

REVIEW PAPER

A REVIEW OF COLLECTOR AND ENERGY STORAGE TECHNOLOGY FOR INTERMEDIATE TEMPERATURE APPLICATIONS†

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Abstract—The technology and thermal performance of intermediate temperature solar collectors is summarized and the status of thermal and thermo-chemical storage methods is reviewed. It is concluded that collector technology is commercially available to achieve delivery temperatures up to 350°F at averaged yearly efficiencies better than 30 per cent in good solar climates and that linear parabolic, single-axis tracking troughs are the best types of collectors currently available for intermediate temperature applications. On the other hand, energy storage options commercially available today are generally limited to sensible heat systems, which are bulky and expensive for long-term storage. More research is necessary to develop new storage concepts, such as intermediate temperature chemical heat pumps based on reversible reactions, suitable for intermediate temperature solar systems with significant storage capability.

1. INTRODUCTION

Solar thermal technology for low-temperature space heating and domestic hot water service is summarized in Ref. [1], and high-temperature solar applications, principally for electric power production, are reviewed in Refs. [2, 3]. On the other hand, solar thermal technology for intermediate temperatures has received little attention to date. This article will present an overview of the solar collector and thermal energy storage technologies suitable for the intermediate-temperature range between approximately 100 and 500°C.

At the present, industry consumes approximately 40 per cent of the United States energy needs as process heat [4]. Almost half of this energy is used at intermediate temperatures between 100 and 350°C. This temperature range is within the reach of commercially available collectors at good efficiency and appears to have excellent near-term potential for market penetration, particularly toward the lower temperature end [5]. Since many industrial processes operate throughout the year, the solar equipment can be used year round and all of the collectable solar energy can be applied to the process. Therefore, the delivered cost of solar energy in the industrial heat sector is potentially less than in space heating in which solar equipment is idle over a large part of the year. In high-temperature applications, solar collector efficiencies are often reduced by large thermal losses, although large-scale electric power production by

power-tower central systems has economic potential provided the cost of heliostats can be reduced appreciably. For the near-term, however, one of the most promising applications of solar energy is in the industrial sector [6]. Therefore, it is important to review and understand the operating characteristics and state-of-development of the thermal collection and storage technologies for such applications.

In this review the solar energy storage and collector technologies will be treated separately. It should be noted at the outset, however, that due to the complex interaction between the collector field and storage device in a system, a total systems study is required to identify the merits of particular components for a given application. Cost and performance data on specific collectors or storage units is only a first step in identifying useful concepts [7]. For example, an inexpensive storage device with low efficiencies requires more nominal storage capacity and collector area than a more costly, but more efficient, storage unit. Since solar collectors usually dominate the total system cost, the extra collector area alone could more than offset the price savings offered by cheaper storage. Even if storage in a system were essentially free, but the storage device inefficient, the total delivered energy cost from the solar energy system could be greater than with a more costly, but also more efficient, storage device. Furthermore, inexpensive collectors or storage units might only be able to deliver energy at lower temperatures where the conversion of solar energy to useful heat or work is less useful in a particular application. Only a study of the integrated solar collector/storage system can clearly establish the

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cost of useful energy and whether system trade-offs are cost-effective.

A trade-off also exists between the collector field size and the storage capacity required to provide a given fraction of the total energy requirements of the load. For example, if storage is inexpensive but collectors are costly, a solar plant designed to provide 100 per cent solar energy should be built near the minimum collector field size that will meet the load and with long duration energy storage. However, if collectors are inexpensive relative to storage the optimum storage capacity would be close to the minimum requirement to last through the longest period without sunshine, while the collector field size would be that required to charge storage quickly and still service the load. In reality, systems will be designed between these extremes with the actual sizes dictated by component costs, equipment performance, load requirements, insolation availability, etc. Back-up energy costs must also be considered in a system analysis, since a reserve source of fossil energy can generally provide energy less expensively for long periods without insolation than a "stand alone" solar facility with the large collector field and storage capacity needed [8] for solar autonomy.

2. SOLAR COLLECTORS

Concentrating solar collectors offer an attractive means of providing thermal energy at intermediate temperatures. At least thirty manufacturers in the United States have developed and marketed, on their own initiative, concentrators that provide some experience at operating temperatures in the range 100 to 350°C. The number of applications at temperatures up to 350°C will grow as more experience is gained in the field. But the total installations by even the most successful manufacturers only now amount to approximately 10,000 m² at all temperatures. Consequently, the net impact in terms of displacing conventional non-renewable energy sources is quite small. However, the U.S. government is attempting to increase the number of concentrators used by funding industrial and agricultural applications as well as providing research funds for performance characterization and improvement efforts. This section outlines the physical aspects of solar concentrating collectors. Attention is directed at the solar resource that can be tapped by concentrators and the collector efficiencies attainable for various thermal conversion processes. Thermal modeling is described, economic considerations highlighted, and topics deserving research attention are identified.

For most all intermediate temperature applications, some means of concentrating solar radiation is necessary. Concentrating solar collectors redirect insolation passing through an aperture onto an absorber of smaller area. The flux redirection may be accomplished by single or multiple reflective (mirror-like) or refractive (lens) elements. The principal

reasons for using concentrating collectors in intermediate-temperature solar thermal conversion systems are:

The smaller absorber size reduces thermal losses in comparison with a flat-plate collector of equivalent aperture. This improves the efficiency of solar energy utilization at a given collection and heat delivery temperature.

Weight can be reduced by replacing a large expensive absorber with a light reflective or refractive element and a smaller absorber.

The energy delivery temperature can be raised and closely matched to a system's thermodynamic needs for process heat or for the production of work.

The use of concentrating collectors appears attractive in the industrial sector because such collectors can heat a working fluid to temperatures as high as 300°C at relatively high thermal efficiency, as discussed in section 2.6 and demonstrated in Fig. 9. Consequently, a concentrator can often deliver more energy per unit cost than the flat plate. Figure 1 shows a breakdown of process heat needs as a function of temperature. Since approximately 15% of the national gross energy input is consumed by industrial processes at end-use temperatures below 250°C [4], it is apparent that intermediate-temperature concentrating solar collectors can be used to supply a substantial part of the U.S. industrial energy needs.

Concentrating collectors can also be used for decentralized, small-scale electric power generation [9] because efficient power generation with a Rankine, Stirling, or Brayton cycle requires that a work-

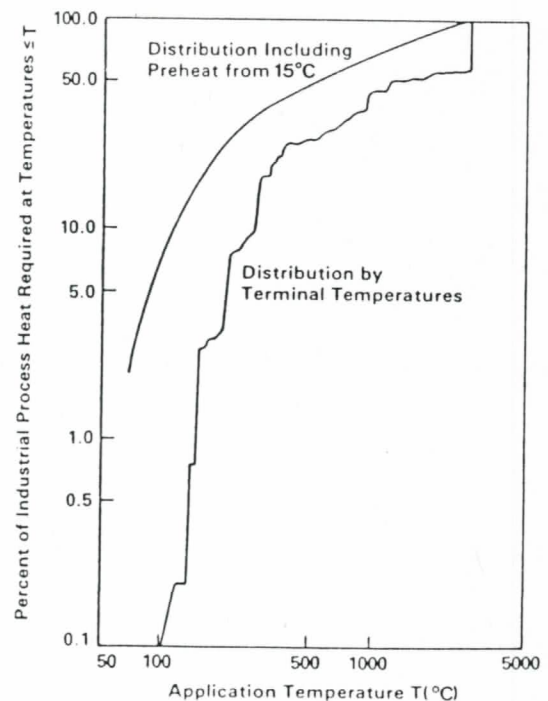


Fig. 1. Distribution of industrial process energy requirements vs application temperature.

ing fluid be available at higher temperature than a flat-plate collector can deliver. Also, the economic potential of direct conversion of solar radiation into electricity by means of photovoltaic devices can benefit from concentration. The high cost of solar cells has suggested the use of concentrators to reduce the cost of the receiving surface and increase the flux incident on the cells [10]. To prevent excessive cell temperatures, the receiving surface must be cooled. The heat removed can be used for thermal applications, an arrangement often referred to as a total energy system.

2.1. Concentrating collector technology

The concentrator *aperture* is that plane area through which the total incident solar energy (called solar *irradiance*) passes. It is established by the physical extremities of the mirror or lens. In *thermal conversion* systems a *working fluid*, which may be a liquid, vapor, or gas, is used to remove energy from the *absorber*, which is, in effect, a heat exchanger. The absorber is designed to receive the concentrated solar flux. In a flat-plate collector the aperture area and absorber area are equal. The sense in which the term *concentration* is used must be clearly understood. *Flux concentration* is the ratio of the flux incident on the absorber to the solar irradiance incident on the aperture. The *geometric concentration ratio* (CR) is the ratio of the aperture area to the surface area of the absorber.

Most concentrating collectors have a moving element (the aperture and/or the absorber) that follows the sun's apparent motion across the sky. Collectors with large acceptance angles need only seasonal position adjustments, whereas collectors with small acceptance angles must track the sun continuously. The *acceptance angle* is the limit to which the incident solar irradiance path may deviate from a normal drawn to the aperture and still reach the absorber. The appropriate parts of the collector may be moved manually or by use of a clock-driven or computer-driven open loop control, or a sun-seeking servomechanisms in closed loop control.

The thermal performance of concentrating collectors, as with flat-plate models, is characterized by their thermal efficiency. The thermal *efficiency* (η) is defined as the ratio of useful energy delivered by the collector to the total solar energy passing through the collector aperture. The enthalpy rise in the working fluid is one measure of useful energy. Solar irradiance consists of direct *beam* irradiance (H_b) and *diffuse* irradiance (H_d). The latter is created by scattering processes in the atmosphere. The direct beam irradiance is contained within the solid angle subtended by the solar disk. The majority of concentrating collectors use only beam irradiance and very little diffuse component [11]. But even on a clear day, the diffuse irradiance can represent 20 per cent of the total irradiance [12]. The sun's black body temperature of 5762 K results in a solar spectrum concentrated primarily in the 0.3–3.0 μm wavelength band. The black

body temperature sets an upper limit to the peak temperature achievable in a concentrator collector [13].

2.2. Generic types of concentrating collectors

Two broad categories subdivide concentrating solar collectors: reflective and refractive units. A variety of geometric shapes have been proposed and prototypes or production units built in each category. Many of these units use optical concepts retained from the astronomical sciences. The two categories provide little guidance, however, in identifying candidate devices to meet a specified system requirement. For this purpose the collector geometric concentrating ratio (CR) is a more pertinent parameter. With increasing concentration ratio it is ordinarily possible to extract useful energy from the collector at a progressively higher temperature without sacrificing efficiency. Geometric concentration ratios may range from 1 to 10 for a compound parabolic concentrator (CPC) or flat mirror device (V-Trough) and up to several thousand for a reflecting paraboloid. The benefit of an increase in temperature of the delivered energy is accompanied by an increase in the sun position tracking accuracy requirement. The additional complexity of one- and two-axis (equatorial or altazimuthal) aiming is reflected in increasing collector cost. The temperature level at which energy is needed then becomes a prime variable impacting system cost. Concentrators with flux concentration ratios in the range of 25–75 are commercially available at \$150–\$250 per square meter of aperture with installed collector field costs varying from \$300 to \$400/m². In selecting a generic type of concentrator when a specific need has been identified, it is also well to consider difficulties and losses incurred in manifolded multiple collector units. The number of flexible or swivel connections and length of interconnecting piping can represent a significant portion of the system cost, increase energy transport losses, and thus reduce thermal system performance [14].

Figure 2 shows schematically the three types of concentrating collectors that are commercially available or are under active development:

- stationary and seasonally adjusted;
- line concentrators; and
- point concentrators.

Within the latter two categories are devices such as parabolic troughs that focus in an optical sense, as well as units that provide no optical image like the hemispherical dish and inflated reflector. Approximate figures for the flux concentration ratio are also given in Fig. 2. The solar disk size of 0.52° set an upper limit on the concentration ratio of the order 200 for two-dimensional collector and 40,000 for a three-dimensional collector with continuous tracking [13].

