

Chapter XI

ENERGY STORAGE

Chapter XI.—ENERGY STORAGE

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MAJOR DESIGN CHOICES

Energy can be stored in thermal form by heating or chilling liquids or solids; in mechanical form by using mechanical or electrical energy to pump water to high reservoirs, spin flywheels or compress air; and in chemical form by driving battery reactions, producing hydrogen or other chemicals to generate heat, or by distilling solutions. This chapter discusses a range of storage technologies which could have a major impact on the cost and performance of onsite solar energy systems during the next 10 to 20 years; it does not attempt to review all possible storage technologies.

Most of these approaches require specialized storage equipment, but in some cases it may be possible to integrate storage into mechanical structures which serve other functions. Careful architecture can increase the **inherent ability** of walls and floors, for example, to store thermal energy.

Energy can be stored at a variety of points in an onsite solar system and some of the opportunities are presented in figure XI-1. The options for the heat engine system are most complex:

1. Energy can be stored at relatively high temperatures before it is used by a heat engine. In this form, high-temperature storage is equivalent to a supply of fossil fuel.
2. Heat rejected by the engines can be stored at relatively low temperatures.
3. Electricity generated by the system can be stored in batteries or other electric storage devices.

It is **unlikely** that all three types of storage would be used in a single installation.

Storage systems can provide a useful buffering role, regardless of whether solar energy is used, since the timing of demands and the timing of generation desirable for peak performance of generating equipment seldom coincide. Most of the equipment discussed in this chapter was developed for systems in which solar energy played little or no part.

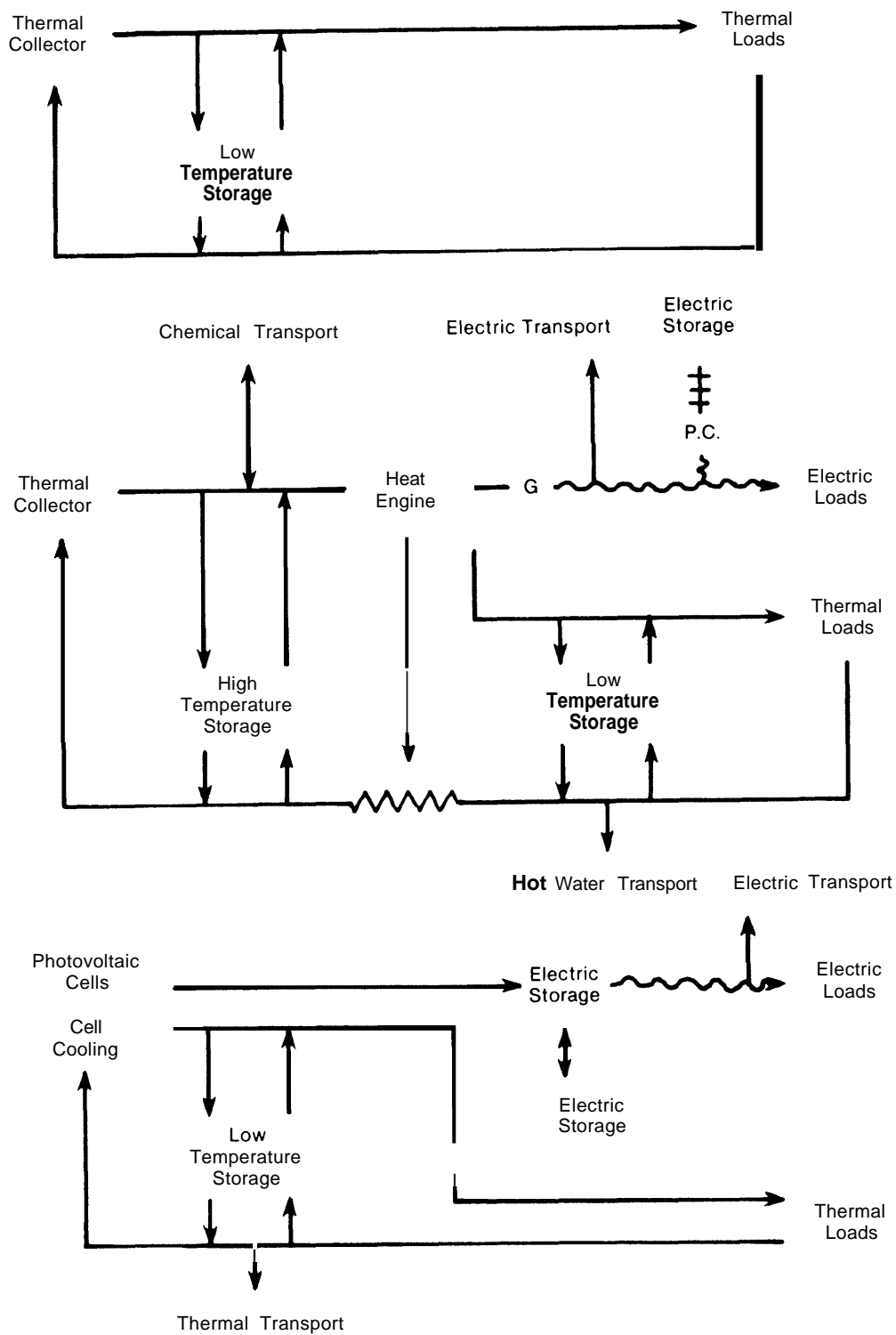
Some of the uses of storage are:

