commodity of world-wide usage that requires only air and water as primary feedstocks. Second, there is the potential for solar uniqueness, since this process would require solar photons to catalyze it.

Optical Properties Calculations

To design a STARR receiver it is necessary to understand the optical properties of absorbing parti-

cle suspensions. Computer codes utilizing the Mie calculation were developed to determine the absorption of *broad band* spectral radiation by gas-particle suspensions. Figure 1 illustrates the result of these calculations by showing the fraction of light absorbed by a particle suspension as a function of the product of particle mass loading and propagation distance.[10,11] Data are plotted for magnetite (Fe_3O_4), hematite (FeO_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; 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 studies.

Integrated Model of Gas-Particle Mixtures

To properly design a STARR receiver, it is important to understand the gas and particle temperatures, densities, and flows inside the receiver. To calculate these quantities requires development of a model to predict the effects of solar absorption and heat transfer within gas-particle mixtures, the fluid flow, and the chemical reactions. Since FY 1984, we have been working on versions of such a model that would include most major effects.[7,11-12]

To study possible chemical reactions carried out by STARR, we implemented the CHEMKIN computer codes at LBL. These state-of-the-art thermochemical codes were obtained from Sandia National Laboratories. This implementation will allow us to calculate chemical kinetics and equilibrium for complex reacting systems including the presence of condensed phase species.

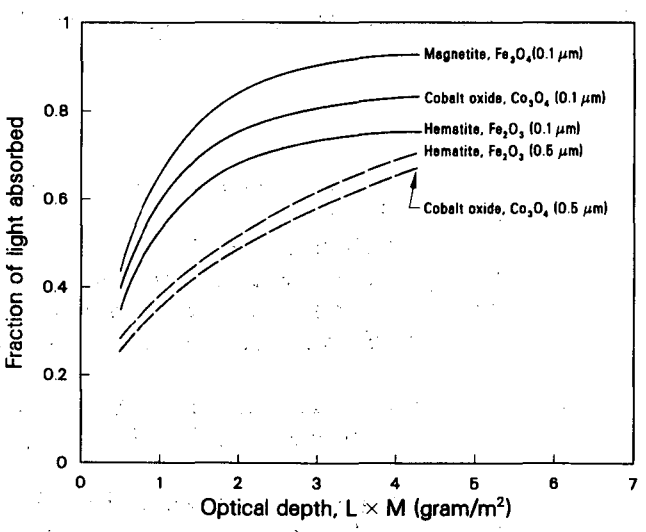

Figure 1. Fraction of the light absorbed from a xenon arc-lamp by a uniform gas-particle mixture as a function of the optical depth (the product of the mass of particles, per unit volume, and the path length). Each curve represents a specific particle. (XCG 862-7101)

Experimental Studies

Laboratory studies were used to validate our understanding of radiantly heated particle suspensions and to explore new ways of inducing chemical reactions with sunlight. Concentrated solar radiation is simulated in the laboratory using a high intensity xenon arc lamp mounted at one focus of an ellipsoidal reflector. The 2.2 kW xenon arc-image furnace is 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 to the solar simulator in FY 1985 to improve the alignment and reduce heat losses. The complete experimental system includes gas supplies, vortex particle entrainer, baffled optical attenuation tube, quartz reactor, dichotomous sampler, electronics, and instrumentation to measure temperature and flow. Particle composition is monitored off-line with an automatic x-ray diffractometer, and gas composition is monitored with a gas chromatograph.

The experimental system was used to investigate chemical reactions induced by radiant heating in the reactor system. Both oxidation and reduction of entrained particles were demonstrated. All the entrained particles were examined using Scanning Electron Microscopy (SEM). In addition to the metal oxides mentioned below, a beneficiated phosphate ore sample from Togo was examined for suitability for solar thermal processing (see Fig. 2).

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 a few 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.