A large number of materials and construction processes have been used in concentrating collectors. Re-

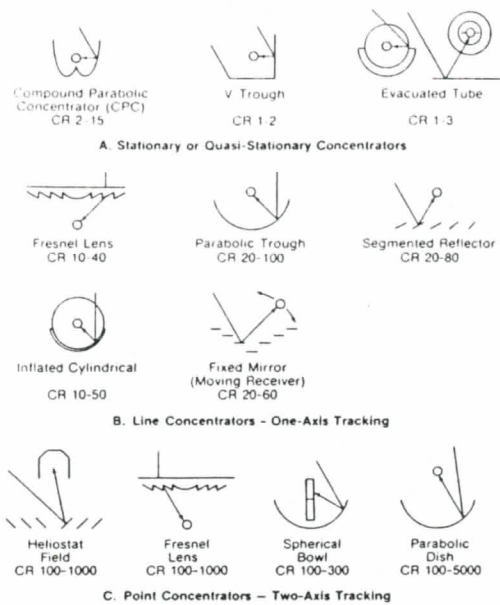


Fig. 2. Generic types of concentrating collectors.

fective surfaces have been made of chrome plate, electropolished aluminum, silvered glass, and metalized film. Plywood, honeycomb sandwich, concrete, metal

plate, and polyurethane foam have been used for supporting substrates. Refractive units are often cast or extruded acrylic. Absorbers are metallic, ceramic, or glass and may be partially or totally enclosed in a glass envelope. Selective coatings (high solar absorptance, low infrared emittance) on the absorber are used when the absorber surface temperature can be maintained at all times below the degradation temperature of the coating. Table 1 lists selective coatings being developed or used in concentrator systems. At this time, black chrome is the most common absorber selective coating. Each choice of materials carries with it a corresponding cost, durability, maintenance requirement, and performance factor. Laboratory instruments are available for measuring such crucial parameters as the surface reflectance, absorptance, and emittance as a function of wavelength and/or temperature.

Conductive and convective thermal losses from the absorbers are reduced by single or multiple glass jackets (possibly evacuated) and insulating blankets (fiberglass, foamglass, and calcium silicates are sometimes used) on unilluminated portions of the absorber. Low conductivity supports that can maintain proper positioning of the absorber despite thermal stresses and gravity effects are necessary to avoid

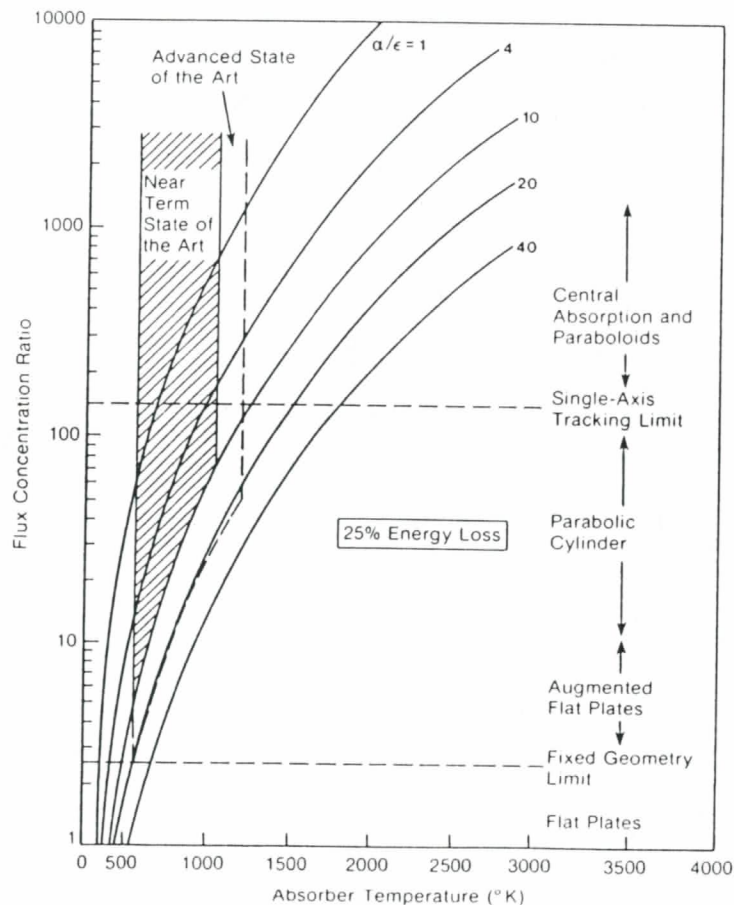


Fig. 3. Effect of concentration ratio and absorptivity/emissivity ratio on absorber temperature for various collectors (Ref. [15]).

Table I. Properties of selected commercial absorber surfaces

Material	Manufacturing Technique	Supplier or Developer	Absorbance α_a	Emissance $\epsilon_c(T, ^\circ\text{C})$	Temperature Stability Limit ($^\circ\text{C}$)
Black Chrome	electro-deposited	Many	0.94-0.96	0.05-0.10(100) 0.20-0.25(300)	300
Pyromark	paint	Tempil	0.95	0.85(500)	<750
S-31	paint	Rockwell Int'l.	0.8-0.85	0.8-0.85	>550
Nonselective					
SOLARTEX	electro-deposited	Dornier (W. Germany)	0.93-0.96	0.14-0.18(310)	700
SOLAROX	electro-deposited	Dornier (W. Germany)	0.92	0.20	200
(Proprietary)					
Black Epoxy	paint	Amicon Corp.	NA	NA	NA
436-3-8	paint	Bostik (U.S.M. Corp)	0.90	0.92	NA
Enersorb	paint	Desoto	0.96	0.92	NA
7729	paint	C. H. Hare	0.96	0.90-0.92	NA
R-412	paint	Rusto-leum Co.	0.95	0.87	NA
5779	paint	Rusto-leum Co.	0.95	0.90	NA
Nextel	paint	3-M	0.97-0.98	>0.90	150
(Nonselective)					
NOVAMET 150	paint	Ergenics	0.96	0.84	800
(Proprietary)					(1 hr)
MAXORB	(proprietary)	Ergenics	0.97(± 0.01)	0.10(± 0.03)	150(20 wks)
Tabor Black	electro-deposited	Miromit	0.91	0.14	<400(1 hr)
(NIS/ZnS)					

stray heat losses and deterioration of thermal performance in the field.

Collector thermal losses can be reduced by selective coatings on the absorber. Consequently, there is an important economic tradeoff between increasing the flux concentration ratio and using more sophisticated, but also more expensive selective coatings when higher energy delivery temperatures are required. Figure 3 indicates the relative merits of concentration ratio enhancement *vis-à-vis* improving the selective coating performance for a constant 25 per cent energy loss [15]. Increasing the absorptivity/emissivity ratio from 4 to 10 is comparable to changing the concentration ratio from 100 to 250 at $\alpha/\epsilon = 4$ in terms of achieving the same absorber temperature.

At the present time, only parabolic trough, evacuated tube, and line focus Fresnel lens concentrators have achieved a large degree of market penetration. Uses for these three units include air conditioning of buildings, industrial process heat, and irrigation pumping systems [16, 17]. Recently, also, commercial versions of the CPC, segmented parabola, and parabolic dish collectors have become available in the United States.

2.3 Working fluids

Selection of a working fluid for use in a concentrator collector-energy delivery system requires consideration of several parameters. The issues impacting the fluid choice are:

- fluid cost, anticipated lifetime, and disposal cost;
- sampling requirements to verify fluid quality (i.e., the absence of decomposition products);
- toxicity;
- flammability (flash point, fire point, auto-ignition temperature);

compatibility with other system materials (such as piping, packing and seals, valve seats, flex-hoses, and storage materials) as well as materials onto which it may leak (insulation, roofing);

- physical properties;
 - freeze point,
 - viscosity at low (startup) and high (operating) temperature,
 - vapor pressure,
 - specific heat,
 - thermal conductivity,
 - thermal expansion,
 - density;
- availability of solvents or other cleanup materials;
- chemical stability at operating temperatures; and
- potential vapor emissions.

Local codes and standards usually provide restrictions with respect to toxicity, flammability, emissions, and/or disposal of waste fluid. Table 2 lists many commercially available liquids that have been considered for intermediate temperature concentrating collector applications with the supplier's recommended temperature range for the fluid.

2.4 Solar resource assessment for intermediate delivery temperature

Solar energy exhibits diurnal and seasonal variations, as well as minute-by-minute changes due to clouds and variations in atmospheric conditions. Concentrating collectors are more susceptible to these transients than flat-plate collectors because of their dependence on beam irradiance. CPC, V-Trough, and evacuated tubular collectors use a portion of the diffuse component and, therefore, do not experience the same transient characteristics [18-20]. When several

Table 2. Heat transfer fluids for concentrating collectors

Manufacturer	Fluid Name	Operating Range (°C)	Flash Point (°C)
Anderson Development Co.	Q-Therm "B"	-34 to 443	260
Bray Oil Co.	Brayco 888	62 to 288	163
Davis-Howland Oil Co.	Light oil	-18 to 218	191
	Heavy oil	4 to 315	315
Dow Chemical Co.	Dowtherm A	16 to 399	124
	E	-18 to 260	69
	G	4 to 343	152
	H	-10 to 288	193
	J	-73 to 288	193
	LF	-32 to 315	127
Dow Corning	Q2-1132	-45 to 204	204
	Syltherm 800	-40 to 427	154
Exxon	Caloria HT43	-10 to 315	304
	Humbletherm 50		
Mark Enterprises	H-30C	-34 to 327	182
Mobil Oil Co.	Mobiltherm Light	26 to 204	121
	600	-15 to 315	177
	603	-7 to 315	143
	605	-7 to 315	204
Monsanto	Therminol 44	-45 to 218	207
	55	-18 to 315	179
	60	-51 to 315	160
	66	-9 to 343	178
	88	149 to 399	191
Ore - Lube Corp.	Ore-Therm 600	-10 to 315	218
Resource Technology Corp.	Sun-Temp	-40 to 355	193
Sunoco	Oil 21	-18 to 315	226
	25	-15 to 315	229
Union Carbide Corp.	UCON HTF-500	to 260	280
	SD-HB-280X	to 260	280

generic types of collectors are being considered for an application, the maximum and average performance of each must be known. Table 3 lists the expressions for the beam radiation incidence angle for stationary

as well as tracking collectors [21]. Integration of these expressions over a full, clear day generates a theoretical maximum collector performance ($\eta = 1.0$) for each tracking mode [22]. These integrated values are also

Table 3. Incidence angle and annual energy yield

Tracking Mode	Incidence Angle†	Long-Term Average Annual Total Radiation (All values normalized to unity for total radiation on horizontal surface at each location ^a)		
		Phoenix, AZ	Omaha, NB	Blue Hill, MA
Stationary (Horizontal)	$\sin \theta = \sin \phi \sin \delta + \cos \phi \cos \delta \cos \omega$	1.00	1.00	1.00
Fully Tracking	$\theta = 0$	1.42	1.44	1.36
N-S Horizontal Axis, E-W Tracking	$\cos \theta = \frac{\tan \delta - \tan \phi \cos \omega}{\tan \delta \tan \phi + \cos \omega}$	1.29	1.30	1.23
N-S Polar Axis, E-W Tracking	$\cos \theta = \cos \delta$	1.38	1.40	1.32
E-W Horizontal Axis, N-S Tracking	$\sin \theta = \cos \delta \sin \omega$	1.16	1.18	1.16

^aTotal long-term average annual radiation incident on a horizontal surface
 Phoenix, AZ 2150 kW/m²-yr
 Omaha, NB 1510
 Blue Hills, MA 1280

† θ - Incident Angle
 ϕ - Latitude
 δ - Declination
 ω - Hour Angle

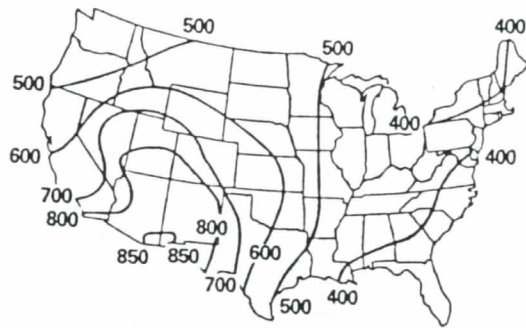


Fig. 4. Average annual direct normal solar total irradiation (1000 Btu/ft²); 1 Btu/ft² = 11.4 kJ/m².

shown in Table 3. The numbers, when modified by an appropriate η for each collector type, indicate the gain in incident energy from various tracking modes relative to a horizontal stationary collector.