1. Storage in solar devices can be used to provide energy during cloudy periods and at night. Storage can also be used to facilitate starting large solar turbine systems in the morning by preheating the equipment and to allow a gradual cooling of the system when it is closed

at night. It can also mitigate the rapid temperature changes which can result from sudden fluctuations in the Sun's intensity during periods of partial cloudiness.

2. Storage equipment can be used to make more effective use of generating equipment. As noted earlier, without storage the output of generating equipment must be continuously adjusted to meet fluctuating demands. This means that generating equipment is either idle or operating at part capacity much of the time—resulting in higher electric costs since capital charges must be paid on the equipment, even if it is not used. Operating plants frequently below full capacity also means that the

Figure XI-1.—Possible Locations for Storage Equipment in Onsite Solar Energy Systems



generators are not operating at peak efficiency. Most large coal and nuclear plants cannot readily be adjusted to meet changing loads; demand fluctuations must be met with generating equipment which burns oil or gas—fuels which are becoming scarce and expensive.

Generating capacity can be reduced with storage equipment if the storage is filled while capacity exceeds demand, and discharged during periods of high demand. In electric utilities, this means that gas- and oil-burning plants can be replaced by storage charged from coal or nuclear plants functioning at close to their top output all year. In the case of solar collectors, it means that collectors can be sized to meet average demands instead of peak demands.

With the exception of pumped hydroelectric storage, no electric storage* device is now economically attractive to electric utilities. The rising cost of oil and gas as well as progress in storage technology may reverse this situation in the near future however, and the industry will demonstrate a number of advanced systems during the next few years. The possibilities have been reviewed in two recent studies sponsored by the Electric Power Research Institute (EPRI).¹²

Electricity which will eventually be used for electric resistance heating can be stored very inexpensively by using the electricity to heat water or bricks in onsite storage devices. Electric air-conditioning can also be

“stored” inexpensively in tanks of ice or chilled water.

Storage in this form will not be used unless prices to consumers are changed during the day to reflect the fact that electricity costs less to generate during off peak hours at night than it does during the day when demands are large. These simple storage devices are extensively used in Europe and Great Britain, where such “time-of-day” rates have been in use for many years and are beginning to be marketed in the few parts of the United States where these rates are being introduced.³

(The circumstances under which storage devices can be used economically in load-leveling applications are discussed in appendix XI-B.)

3. Storage can improve the performance of heating, cooling, and other energy-consuming equipment in much the same way that it can reduce the cost of generating electricity. Without storage, the equipment must be large enough to meet peak demands. This means that the equipment must be operated at less than its maximum capacity much of the time, increasing the need for generating equipment and decreasing system efficiency. Storage can have the additional benefit of permitting heat-pump devices and air-conditioning devices to operate when ambient conditions are most favorable. Air-conditioning systems, for example, are much more efficient at night when ambient air temperatures are relatively low.