Powders of hematite, magnetite, cobalt oxide

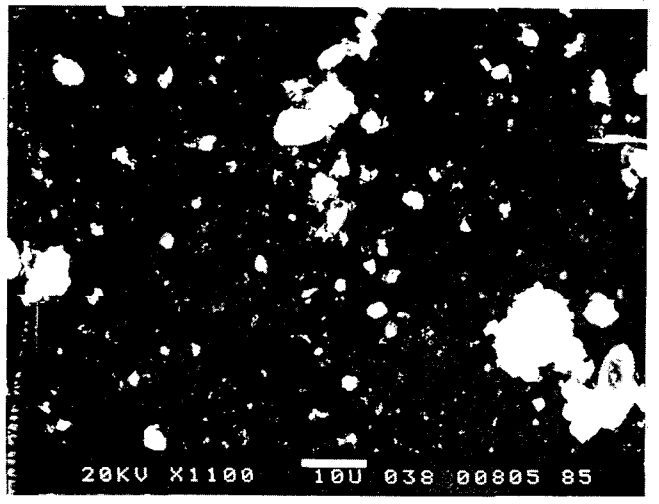

Figure 2. Scanning electron micrograph of beneficiated phosphate ore from Togo. (XBB 863-1734)

(CO_3O_4), copper oxide (CuO), zinc oxide (ZnO), and manganese dioxide (MnO_2) were separately entrained in argon and passed through the reactor to determine if they could be reduced by direct radiant decomposition (such reductions are important for hydrogen-producing multistep thermochemical cycles). Because of the limited size of the reactor, 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%. Figure 3 gives the x-ray diffractometer measurements of the 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.

PLANNED ACTIVITIES FOR FY 1986

The research in direct radiant heating of small particle suspensions will continue in FY 1986 with support from SERI. The proposed work will concentrate on detecting and exploiting photolytic effects at high fluxes and temperatures to produce useful fuels and chemicals. Both experimental and analytical techniques will be used to explore radiantly induced chemical reactions. In particular, reactions involving the oxidation of nitrogen and the reforming of methane with carbon dioxide will be studied. Experiments using the solar facilities at Sandia National

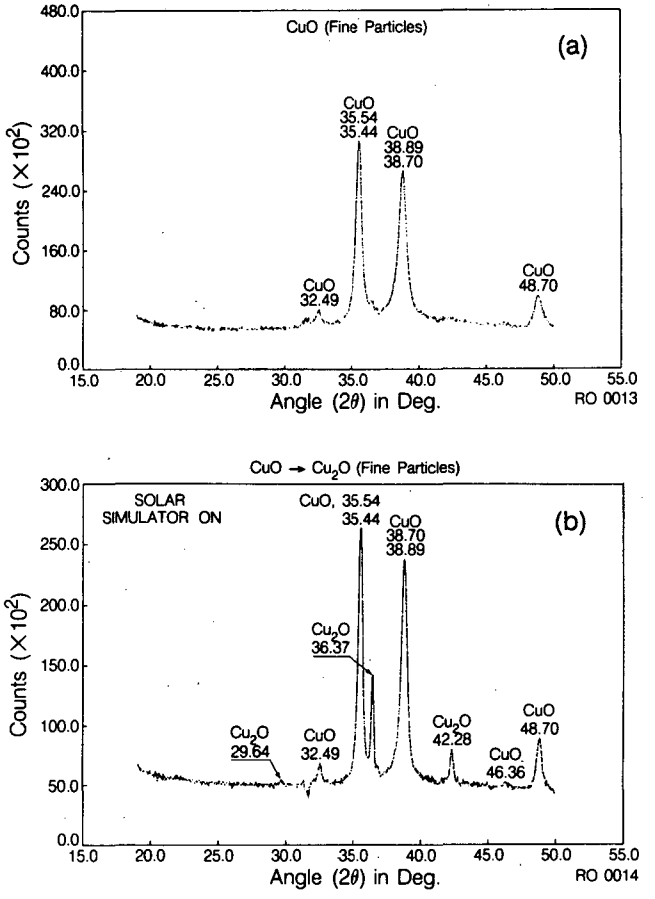

Figure 3. X-ray diffractometer measurements of copper oxide powder before and after solar simulator turned on. [(a) XBL 855-9323, (b) XBL 855-9325]

Laboratories in Albuquerque are planned for FY 1986 or FY 1987.