From long-term insolation records that are available for several sites in the United States the mean daily insolation may be computed. A plot for an average year is shown in Fig. 4 in the form of isopleths that are based on long-term beam irradiance measurements. Such maps provide general guidelines in evaluating the nominal solar resource on a geographical basis. The National Oceanographic and Atmospheric Administration is continuously upgrading the insolation monitoring systems and increasing the number of station locations. The data generated to date have been used to create a standard insolation database (SOLMET) that is being promulgated by the

U.S. Department of Energy for use in its solar research programs. SOLMET gives hourly data for total insolation on a horizontal surface [23]. Analytic models must be used to transpose this nominal data record onto surfaces of other orientation and for different atmospheric conditions [24, 25].

2.5 Long term average collector performance

Instantaneous efficiency tests (see Section 2.6) will provide data on collector performance under standard conditions. This data can be combined with site specific long-term irradiation conditions to predict average collector field performance on a yearly basis. A summary of average parabolic trough collector performance for the entire United States is presented in Ref. [26]. Figure 5, taken from this reference, is a plot of the annual energy output for a tracking parabolic trough with a north-south horizontal axis operating at 70°C. Such plots are useful in providing a qualitative comparison of collector energy at different locations on a nationwide basis.

The utilizability method [27] is a technique for making such detailed long term average performance calculations for systems that operate at constant or nearly constant temperature. The result is a plot of collector yearly average energy delivery (\bar{Q}_{year}) vs operating temperature. The utilizability method provides a realistic, long-term assessment of collector field performance than predictions based on calculations with detailed weather data for a specific year are more tedious. Examples of the latter, detailed calculation process using small (typically 1 hr or less) compu-

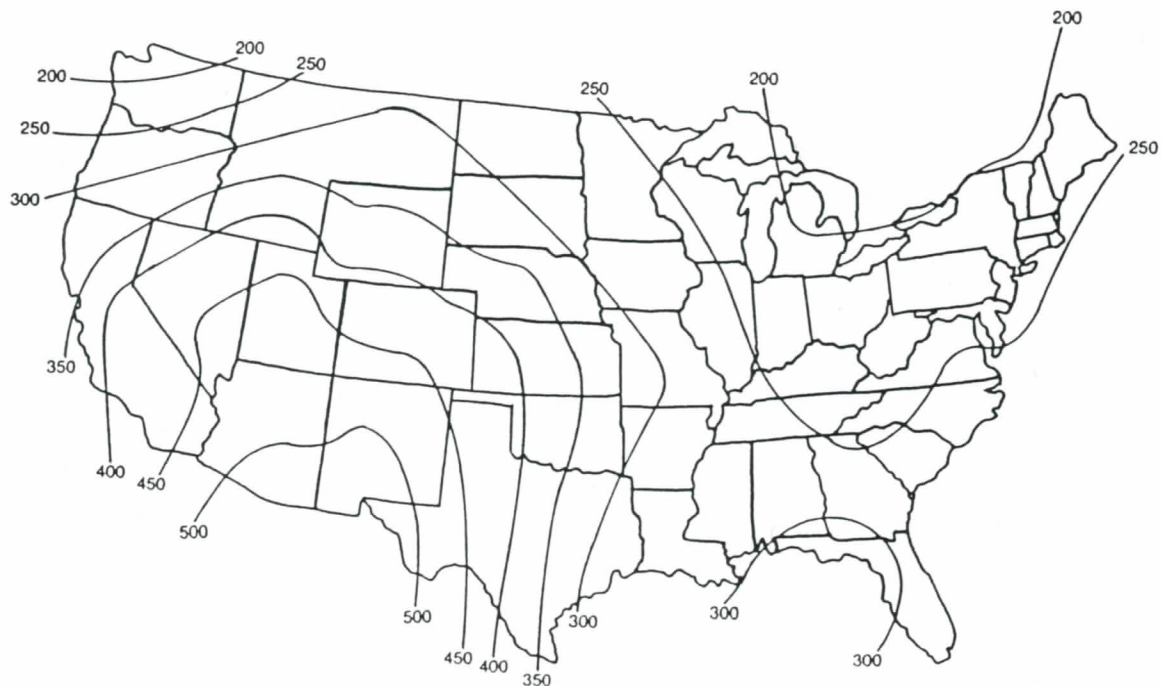


Fig. 5. Annual energy output for a parabolic trough with a north-south horizontal axis operating at 70°C (1000 Btu/ft²); 1 Btu/ft² = 11.4 kJ/m².

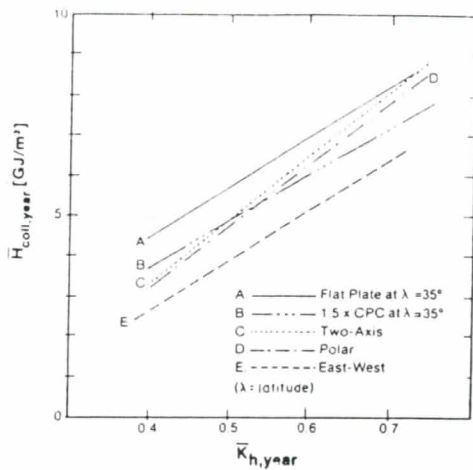


Fig. 6. Yearly radiation availability vs clearness index for the principal collector types.

tation steps, are the SOLTES [28] and TRNSYS [29] codes. Calculations of the SOLTES and TRNSYS type provide the collector system energy delivery characteristics on an hourly and daily basis—information unavailable from the utilizability method.

Collares-Pereira and Rabl [27] provide a description of utilizability method calculations. Their results are directly applicable to concentrating collectors. Calculating the long-term average total solar irradiation available at the collector aperture (\bar{H}_{coll}) is a first step in computing \bar{Q}_{year} , or

$$\bar{H}_{coll} = (R_h - R_d \bar{d}) \bar{K}_h H_0$$

Here R_h and R_d are functions of the collector type, tracking features, latitude, time of year, and daily operational period. Reference [1] provides specific values for R_h and R_d . The ratio of terrestrial over extraterrestrial irradiation, (H_0) is \bar{K}_h (clearness index, called K_t in Ref [30]); it is available from long-term weather records at many sites [30]. The ratio of diffuse to hemispherical irradiation, \bar{d} , can be correlated with the clearness index [31] by the equation

$$\bar{d} = 0.775 + 0.347(w - \pi/2) - \{0.505 + 0.261(w - \pi/2)\} \cos(2\bar{K}_h - 1.8)$$

where w is the sunset hour angle in radians.

The value of \bar{Q}_{year} is the product of \bar{H}_{coll} , the long-term average optical efficiency ($\bar{\eta}_0$), the collector heat extraction efficiency factor (F), and the utilizability ϕ :

$$\frac{\bar{Q}_{year}}{A} = F \bar{\eta}_0 \bar{H}_{coll} \phi \left[\frac{GJ/year}{m^2} \right]$$

Expressions for ϕ are given in Ref. [1].

The average optical efficiency is dependent upon the collector type and tracking features. Reference [32] describes the generation of $\bar{\eta}_0$ from standard collector tests conducted at *non-normal* incidence. The factor F appears in the Hottel-Willier-Bliss collector model,

and its specific form depends on the collector temperature used as a reference (i.e. absorber surface temperature or one of several fluid temperatures). Figures 6 and 7 show results obtained by the utilizability method. The figures compare the long-term average energy delivery of several concentrators at specific locations and in specific tracking orientations. The utilizability method also reveals the month-by-month performance figures. The monthly figures identify unique characteristics such as the superior winter-time performance of an east-west oriented axis trough as compared to a horizontal trough with north-south tracking axis. This utilizability approach is useful in selecting, sizing and optimizing solar equipment for specific applications. When installed system costs for different types of collectors are available, increased performance can be weighed against higher equipment costs resulting from more sophisticated collectors to select an economically optimum system for a given application.

2.6 Performance evaluation

The first step in an analytical performance prediction for a concentrating collector is usually an optical assessment in the solar wavelengths using ray-tracing techniques. If it is assumed that the optical characteristics are independent of temperatures, this portion of the analysis can be decoupled from the thermal assessment. The ray-trace analysis uses as inputs the collector geometry, solar disk size, irradiance, and material properties (transmittance, reflectance, and absorptance along with their angular dependence). The output is the rate of radiant heat transfer to the absorber that, in turn, becomes an input to the ther-

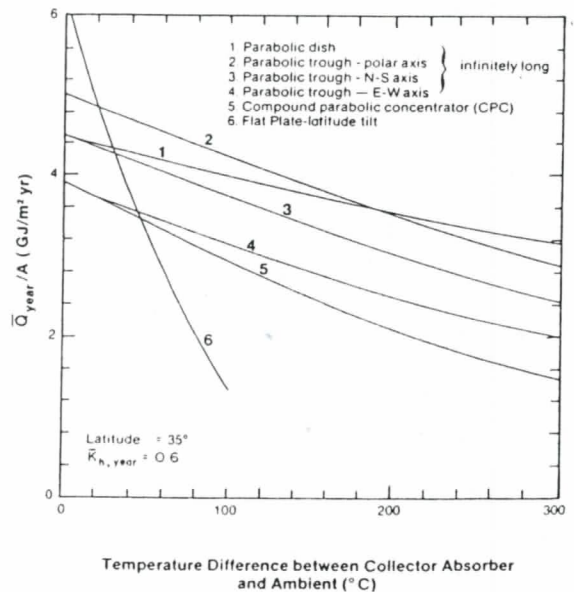


Fig. 7. Yearly energy delivery vs ΔT above average ambient for typical collectors for $\bar{K}_{h,year} = 0.6$ Latitude = 35° (based on test results of Ref. 33).

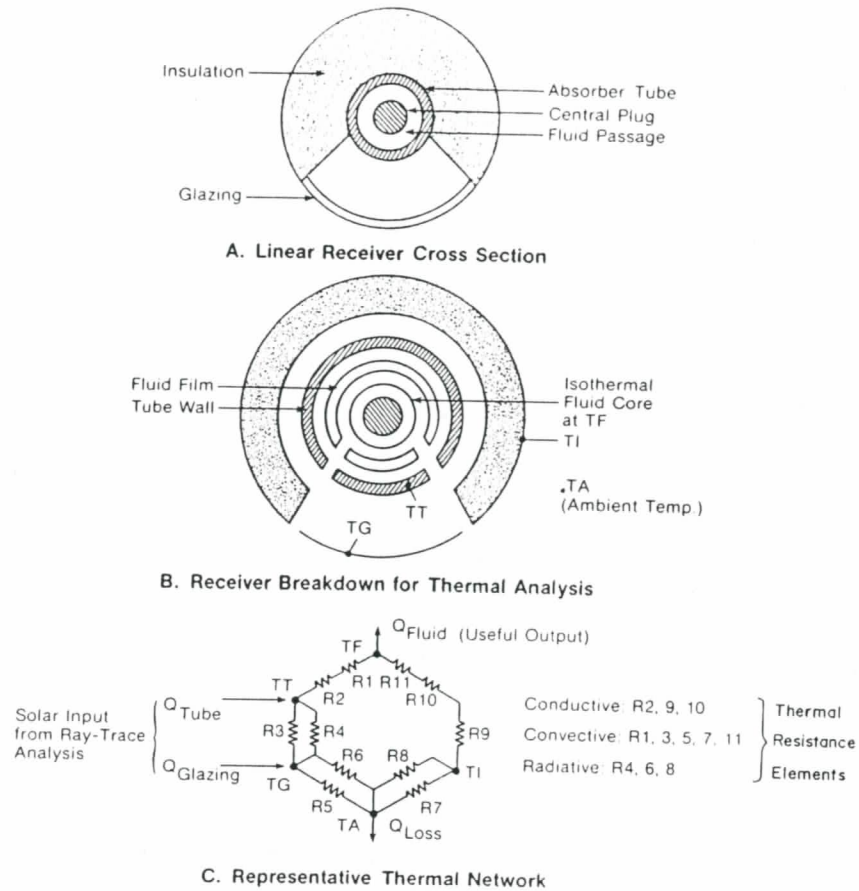


Fig. 8. Example of receiver thermal modeling.

mal analysis. The second step is a thermal analysis that determines the portion of this radiation heat input that is transferred to the working fluid by calculating the heat loss by conduction, reradiation, and convection to the environment. In one approach to the analysis of linear concentrators the device is sliced into transverse segments that are assumed isothermal in the longitudinal direction. Figure 8 illustrates a model of an absorber intended for a parabolic trough

reflector. Also shown is the thermal resistance network for the thermal analysis. By using an iterative process, one solves for the nodal temperatures and working fluid energy gain, even though the reradiative resistances are nonlinear due to their T^4 dependence. The wide variations in collector geometrical shape, optical characteristics, and insulation placement indicate that no single analytical model will be sufficient to encompass all the concentrating collectors of interest.