* The term “electric storage” is used throughout this chapter to mean storage which is charged by and which discharges electricity, even though the energy in the storage device is not in the form of electricity.

¹²Ralph Whitaker and Jim Birk (EPRI), “Storage Batteries: The Case and the Candidates,” *EPRI Journal*, October 1976, p. 13.

¹³*An Assessment of Energy Storage Systems Suitable for Use by Electric Utilities*, EPRI project 225, ERDA E (11-1)2501, July 1975.

³William H. Wilcox, statement delivered to the Pennsylvania Public Utility Commission (76 P. R. M. D-7), July 25, 1977.

THERMAL STORAGE

OVERVIEW

There are three basic approaches to storing thermal energy:

- Heating a liquid or solid which does not melt or otherwise change state during heating. (This is called "sensible-heat" storage, and the amount of energy stored is proportional to the system's temperature.)
- Heating a material which melts, vaporizes, or undergoes some other change of state at a constant temperature. (This is called "latent-heat" storage.)
- Using heat to produce a chemical reaction which will then release this heat when the reaction is reversed.

Equipment for storing energy as sensible heat can be simple and relatively inexpensive if fluids are stored at temperatures below 400°F. One difficulty with sensible-heat storage is that it can be difficult to ensure a constant output temperature.

If a constant temperature is desired to operate a heat engine, or for some other purpose, two separate storage tanks are required: one to store the hot liquids and one to store the low-temperature fluids emerging from the engine.

Latent-heat storage can supply energy at constant temperature from a single container and can usually store greater amounts of energy in a given volume or weight of material. The materials used, however, are relatively expensive and problems are encountered in transmitting thermal energy into and out of the storage medium.

Chemical storage techniques can be used at a great variety of temperatures and have the advantage of allowing storage of reduction products at ambient temperatures (eliminating the need for expensive insulation). Chemical energy can also be transported conveniently. Recovering energy

from storage could be expensive, however, if expensive catalysts are required. Chemical storage can be expensive if some of the chemicals which must be stored are in the form of gases requiring large pressurized tanks.

A number of promising reactions are being examined, however, and there is reason to be optimistic that an attractive technology can be developed. Research in this area is in a formative stage.

Table XI-1 summarizes some of the materials and approaches which have been suggested for thermal energy storage,

LOW-TEMPERATURE STORAGE 0° to 150°C (32° to 302° F)

Sensible-Heat Storage in Water

A variety of techniques have been examined for storing relatively low-temperature thermal energy, but the use of water as the storage medium for liquid systems has been the dominant approach and is likely to remain so for at least a decade.⁴⁵ Most solar heating and hot water systems use an insulated hot water tank located in the building equipment room or buried in the ground. Figure XI-2 shows a cross section of a typical installation, and figures XI-3 and XI-4 show the installation of steel and fiberglass tank. Tanks can be made from a variety of materials, and the costs of a number of commercially available containers are summarized in figure XI-5. It may be possible to reduce the cost of large tanks significantly by simply lining an excavation with a watertight

⁴⁵C L Segaser (Oak Ridge National Laboratory), *Thermal Energy Storage Materials and Devices*, OR NL-HUD-M IUS-23, August 1975

⁴⁶George C. Szego, "Hot Water Storage Systems Group Report," in *Proceedings of the Workshop on Solar Energy Storage Subsystems for the Heating and Cooling of Buildings*, NSF-RA-N-75-041, ASH RAE, Apr 16-18, 1975, pp 17-23.