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High Temperature Ceramics Development Using the Sol-Gel Process*

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The goal of this research is to develop advanced ceramics for high temperature applications based on microstructural fabrication techniques using sol-gel processing. In traditional ceramic preparation, the principal sources of unreliability in performance derive from the processing techniques and the state of the starting materials. It has been postulated by some research groups that uniform agglomerate-free fine *particles* can be used to produce more reliable and reproducible ceramics than those prepared traditionally from irregular shaped commercial powders. Other groups have suggested that controlling *pore* uniformity in green bodies (ceramic preforms before sintering) is the important factor and the particles do not necessarily have to be uniform. Evidence for improved performance in laboratory scale samples has been presented by proponents of both the "uniform particle" and "uniform pore" hypotheses.

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We are developing a high density sol-gel processing technique that offers the possibility of controlling both the uniformity of particle *and* pore sizes and thereby better control of the microstructure and reliability in the ceramic material. Work was initiated late in FY 1984 with a review of sol-gel preparation techniques for making metal oxide ceramics from alkoxide precursors.

ACCOMPLISHMENTS DURING FY 1985

Currently, the production of ceramics by sol-gel processing is carried out using two distinctly different processes. In one, hydrolysis of a metal alkoxide in alcohol leads to condensation and formation of a monolithic gel. This alcolgel is then air-dried slowly and sintered to obtain small samples of a ceramic or glassy material. In the second process, fine spherical metal oxide particles are produced by hydrolysis and condensation of metal alkoxides. The fine powders, without large agglomerates, are used to prepare ceramic "green bodies" that are subsequently sintered to produce experimental ceramic materials. We have been studying the monolithic approach because this technique offers a real possibility to control both particle and pore sizes as well as the interparticle bonding. In addition, this approach offers promise for producing multicomponent but homogeneous ceramics and glasses difficult to produce by conventional means.

The experimental research on monolithic gels at LBL was initiated by studying single component systems of silica. In the past, preparation of silica

alcogels was limited to rather low densities of solids. This occurred because of a solubility limit of the alkoxide in the alkoxide-water-alcohol ternary system. When this solubility limit is exceeded, phase separation or precipitation occurs; this sets an upper limit on the solid content in the alcogel. An important accomplishment of our research in FY 1985 was to find ways to overcome this solubility problem and allow the preparation of materials with much higher solid content, more suitable for ceramic applications.

In addition to the preparation of single component sol-gel solids, we have also synthesized the mixed oxide system SiO_2:Al_2O_3. Transmission Electron Microscopy (TEM) of this system shows that the Al_2O_3 particles are fine needles 5 nm diameter and 25–30 nm in length. The SiO_2 surrounds the Al_2O_3 needle. More definitive study to characterize the microstructure is in progress.

In addition to the synthesis work, we have developed several new techniques to study the evolution and details of gel microstructures. Special sample preparation methods were developed to overcome significant difficulties in stabilizing these very fine, electrically insulating, low thermal conductance materials for TEM studies. The kinetics of gelation were studied by following the intensity of scattered laser light. These studies and the resulting structural data help define the state of the starting material. By relating the properties of the starting material-microstructure with the final properties of the ceramics, not only a correlation between microstructural properties and final properties can be established, but one can tailor a ceramic property based on the starting microstructural properties.

PLANNED ACTIVITIES FOR FY 1986

The preparation of mixed oxide gels will be continued in FY 1986 with emphasis on obtaining very fine and homogeneous alcogels and ceramic precursors. The drying and sintering kinetics of the mixed oxide ceramics will be studied and their physical and mechanical characteristics will be measured. Further studies will be carried out to elucidate the relationship between the microstructural properties and the characteristics of the finished material.

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