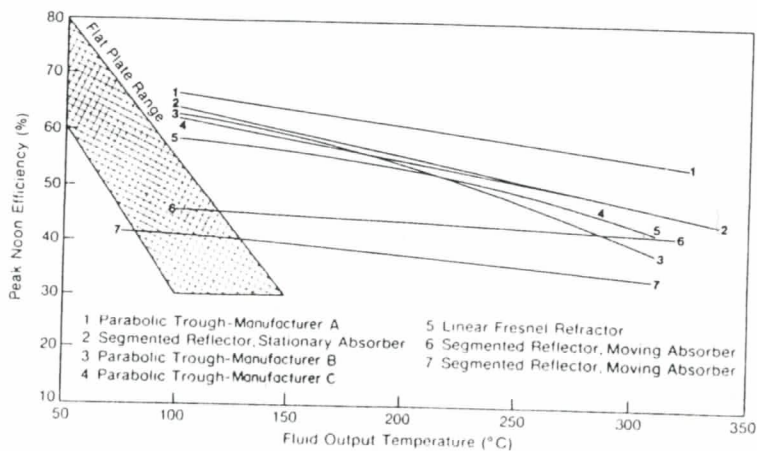


Fig. 9. Linear concentrating collector efficiency (experimental data).

Analytically predicted performance is subject to uncertainties because of the assumptions used. For reliable performance data, concentrating collectors should be tested in an outdoor test loop. Instantaneous thermal performance data can be obtained by monitoring the enthalpy rise in a working fluid. Variables that should remain constant during such a test are the solar flux, incident angle, fluid flowrate, fluid inlet temperature, and ambient conditions. Figure 9 shows the experimentally measured performance characteristics of several generic types of concentrating collectors [33], as well as of high quality flat-plate collectors. Efficiency calculations for the concentrators are based on the beam irradiance, whereas the total irradiance is used to evaluate the efficiency of the flat-plate devices. Possible confusion can be avoided if the reference irradiance is clearly stated when efficiency values are published.

The dependence upon experimental tests to assess concentrating collector thermal performance underscores the need for standard test procedures to generate performance factors of general usefulness. The ASHRAE standard 93-77 [34] satisfies this need for flat-plate collectors, but no similar procedure is available for concentrating collectors.

Issues that should be addressed in a thermal performance testing standard for concentrating collectors include:

Efficiency at normal incidence;

Bidirectional incidence angle modifiers for stationary or seasonally adjusted concentrators such as the V-Trough and CPC;

Collector time constant;

Fluid properties (density, specific heat and viscosity) must be accurately known at high temperatures if a computation of $m\dot{C}_p\Delta T$ is to be relied upon as a measure of the useful energy gain in the collector. Allowance may be made for other measurement techniques that do not rely on accurate flow detection and fluid property assumptions at high temperatures (such as the calorimetric ratio technique) [35];

Optical end loss effects should be factored out in linear concentrators (e.g., parabolic trough) that are tested as a single module but erected in long, closely spaced arrays;

The influence of circumsolar irradiance. A conventional field of view pyrheliometer may not accurately measure the portion of the incident radiation used by a high concentration ratio collector, if the latter has a more restricted field of view than the pyreheliometer itself;

Stagnation conditions, regularly imposed on flat-plate collectors, may destroy the effectiveness of some concentrator absorbers;

The time constant of a concentrator that is too small will be difficult to measure and of no practical interest;

Common terms such as concentration ratio and aperture must be clearly defined; and

Performance may be sensitive to collector orientation since this can influence convection loss patterns in some cavity-type receivers.

2.7 Research topics

Concentrating solar collectors are amenable to quantitative improvement. Research topics about heat transfer in concentrator devices and systems over the specific behavior of major elements such as the absorber as well as the interaction between elements.

The collector absorber merits principal attention because it is the essential heat exchange element in the collector. Direct impingement of solar radiation on a "black" fluid, either as a falling film or contained within transparent piping, is being pursued [36]. Here no penalty is incurred due to a temperature drop across the pipe wall and the fluid film. Cavity-type receivers incorporating heat pipes or porous ceramic materials are being investigated for point focus concentrators [37]. A phase change process that permits the direct generation of steam in the collector is also of interest [38].

The beneficial impact of specific improvements in line focus parabolic trough technology is indicated in Fig. 10 [39]. A state-of-the-art parabolic trough served as a reference collector in order to establish the relative performance levels shown. Analytical techniques that incorporate a thermal resistance model were used to compute the expected performance gain resulting from specific technology advancements such as a reduction in receiver emittance. Other improvements from additional R & D effort are a better reflector shape (reduced slope error), evacuated jacket (reduced slope error), evacuated jacket

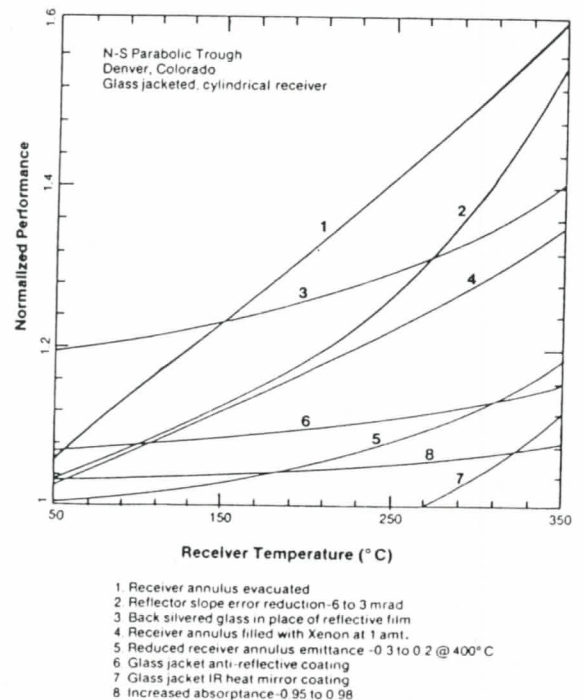


Fig. 10. Parabolic trough performance benefits of several improvements.

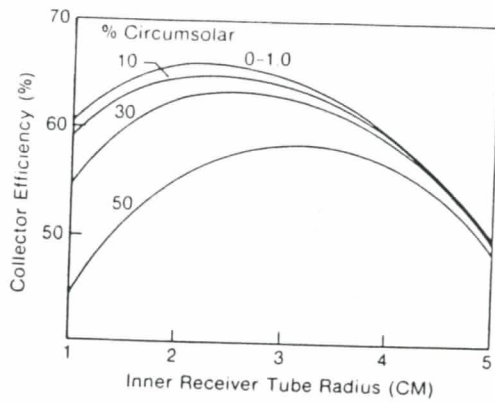


Fig. 11. Computed influence of circumsolar conditions on the linear receiver of Fig. 8.

receiver, and heat mirror treatments on receiver glazing. Comparative analysis such as that shown in Fig. 10 helps to indicate where funding can be most wisely expended for collector thermal performance improvement.

The degradation of the crucial optical components over a 10–20 year lifetime is unknown. Research and development are needed to increase the operating temperature range and durability of absorber selective coatings. Simple cleaning procedures that do not adversely affect reflectivity when repeated over a long time should be developed.

Circumsolar radiation may significantly affect concentrating collector thermal performance. Circumsolar radiation results from forward scattering of the solar flux by atmospheric molecules and aerosols and causes wings to appear on the intensity profile of the sun. The broadening of the apparent solar disk can result in optical spillover with a receiver designed for the ideal solar disk diameter of 0.52° . Figure 11 shows the computed influence of circumsolar radiation on the selection of a linear receiver for a parabolic trough collector. The calculations are the result of a ray-trace analysis combined with a receiver thermal model, both apply to the geometry shown in Fig. 6. The circumsolar percentage was varied while the beam irradiance was assumed fixed at 1000 W/m^2 . Average circumsolar ratios to be expected during operation will probably range to 10 per cent. Values larger than approximately 10 per cent are associated with rapidly decreasing beam irradiance; collector operation would be terminated in those instances. Figure 8 indicates that a linear receiver optimized at a radius of 2.1 cm for 0 per cent circumsolar would cause a minimal drop in performance at 10 per cent circumsolar compared to an optimum radius at 10 per cent circumsolar. Lawrence Berkeley Laboratories have measured and recorded circumsolar profiles at various geographic locations [40]. Detailed studies should be conducted to judge performance degradation in point focus collectors due to circumsolar radiation.

Successful incorporation of concentrating collectors into an energy delivery system will be dependent on proper flow and temperature control of the working fluid. Satisfaction of stringent energy delivery temperature prevention of fluid and equipment damaging temperature excursions, or minimization of parasitic pumping losses require that flow strategies be developed and implemented. These strategies will need to consider feed-forward control concepts, flow rate optimization, hourly variations in back-up fuel costs, system time constants, and related issues [41].

Significant improvements are needed in the thermal modeling of concentrating collector absorbers. Current analytic models are restricted to simple geometries. They incorporate simplifying assumptions, and consequently, the agreement between predicted and measured performance has been poor. Convection, in particular within the odd-shaped enclosed spaces about the hot absorber, is poorly quantified. Laser interferometry may be helpful in studying convection in such cases. Lasers are also useful in evaluating the shape accuracy of reflective surfaces [42]. Computerized ray-trace models are needed to map the IR loss patterns about the absorber. Ray-trace models would also be helpful in judging the performance of secondary concentrating elements that may be positioned at the absorber and the optical qualities of multifaceted reflector surfaces [43]. Convection suppression by baffling and evacuation needs further research.

Thermal system models have been developed for specific applications such as the large-scale power tower [44]. This approach is required to judge the collector interaction with thermal storage when both load and solar input vary in time. Models having more general application are required for other concentrating collector systems. Collector system studies are also needed to determine the minimum concentration ratio that is capable of delivering energy at a specified temperature with each generic type of concentrating collector. Reducing the concentration ratio may help to lower collector cost. Such a reduction is often traded off against a more expensive absorber selective coating that, when combined with the smaller concentration ratio, still permits the collector to meet the load requirements at the specified energy delivery temperature.

Related to research about concentrating collector thermal conversion systems are Rankine and Brayton cycles and Stirling engines matched to the thermodynamic output characteristics of the collectors. Several of these cycles are being proposed for incorporation advanced, high temperature systems [45]. Economic models that tradeoff thermal performance with life-cycle costs are crucial in any solar system and especially so in concentrator systems where the capital investment may be quite large [7]. Thermal performance gains must be balanced against added capital and maintenance costs.