Table XI-1.—Proposed Thermal Storage Materials

Storage type	Temperature Regime			
	0°-15 °C (32 °-50°f=) (stores cooling for air-conditioning)	30°-150 °C (86°-302°F) (process heat and low-temperature heat engines)	200°-350 °C (392°-662°F) (heat engines and process heat, absorption air-conditioning)	400 °-1,000 °C(752°-1,832°F) (heat engines)
Sensible heat	— water	—pressurized water — rocks	—fuel oil —organic heat-transfer liquids (e. g., Therminol, etc.) — rocks —steel —pressurized water	— rocks —steel —heat-transfer salts (e. g., HITEC)
Latent heat	— C ₁ / C ₁₆ paraffin — 1-Decanol —other paraffins — Inorganic salt, hydrate eutectics — ice	— Inorganic salt, hydrate eutectics (e. g., CaCl ₂ ·6 H ₂ O) —organic compounds (e. g., paraffin & CC1 ₄)	— NaOH	— in organic compounds (LiH, NaOH, KNO ₃ /NaNO ₂) —eutectic salts (LiF, NaF, etc.]
Chemical reaction		—metal hydrides (e. g., LaNi ₅ H ₂)		CO + H ₂ ·CH ₄ + H ₂ O 2 S O ₃ = 2SO ₂ + O ₂

(and possibly insulating) material. Plastic insulations (such as polyurethane) can simply be floated on the surface of the thermal lake thus produced.

Insulation can represent a significant part of the cost of small water tanks, but in very large devices (i. e., in systems capable of holding more than about 30,000 kWh, or about 160,000 gal.) the insulating value of dry earth surrounding the tank may be adequate. The insulating value of dry soil 10 meters (33 feet) thick is roughly equivalent to that of a layer of polyurethane foam 30 cm (12 inches) thick. Very dry, low-conductivity soil would be equivalent to 1.3 m (4.3 ft) of polyurethane. The heat conduction of moist soil should decrease to this value as it is heated by energy escaping from the tank and dries out.^b Since most buildings are located in areas where ground water is quite deep, earth insulation may be able to provide the bulk of the insulation required for large thermal storage systems. It must be recognized, however, that it can take as

much as a year for the earth around a large storage tank to reach equilibrium by heating and drying, and a considerable investment of energy may be required to achieve this equilibrium. ' Earth insulation is examined in greater detail in appendix XI-B.

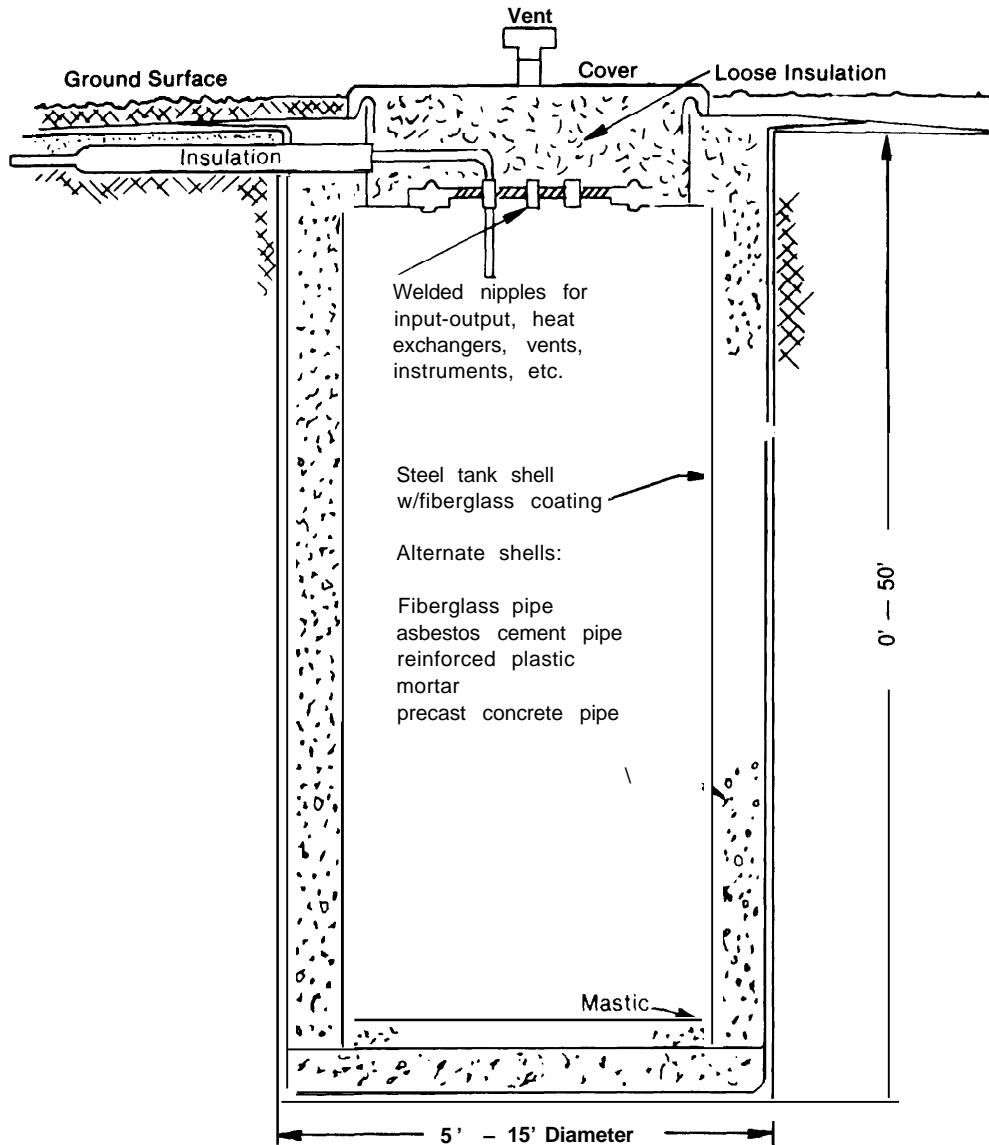
The value of a sensible-heat storage system is increased if it is able to return energy at a temperature close to the temperature at which fluids were delivered from the collectors.