3. SOLAR THERMAL ENERGY STORAGE

Because solar radiation is intermittent, fossil fuel back-up or energy storage must meet energy needs at night or during periods of cloud cover. Short-term storage provides a reservoir of energy that can adjust for small phase differences between local solar energy supply and the load demand. Longer term storage can aid in matching seasonal demands to the solar availability, thereby allowing an increased solar contribution to total energy needs. The optimum energy storage duration is usually that which provides the minimum final delivered energy cost when integrated with the collector field and back-up into a final application.

Intermediate-temperature thermal energy storage can be used for industrial processes, air conditioning, and agricultural applications. The factors that influence the cost of energy from storage will be reviewed first. Then, the energy storage capabilities and costs of storage media will be reviewed for representative materials. Selected heat exchangers and storage vessels that offer possible reductions in system costs for the various modes of operation will also be discussed. The latter two topics will be illustrated by examples developed for temperatures outside the intermediate range to give a rounded picture; but the concepts could be modified slightly to service the intermediate temperature applications. Research needs will be identified at the end.

3.1 Stored energy cost

The total cost of a thermal energy storage unit depends on the storage capacity costs (energy-related costs) and the energy removal or additional costs (power-related costs):

$$\begin{aligned} \text{Total cost} &= \text{energy related cost} \\ &+ \text{power related cost} \quad (3-1) \end{aligned}$$

The energy-related costs include the storage medium, container, insulation, and other items used for storage of heat, whereas, heat exchangers, pumps, plumbing, heat transfer fluids, and other components needed to transfer heat to and from storage are included in the power related cost. To minimize the cost of storage, the energy storage capacity and power capability should be kept as small as possible since they directly affect the costs in eqn (3-1). However, they must provide adequate energy transfer and the necessary storage duration time T [46]:

$$T = \frac{\text{Energy storage capacity}}{\text{Power capability from storage}} \quad (3-2)$$

For long term storage (large T), the energy storage capacity is larger than the power capability, and the energy-related costs will generally dominate the total cost in eqn (3-1). Therefore, very inexpensive storage materials, containers, etc. are essential while the cost of heat exchangers and other power related

components are somewhat less important. For short term storage (small T), the power capability must be larger than the storage capacity; power related unit costs must, therefore, be kept low while the unit energy costs may be higher than for seasonal storage. Of course, in the final application, the total storage unit cost must be that which will minimize the delivered cost of energy, regardless of the factors affecting it.

To conceptualize the effect of the utilization of storage capacity on the cost of energy from storage, the storage unit is divided into fictitious elements. Adding initial elements of storage capacity produces a large increase in the per cent of the load met by solar since they will be used each evening following a sunny day as well as for periods of cloud cover. The storage elements beyond one night's capacity will be used only for cloudy days following sunny days, and these elements will have a continually declining impact on the solar contribution. The degree of utilization has important consequences on the price of energy delivered from storage. For example, if the total storage system costs \$3/kW_r-hr and 20 per cent of this cost will cover yearly charges for operation and maintenance, taxes, and the return on investment, the yearly cost is about \$0.60/kW_r-hr. If initial elements of storage capacity are used 300 times per year to meet evening loads and cloudy periods, the cost of energy from these storage elements is:

$$\begin{aligned} &\frac{\$0.60/\text{kW}_r\text{-hr-yr}}{300 \text{ uses/yr}} \\ &= \$0.002/\text{kW}_r\text{-hr} (\$0.586/\text{MBtu}) \text{ delivered} \quad (3-3) \end{aligned}$$

This cost does not include the price of extra collectors, hardware, etc. required to charge the unit, but it is low enough that storage is probably not a major cost barrier for many applications. However, long term storage elements are used far less frequently. With the same yearly charges, but assuming a use of only four times per year use, the delivered energy cost from an element with such low use is approximately:

$$\begin{aligned} &\frac{\$0.60/\text{kW}_r\text{-hr-yr}}{4 \text{ uses/yr}} \\ &= \$0.15/\text{kW}_r\text{-hr} (\$43.95/\text{MBtu}) \text{ delivered} \quad (3-4) \end{aligned}$$

When costs of collectors, hardware, etc. are added, the final delivered energy cost is not promising. As more storage capacity is incorporated, the average utilization decreases and the delivered energy cost increases further. Therefore, unless the storage costs are very low, hybrid solar systems that use a backup source of energy tend to be more economical than seasonal storage.

The fraction of the energy charged to storage that can be delivered to the load at the required rate (round trip efficiency) also has important consequences on the delivered energy cost. First, more storage capacity must be provided than is theoretically required. For example, if 67 per cent of the energy

used to charge storage can be actually delivered to the load, than 50 per cent more storage capacity must be provided to allow for these losses. Thus, the energy related cost is about 50 per cent higher than if the devices were 100 per cent efficient.

The efficiency has perhaps more important consequences on collector cost. To provide the "lost" energy, the collector area must be increased beyond the theoretical minimum. In the example above, the energy output from the collector field to storage must be 50 per cent greater than that from the storage device. The cost of energy from storage will be considerably higher than the cost from the field since not only must the minimum collector field and storage capacity be paid for, but the cost of extra components must also be covered. Low efficiency storage systems will probably not provide competitively-priced energy unless both collector and storage costs are very low or excess energy available during periods of low demand can be provided during time of high demand, thereby reducing collector size.

The penalty associated with the delivered energy temperature must be considered in energy storage costs. If heat is required at a temperature T , the collector field must operate at a higher temperature $T + \Delta T$ to transfer heat to the process. However, if energy passes through storage, allowances must be made for temperature drops between the collector field and storage and between storage and the load. The collector field must operate at a higher temperature, perhaps at $T + 2\Delta T$. A further complication is that some thermal storage media go through a continuous temperature drop as they are discharged (sensible heat liquids) or must drop in temperature to release energy (reversible chemical reactions). The

lowest storage temperature during discharge must be above that required by the load; the collector field temperature must be above the highest storage temperature required during charging. In each case, an increase in collector temperature results in a decrease in collector efficiency, and the field size (and cost) will accordingly increase. Alternatively, if the collector temperature is fixed, heat can be converted to work with a lower efficiency in thermodynamic cycle processes. The effect of temperature on system cost and performance depends on the collector characteristics and the use of the heat.

3.2 Thermal storage methods and media

Thermal energy can be stored as a change in internal energy of a material as sensible heat, latent heat, heat of reaction, or combinations of these. In general, materials that have a large change in internal energy per unit volume minimize the space needed to store energy. However, vapor pressure, toxicity, corrosiveness, and other properties also must be considered since they influence the price of the containment. The cost per unit storage capacity must be low if the system economics are to be reasonable. This requires not only that the cost of the storage media be low, but also that containment and heat exchange costs be reasonable. In this section, material costs and some of the important properties that influence thermal storage costs will be reviewed for some presently considered thermal storage media.

3.2.1 Sensible heat

Raising the temperature of a solid or liquid stores thermal energy. Presently most thermal storage devices use sensible heat storage since current tech-

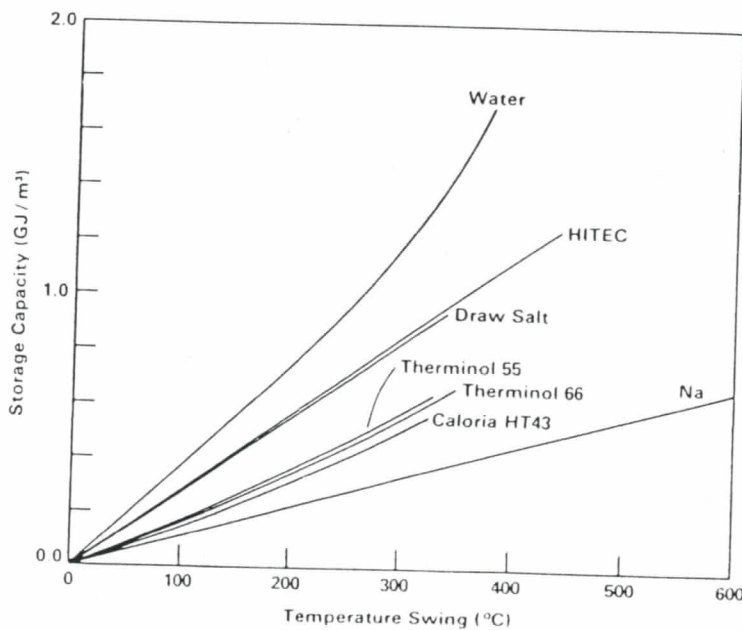


Fig. 12. Storage capacity per unit volume as a function of temperature swing for selected liquid sensible heat storage media [47].

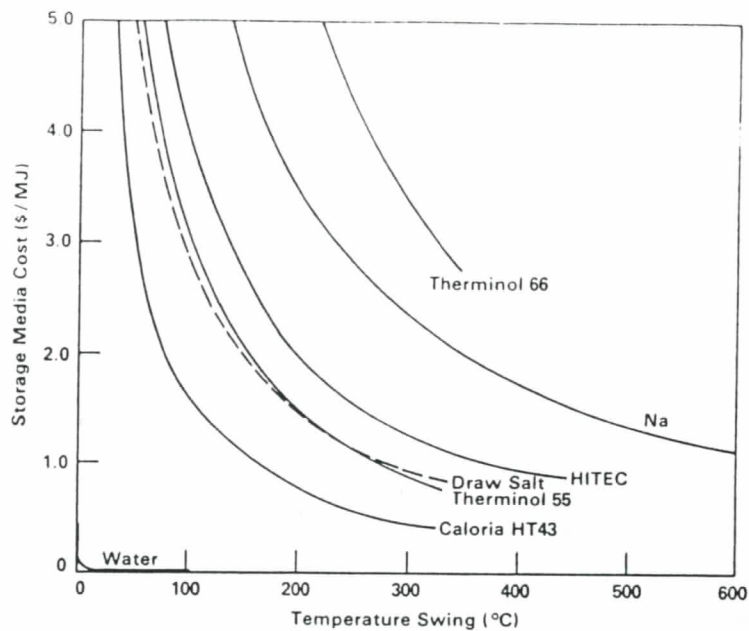


Fig. 13. Storage media costs in dollars per unit energy stored as a function of temperature swing for selected liquid sensible heat storage media [47].

nology is adequate for good system design. The energy storage capacities per unit volume of selected liquids for sensible heat storage are shown approximately in Fig. 12 as a function of the temperature swing of the storage media between the temperature limits of the liquids shown in Table 4. Figure 13 shows the storage media capacity costs in 1978 dollars per unit energy stored for large quantities of the same liquids. Commercial grade materials are assumed to be acceptable.

Water appears to be the best sensible heat storage liquid available because it is inexpensive and has a high specific heat. However, above 100°C, the storage

tank must be able to contain water at its vapor pressure, and the storage tank cost, which is not included in Fig. 13, rises sharply with temperature beyond this point. Organic oils, molten salts, and liquid metals circumvent the vapor pressure problems, but limitations in handling, containment, storage capacities, cost, and useful temperature range are evident for each as shown in Table 4 [48-50]. Although these fluids are used in commercial operations, the lifetime and cost requirements for solar storage limit their use.

The difficulties of the vapor pressure of water and the limitations of other liquids can be avoided by storing thermal energy as sensible heat in solids. But

Table 4. Liquid sensible heat storage media

Medium	Fluid Type	Cost (\$/kg)	Temperature Range (°C)	Heat Capacity ($\text{Jkg}^{-1}\text{K}^{-1}$)	Comments
Water	—	0	0 to 374	4190	Pressure vessel required above 100°C.
Caloria HT43	Oil	.30	-10 to 315	2300	Cracking occurs at high temperatures and may form volatile products lowering flash point. May polymerize at high temperatures to increase viscosity. Nonoxidizing environment required at high temperatures.
Therminol 55	Oil	.60	-18 to 315	2400	
Therminol 66	Oil	2.03	-9 to 343	2100	
Hitec	Molten Salt	.59	150 to 590	1550	Long-term stability unknown above 550°C. Stainless steel or other expensive containers probably required above 450°C. Inert atmosphere required at high temperatures. Heated lines required to prevent freezing.
Draw Salt	Molten Salt	.44	250 to 590	1550	
Sodium	Liquid Metal	.90	125 to 760	1300	Stainless steel or suitable alternate containers required. Requires sealed system. Reacts violently with water, oxygen, and other materials.

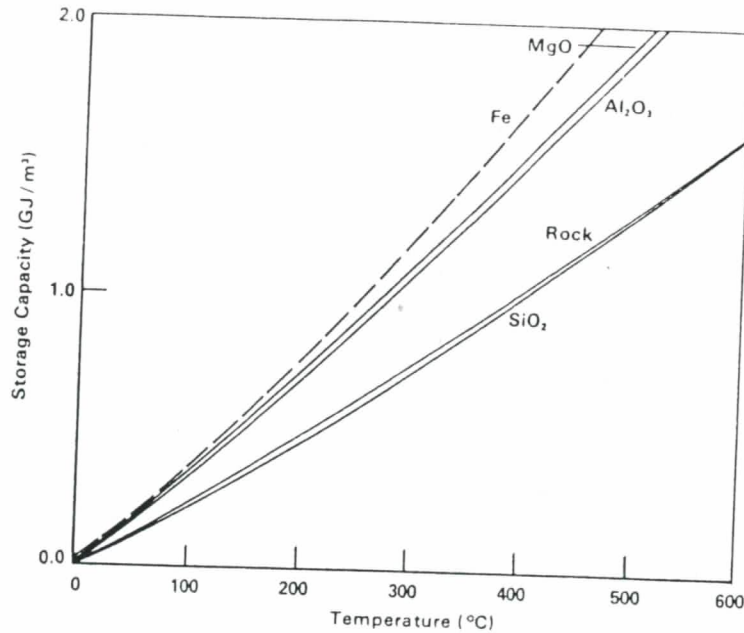


Fig. 14. Storage capacity per unit volume as a function of temperature for selected solid sensible heat storage media [47].

larger amounts of solids are needed than are water since the heat storage density of solids is usually less than water as shown approximately in Fig. 14 relative to a lower temperature limit of 0°C [47]. The cost of the storage media per unit energy stored, although not as low as for water, is still acceptable for rocks as shown in Fig. 15. Direct contact between the solid storage media and a heat transfer fluid is vital to minimize the cost of heat exchange in a solid storage

medium, and the storage volume must be increased beyond that of Fig. 14 by up to 50 per cent to provide for adequate fluid flow at a reasonable pressure loss. Fluids such as high pressure helium or heat transfer oils are generally required for high-temperature storage in solids to provide adequate heat transfer [50, 51]. The heat transfer fluid must also be compatible with the solids, and the problems of finding a fluid with low vapor pressure, high heat capa-

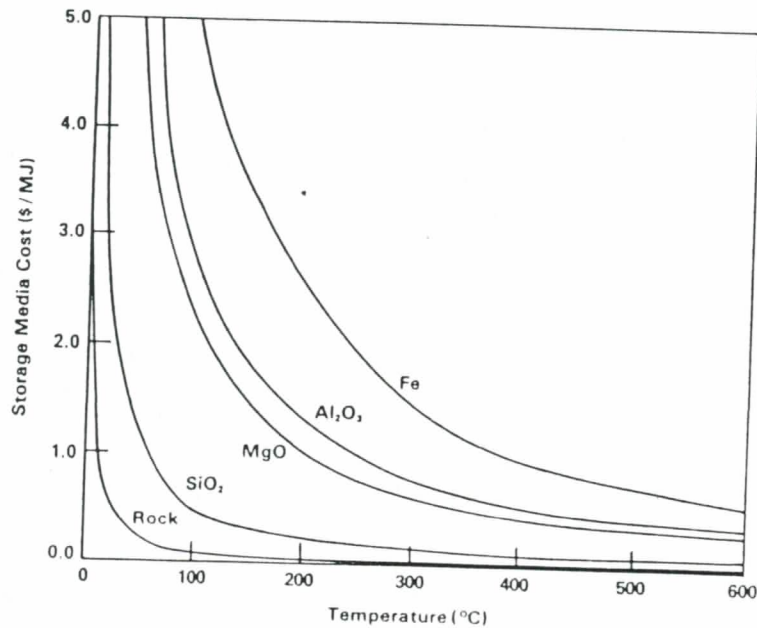


Fig. 15. Storage media costs in dollars per unit energy stored as a function of temperature for selected solid sensible heat storage media [47].

city, and low cost are similar to those for storage in a liquid.

3.2.2 Latent heat of phase change

A substantial change in internal energy accompanies a phase change. High energy storage densities over a narrow temperature range make latent heat storage materials attractive for thermal energy storage. However, since a high volumetric energy storage density is essential, only solid-liquid or possibly solid-solid transformations with significant enthalpy changes are practical. Material requirements include low cost, high heat of transition, high density, appropriate transition temperature, low toxicity, and long-term performance.

For higher temperatures, some generalizations are possible about latent heat materials [52]. Carbonates and possibly carbonate-chloride systems are serious candidates because their good corrosion characteristics make containment costs reasonable and the costs of the materials are typically low. Nitrates and nitrites are good choices for applications below 500°C since they are fairly noncorrosive and inexpensive. Chloride systems are cheap enough to be attractive but are more corrosive than the previous compounds. Hydroxides, as a group, tend to be both more expensive and corrosive and are less serious candidates for inexpensive storage units. Fluorides offer relatively high heat storage densities, but they are often expensive and their corrosiveness makes the fluorides more expensive to contain than the other salt systems discussed.

Figure 16 approximately presents the volumetric energy storage densities for some intermediate temperature storage salts of the types discussed. The density of the lower density phase near the transition temperature of the material was used to transform the data of Ref. [52] to a volume basis for this plot. Salt mixtures were used in some cases to lower the transition temperature, and the densities were computed assuming the compound volumes are additive. Because constant properties and several approximations were employed to estimate properties, the plot should only be used as an approximation to compare materials, but not for engineering design. The compositions of the mixtures by mole per cent are shown in parenthesis on the plot. The lower temperature on the curves was arbitrarily chosen as 100°C. The two sharp increases in energy storage density exhibited by sodium hydroxide are due to a solid-solid phase change within about 25°C of the solid-liquid transformation. Again, a volume penalty must generally be assessed against the storage densities shown to provide adequate heat transfer required for the phase change.

Figure 17 presents the storage capacity costs for storage materials only as a function of the temperature swing around the transition temperature shown in parenthesis assuming commercial grades are acceptable. The costs of some salts are competitive with the cost of sensible heat liquids for high-temperature storage, but significant problems in containment, heat exchange, and possibly corrosion must be overcome to make latent heat storage systems cost-effective.

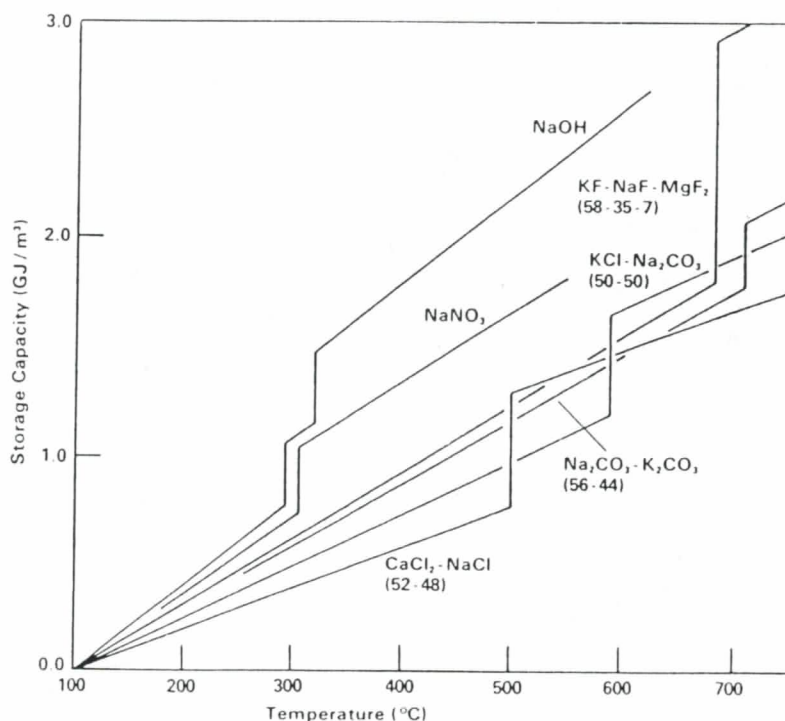


Fig. 16. Storage capacity per unit volume as a function of temperature for selected latent heat storage materials. The molar composition of mixtures is shown in parenthesis [47].

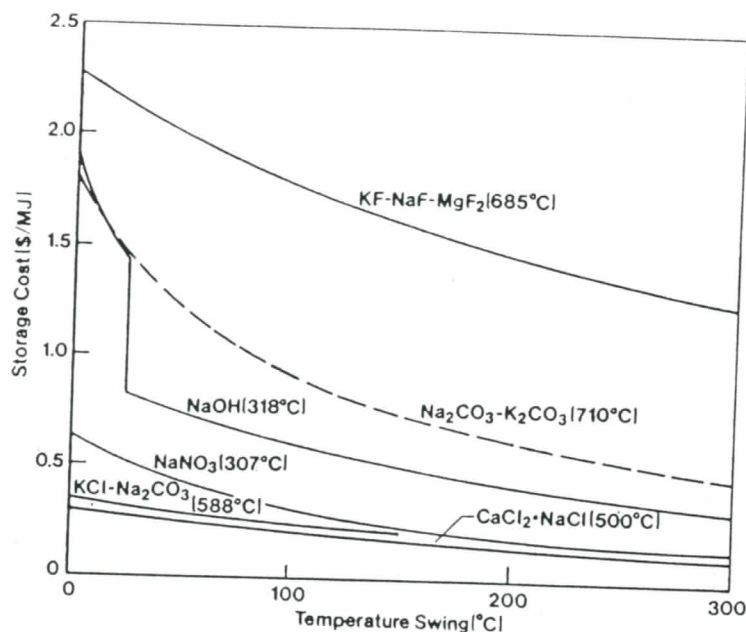


Fig. 17. Storage media costs in dollars per unit energy stored as a function of temperature swing for selected latent heat storage materials. The transition temperature is in parenthesis [47].

3.3 Reversible chemical reactions

Thermal energy may also be stored as the bond energy of a chemical compound, and energy can be repeatedly stored and released in the same materials by reversible chemical reactions. The energy storage density by reversible chemical reactions is generally higher than heat-of-fusion transitions. Chemical storage may also have cost potential since some of the materials could be available for as little as a few pennies per pound. Chemical storage has the added advantage that significant energy storage densities are possible even at ambient conditions. Despite all the promise offered by chemical reaction storage, the technology is at an early stage of development; and economic and efficient systems have not been actually demonstrated for commercial applications. It is not known, for example, whether many of the reactions will cycle over the long-term. Reasonable cost projections must await further research to clarify the ultimate capabilities and design of storage systems.

3.3.1 Thermochemical energy storage

The operating concepts for reversible reactions storage can be broken into three categories: thermochemical energy storage, chemical heat pump storage, and thermochemical pipeline energy transport. Table 5 presents a few of the possible reactions considered suitable for thermochemical energy storage of thermal energy in the temperature range covered here [53-55]. The heats of reaction are calculated at 25°C from standard tables [56]. Since a high energy storage density is necessary in such applications, only reversible reactions with reactants and products that can be easily stored as liquids and solids are practical. Reac-

tions that produce two distinct phases such as a solid and a gas facilitate the separation of products to prevent back reaction. For example, solid calcium hydroxide (slaked lime) will endothermically decompose to solid calcium oxide (quicklime) and water vapor if it is heated to about 500°C at one atmosphere pressure. The water vapor is condensed for storage in a separate vessel. When heat is required from storage, water and the calcium oxide are mixed, somewhat as in slaked lime manufacture, and the exothermic reverse reaction of the two species produces energy [57-59].