One way of doing this is simply to use two storage tanks, one of which holds water at a relatively low temperature (i. e., at the temperature of fluids returned from heating radiators) and another which holds fluids emerging from the Collectors. This is more expensive, although it does not necessarily require doubling the cost. In a large system, several tanks may be needed to provide adequate storage. All that is needed in this circumstance is to maintain one empty tank for shifting liquids from hot to cold storage.

^bJ Shelton, "Underground Storage of Heat in Solar Heating Systems," *Solar Energy*, 17 (2), 1975, p 138

^cShelton, op cit , p 143

Figure XI-2. - Vertical Tank in a Drilled Hole With Foamed-in Place Insulation (for cohesive soils only)



Typical Capacities

4' Diameter x 10' Depth	— 940 Gallons
6' Diameter x 12' Depth	— 2,538 Gallons
8' Diameter x 16' Depth	— 6,015 Gallons
10' Diameter x 30' Depth	— 17,624 Gallons

Vertical tank in a drilled hole foamed-in-place insulation (for cohesive soils only)

SOURCE: E. E. Pickering, "Residential Hot Water Solar Energy Storage," *Proceedings of the Workshop on Solar Energy Storage Subsystems for the Heating and Cooling of Buildings*, NSF-RANN-75-041, April 1975, P.P. 24-37

Figure XI-3.— Installation of Insulated, Underground, Storage Tank at
Solar Heated and Air-Conditioned Burger King, Camden, N.J.