The "turning temperature" T^* in Table 5 is defined as the temperature at which the equilibrium constant is one and is approximated by the ratio of the standard enthalpy change to the standard entropy change for the reaction [54]:

$$T^* = \frac{\Delta H^\circ}{\Delta S^\circ} \quad (3-5)$$

At this temperature, the reactants and products will be present in approximately equal quantities for a pressure of one atmosphere with the actual concentrations determined by the stoichiometry of the reaction. When $T > T^*$, the endothermic storage reaction

Table 5. Thermochemical storage reactions

Reaction	$\Delta H^\circ, \text{kJ}$	T^*, K
$\text{NH}_4\text{F}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HF}(\text{g})$	149.3	499
$\text{Mg}(\text{OH})_2(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{H}_2\text{O}(\text{g})$	81.06	531
$\text{MgCO}_3(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$	100.6	670
$\text{NH}_4\text{HSO}_4(\text{l}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{SO}_3(\text{g})$	337	740
$\text{Ca}(\text{OH})_2(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{g})$	109.26	752

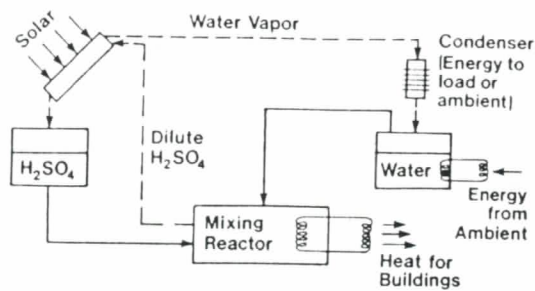


Fig. 18. Chemical heat pump storage for sulfuric acid concentration/dilution with the charging cycle represented by dashed lines (---) and the discharging cycle by solid lines (—).

is favored; but when $T < T^*$, the exothermic reaction dominates. For significant swings in conversion for homogeneous phase reactions at constant pressures, the storage temperature must be significantly higher than it is for energy release. The forward and reverse reactions for gas-solid reactions occur at essentially the same temperature in principle although some temperature swing is required to achieve satisfactory rates. Gas-solid reactions are also desirable since they offer high energy storage densities, ready product separation, a wide range of temperatures, and low cost; but they are complicated by the problems of heat and mass transfer in a solid.

3.3.2 Chemical heat pump storage

Figure 18 illustrates the chemical heat pump mode of operation in which a dilute sulfuric acid solution is concentrated by using solar energy to evaporate water. The water vapor is then condensed for storage and the heat of condensation can be transferred to a load if it can be used at the condensation tempera-

ture. When heat is demanded from storage, energy from the atmosphere can be used to evaporate the liquid water provided the water will not freeze. If the temperatures of the water and acid solution are properly regulated, the water vapor will condense in the solution. Consequently, the heat of condensation as well as the heat of mixing can be released to the load, and energy is "pumped" from the environment. In principle, the total energy released during charging and discharging of storage exceeds that supplied by the sun because of the heat pump action. If all of that energy can be used, the collector field size is reduced relative to a conventional storage system with potential savings in system cost. By interchanging the load and environment positions in Fig. 18, the chemical heat pump may be used for air conditioning as well. This combination of heating and cooling offers more use of the solar collection system, than if the collectors are only used for heating. These systems are being developed largely for heating and cooling applications, and their use for process heat applications has received far less attention.

Table 6 presents a number of reactions thought to be suitable for chemical heat pumping [53, 59–61]. The temperatures are approximate values currently considered although other values are possible depending on the operating pressure. The reactions of Table 5 could be used in a chemical heat pump mode to recover the heat of condensation given off when the vapor is condensed, and the distinction between the modes is quite arbitrary. Some of the gaseous components in Table 6 such as ammonia are not readily liquified near atmospheric pressures and ambient temperature. A second salt such as CaCl_2 that reacts with the gas at a temperature appropriate for heat pumping is used to store the gas as a solid to avoid high pressure containment of the liquids. Liquid com-

Table 6. Chemical heat pump reactions

Reaction	Temp., K
<u>Ammoniated Salt Pairs</u>	
$\text{CaCl}_2 \cdot 8\text{NH}_3(\text{s}) \rightleftharpoons \text{CaCl}_2 \cdot 4\text{NH}_3(\text{s}) + 4\text{NH}_3(\text{g})$	305
$\text{NH}_4\text{Cl} \cdot 3\text{NH}_3(\text{l}) \rightleftharpoons \text{NH}_4\text{Cl}(\text{s}) + 3\text{NH}_3(\text{g})$	320
$\text{MnCl}_2 \cdot 6\text{NH}_3(\text{s}) \rightleftharpoons \text{MnCl}_2 \cdot 2\text{NH}_3(\text{s}) + 4\text{NH}_3(\text{g})$	364
$\text{MgCl}_2 \cdot 6\text{NH}_3(\text{s}) \rightleftharpoons \text{MgCl}_2 \cdot 2\text{NH}_3(\text{s}) + 4\text{NH}_3(\text{g})$	408
$\text{MnCl}_2 \cdot 2\text{NH}_3(\text{s}) \rightleftharpoons \text{MnCl}_2 \cdot \text{NH}_3(\text{s}) + \text{NH}_3(\text{g})$	521
$\text{MgCl}_2 \cdot 2\text{NH}_3(\text{s}) \rightleftharpoons \text{MgCl}_2 \cdot \text{NH}_3(\text{s}) + \text{NH}_3(\text{g})$	550
<u>Hydrated Salts</u>	
$\text{MgCl}_2 \cdot 4\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{MgCl}_2 \cdot 2\text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$	380
<u>Concentration-Dilution</u>	
$\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{SO}_4 \cdot (n-m)\text{H}_2\text{O}(\text{l}) + m\text{H}_2\text{O}(\text{g})$	<600

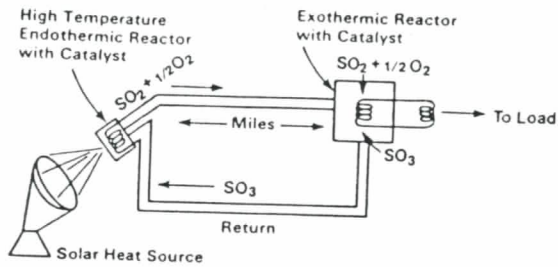
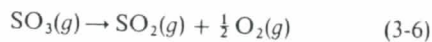


Fig. 19. Transmission of thermal energy by the thermochemical pipeline sulfur trioxide reaction.

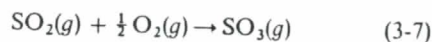
ponents are also being investigated for chemical heat pump systems to avoid the problems of heat transfer in a solid.

3.3.3 Thermochemical pipelines

Significant enthalpy changes also accompany reactions involving one or more gaseous reactants that are not easily condensed. Since the energy storage density is low and the cost of compressed gas storage is high, these reactions are not considered as attractive as the preceding ones for thermal energy storage, although some workers have proposed using massive underground caverns or compressing the reactants/products for storage of the gaseous materials. However, most applications utilize the reaction products for transmitting thermal energy over long distances in a thermochemical pipeline operation (chemical heat pipe). For example, the endothermic decomposition reaction



is driven catalytically at the energy source (Fig. 19) [53, 62]. The gaseous reaction products exchange heat with the reactants and are then transmitted at lower temperatures to a remote load site where the reverse exothermic reaction proceeds catalytically, liberating energy:



The products of this reaction are sent back to the solar source to repeat the cycle. A number of reactions potentially suitable for thermochemical pipeline applications are listed in Table 7 with their standard heats of reaction [53, 54, 62, 63]. All of the tabulated reactions are triggered catalytically to avoid the

Table 7. Thermochemical pipeline reactions

Reaction	$\Delta H^\circ, \text{kJ}$	T^*, K
$\text{CH}_3\text{OH}(g) \rightleftharpoons 2\text{H}_2(g) + \text{CO}(g)$	90.18	420
$2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$	92.26	466
$\text{C}_6\text{H}_{12}(g) \rightleftharpoons \text{C}_6\text{H}_6(g) + 3\text{H}_2(g)$	206.2	568
$\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$	108	801
$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g)$	206.2	960
$\text{CH}_4(g) + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g) + 2\text{H}_2(g)$	247.4	960
$\text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g)$	98.94	1040

necessity of separating the materials prior to transit, and the exothermic reactions take place at temperatures generally well below the turning temperature of Table 7.

3.4 Storage vessels and heat exchangers

Equation (3-1) shows that the cost of the storage media and the container could constitute a significant portion of the energy related costs and must be kept to a minimum. In addition, power related costs frequently are a substantial portion of the total system costs. Therefore, it is important to consider the design of low cost containers and heat exchangers as well as the selection of low-cost materials for storage. In this section, attention is focused on a few concepts that could lower the cost of heat exchange and containment. Most are in early development stages and require extensive effort to achieve that goal.

3.4.1 Sensible heat systems

In order to charge and discharge storage, a heat transfer fluid must be circulated between storage and either the energy source or the load. For liquid storage media, the storage fluid frequently can be used directly for heat transfer. If practical considerations such as freezing of the liquid prevent this, the storage liquid can be brought into thermal contact with an auxiliary heat transfer fluid via a conventional shell and tube type heat exchanger, although at additional expense. Alternately, a second fluid that is immiscible with the storage media can be bubbled through the storage device, and direct contact heat exchange thereby achieved between the heat transfer fluid and the storage media. Research is in progress on such a system for heating and cooling applications.

For solid sensible heat storage media, current practice is to directly contact the heat transfer fluid with the storage media. A dual media unit is being considered for applications to commercial power plants of 100 MW_e and larger [50]. The concept originally used a mixture of sand and granite to reduce the amount of more expensive organic oil, Caloria HT43, used in storage. However, the addition of solids facilitates temperature stratification in the storage vessel. In the device pictured in Fig. 20, oil is circulated from the bottom of the storage vessel, through a heat exchanger to pick up heat, and back to the top of the storage tank. A fairly sharp temperature transition or thermocline will naturally occur between the hot and cold regions in the storage bed, and this thermocline will move downward through the bed during charging. If the direction of oil flow is reversed, the thermocline will move upward through the bed during discharging. A relatively constant discharge temperature is produced from storage as a result of this temperature stratification.

Inexpensive containment of liquid sensible heat storage media is a major challenge in reducing system cost. For high-temperature thermal storage in water or other liquids with significant vapor pressures at the

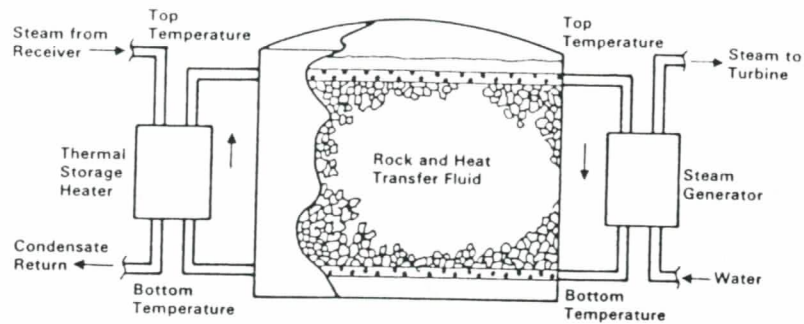


Fig. 20. Dual medium thermal storage concept [50].

storage conditions, a low-cost pressure vessel is required. A vessel made of inexpensive cast iron blocks held together by axial steel tendons offers one possible solution. Underground solution caverns created in salt domes may be an economical way to contain high pressure water or heat transfer oils (Fig. 21).