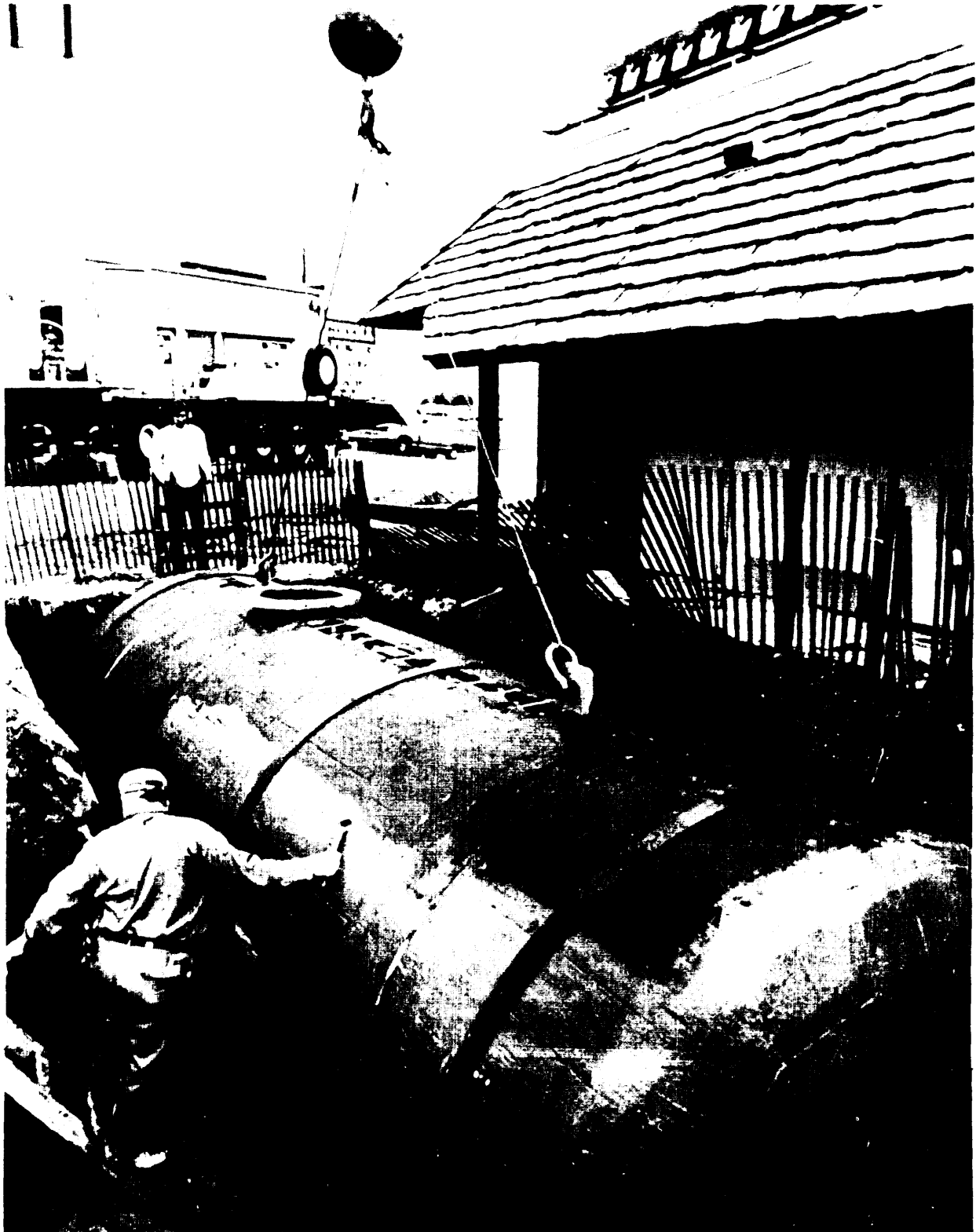


PHOTO: Courtesy of Burger King Corporation.

Figure XI-4.— Installation of Fiberglass Underground Tanks



During Construction, a 1,500gallon underground water storage tank is eased into position at a prepared excavation. The tank, made of lightweight resin-reinforced fiberglass, is one of the two installed as part of the solar climate control system.

SOURCE: September 1976 *Solar Engineering*, page 23.

Such a device would require a control system and a series of adjustable valves.

In most single-tank systems, the cold water returning from a heating system mixes with the hot water in the storage tank, gradually lowering the temperature of the fluids. It would be desirable to maintain a temperature gradient across the tank. A recent set of measurements on the behavior of a typical vertical cylindrical tank indicated that while the water in the tank did not maintain a perfect "stratified" temperature gradient, the hot and cold liquids did not mix completely, and a substantial temperature gradient remained. '

Most techniques suggested for increasing the temperature gradients possible in single-

tank systems involve the use of internal partitions or one-way valves inside the tanks.⁹ Another method being studied involves maintaining a gradient in the density of a salt mixture inside the tank. Heated, high concentrations of salt remain near the bottom of the storage tank if the drop in density due to heating is offset by the higher density resulting from the salt mixture. System stability has been difficult to maintain and experiments are continuing.