3.4.2 Latent heat systems

Heat transfer in latent heat storage materials is complicated by the phase change that occurs during storage or release of energy. During extraction of energy from storage, the liquid freezes on the heat transfer surfaces and an immobile layer of solid material continually grows as it gives up the heat-of-fusion. This solid layer often has a low thermal conductivity, and as it grows, heat transfer is impeded. In most operational latent heat storage devices, heat

transfer to the load or from energy source is through the container vessel walls. In order to provide adequate heat transfer through the frozen material, a high surface area to volume ratio is required for the combined container-heat exchanger. The cost of such units can be substantial, and a good deal of the volume advantage offered by latent heat storage is sacrificed to allow passage of a heat transfer fluid. Volume changes during the phase change can further complicate system design and add to system costs.

One way to lower the cost of heat exchange is to eliminate the need for containers between the latent heat materials and the heat transfer fluid. A direct contact low-temperature latent heat storage unit is illustrated in Fig. 22. This device uses a heat transfer fluid that is immiscible in the storage medium and lower in density. The fluid enters the bottom of the storage unit and rises through the latent heat material, transferring heat and stirring the storage media as it moves. The heat transfer fluid coalesces in a pool at the top the storage vessel and is then pumped back to exchange heat with the energy source or load prior to returning to the bottom of the storage vessel. In order for the heat transfer fluid to coalesce properly, the viscosity apparently must be below 4.5 cP for the salts

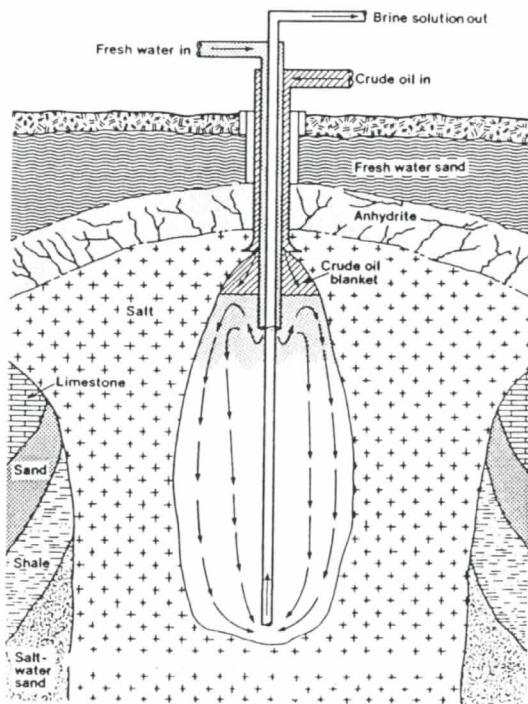


Fig. 21. Salt cavern leaching operation to produce an underground storage cavern [64].

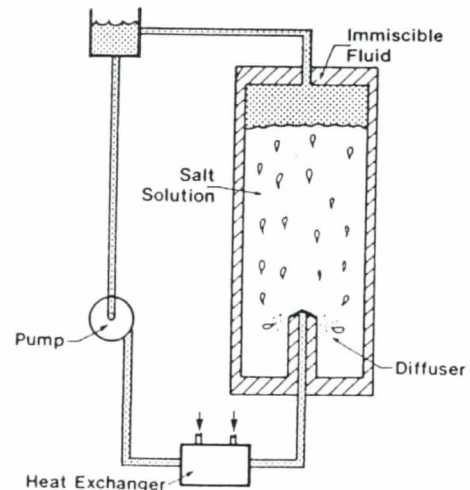


Fig. 22. Direct contact system for heat transfer between a latent heat storage medium and an immiscible heat transfer fluid [65].

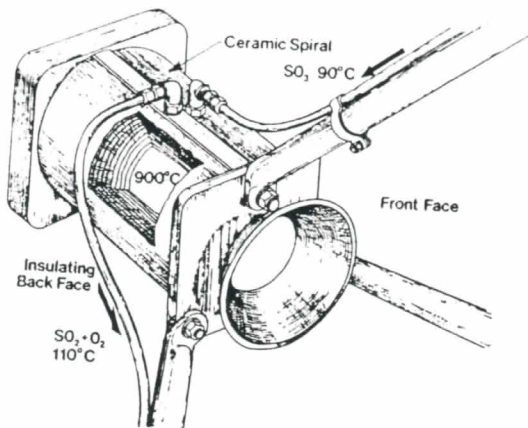


Fig. 23. Cavity converter-heat exchanger for SO_3 decomposition [67].

used in one storage study [65]. This requirement may restrict the choice of heat transfer fluids.

A similar high-temperature system using fluoride salts for storage and liquid lead for heat transfer has been proposed [66] and work is in progress on other high temperature direct contact latent heat storage concepts. However, the viability of such devices has not been demonstrated for intermediate temperatures.

3.4.3 Reversible chemical reaction systems

Storage of solar energy in reversible chemical reactions is in the early stages of concept development, and the problem of providing an inexpensive means of heat transfer has not been adequately dealt with. As a class, gas-solid reactions show promise for chemical storage but possess the inherent problem of poor heat transfer through the solids. Many of the current devices under development use fixed beds of solids with multiple tubes imbedded for heat exchange with a working fluid. Due to the low conductivity of the packed bed, the tubes have to be placed close together to obtain satisfactory heat addition and withdrawal rates. The cost of these heat exchanger-containers is very high and is far more than the price of many of the storage materials. Alternate methods of reacting solids are needed.

Some of the reactions discussed involve either gases or gases and liquids for thermal energy storage or transmission. A heat exchanger-reactor-receiver is being developed to handle these types of reactions and, in particular, the $\text{SO}_3/\text{SO}_2/\text{O}_2$ reaction [67]. A diagram of the system is shown in Fig. 23. Here SO_3 flows into the receiver cavity through a spiral counterflow ceramic heat exchanger that heats the SO_3 up to a temperature close to that in the reaction chamber. The SO_3 dissociates on the catalyst dispersed on the cavity walls while simultaneously absorbing solar energy to drive the endothermic reaction. The dissociated gas then exits through the counterflow spiral heat exchanger and releases its sensible heat to the inflowing SO_3 . By exchanging heat, the

gases may be transmitted more efficiently at lower temperatures. This device is still in the early stages of development, and considerable work is still required to make it operational and establish its utility in a solar application.

3.5 Storage research needs

For intermediate temperature sensible heat storage, the commercially available liquids are generally expensive. Containment of pressurized liquid is also expensive. For short-term storage durations with large temperature swings, these materials may have acceptable economics; but they do not appear attractive for long-term storage although a full system study must be done to establish their merits. Many of the liquids, except water, degrade at high temperatures, and new fluid must be periodically added to the system with additional costs. Some of the materials require stainless steel vessels thereby driving the cost up further. Research directed toward improving the lifetime of sensible heat storage fluids could be useful. In addition, new fluids might be developed that are more suitable for intermediate temperature storage provided the projected costs of such specialty fluids and their containers would be acceptable. Approaches such as underground caverns and prestressed cast iron vessels offer promise of reducing containment costs, and more innovation is needed in this area. Solid materials are economically more attractive for high-temperature storage than the fluids mentioned and their volume requirements are nearly comparable. However, research and development are needed to find heat transfer fluids that can be used in direct contact with the solids over long time periods. The effect of temperature cycling on solid integrity and on the interaction of the solid and a storage vessel must be studied as well. Some work has been initiated in these areas, but there are enough problems that more effort should follow. Finally, lower cost containment is still desirable for these storage materials.

Materials that undergo a phase transition at an essentially constant temperature are conceptually attractive for thermal energy storage, particularly for small storage temperature swings. A number of studies have been and are being undertaken to identify low cost storage materials to satisfy a range of temperatures. The price of providing adequate heat transfer is a significant part of the total storage system cost for latent heat materials. Innovative research and development are required to overcome this cost barrier. Immiscible fluid heat transfer devices may reduce the cost of heat transfer although performance and costs must be demonstrated for intermediate-temperature latent heat storage. Research has also been initiated on active heat exchangers that prevent buildup of the frozen layer. Continued efforts are required to improve the understanding of heat transfer in latent heat systems and apply that knowledge to reduce storage system costs. The economics and thermal performance of each new system must be

carefully evaluated in a total system context; otherwise, it is not certain if a concept has sufficient merit to warrant further development for solar applications. In addition, promising phase change storage systems should be subjected to long-term cycling to ascertain their reliability.

Thermal energy storage by reversible chemical reactions offers potential advantages over the previous storage technologies. Reactions have been identified that have potential for thermal energy storage, and as a class, gas-solid reactions have a number of significant merits for solar energy storage. However, storage by reversible gas-solid chemical reactions is both new and complex, and limited experience has been assembled in the design and operation of storage devices. Most systems under current development are for heating and cooling applications and require a large heat exchanger surface area at significant costs to allow adequate heat transfer through the solid phase. In addition, the source of a number of problems in the use of reactants such as magnesium hydroxide is not understood. Substantial further research is necessary to understand the complexities and limitations of reversible chemical reactions and develop the most cost effective means of storage for the final applications. One must understand fundamental analyses of the heat and mass transfer and kinetics of gas-solid reactions and determine whether cost-effective efficient reactors can be designed for intermediate temperature storage and release of thermal energy. Additional reactions involving low cost materials are also needed for the intermediate temperature ranges.

Other reactions besides the gas-solid type may be suitable for solar energy storage, but important questions must be satisfactorily answered to clearly establish their role. For instance, catalyzed reactions are attractive because no material separation step is necessary. However, gaseous components are involved in known reactions, and they must be compressed for storage. The parasitic power requirements for compression must be carefully evaluated to determine what fraction of the stored energy must be used to process the gases. The cost of pressure vessels is likely to be high. For some systems such as the $\text{SO}_3/\text{SO}_2/\text{O}_2$ reaction, atmospheric oxygen might be used in the system to eliminate the compressor power requirements, but the technical and economic feasibility and environmental acceptability of this concept must be demonstrated. Noncatalyzed liquid reactions such as the NH_4HSO_4 system are attractive because they could avoid the solid heat transfer problems, but separation of the gases must be demonstrated and satisfactory economics achieved. The likely acceptability of toxic substances must also be assessed early in each of the programs to be certain the technology will be accepted later. In all storage systems, careful analyses are required to establish the parasitic power requirements, energy delivery efficiencies, storage costs, and energy delivery temperatures once sufficient

knowledge is available to be certain they are useful in the context of an entire solar application.

4. CONCLUSIONS AND RECOMMENDATIONS

There is a near-term market potential for intermediate-temperature solar thermal conversion systems.

Current collector technology can provide linear concentrating collectors capable of heating a working fluid to 300°C at peak efficiencies up to 60 per cent in favorable locations. However, basic and applied research and development is needed to improve performance analysis, develop methods of mass production, reduce cost of installed systems, assure their long-term trouble-free operation, and improve their efficiency.

Working fluids are commercially available for heat transfer in the intermediate-temperature range.

The long-term durability (10–20 years) of collector reflective, refractive, and selective absorbing surfaces has not been demonstrated.

Analytical models for predicting concentrating collector thermal performance often disagree with experimentally measured performance.

The temperature range over which mid-temperature collectors are reaching commercial viability can at present be supported by sensible heat storage. However, available thermal storage methods in the intermediate temperature range are only economical for short duration when utilization is high.

Development of low cost containment and direct heat exchange technology could significantly reduce solar system cost in the intermediate temperature range.

Reversible chemical reactions are a conceptually attractive storage technology for the intermediate temperature range, but intensive basic and applied research will be required to develop this technology.

There are problems with repeatable cycling, heat transfer rate and containment that need to be solved before latent heat storage systems can become commercially and economically viable for intermediate temperatures.

At the present time, hybrid intermediate temperature solar systems that use fossil fuels for back-up and storage appear promising for near-term market penetration as fossil fuel saving devices, but applied research is needed in short-time buffer thermal storage and control technologies to provide hybrid solar-fossil industrial process heat efficiently.

Heliostats with central receivers could be used for the upper range of intermediate temperature applications, but development of inexpensive heliostats and associated storage technology for such systems is needed.

In each application, system studies with realistic cost estimates are needed to define the economic value or worth of storage in the intermediate temperature range.

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