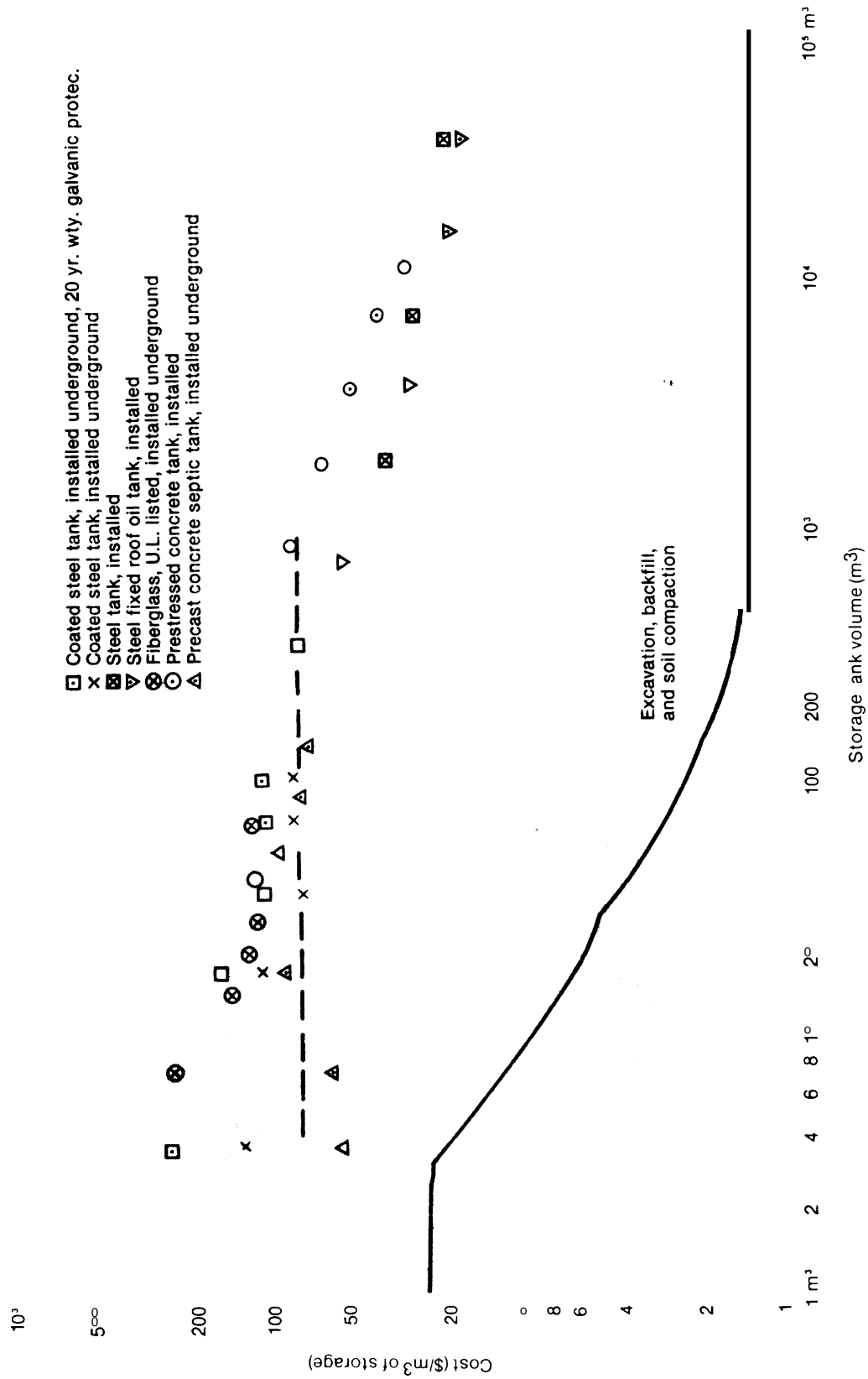
Given that the technology of large thermal-storage devices is simple, and its potential for energy savings so great, the small amount of work done in the area is astonish-

⁹Warren F. Philips and Robert A. Pate, "Mass and Energy Transfer in a Hot Liquid Energy Storage Systems," *Proceedings, 1977 Meeting of the American Section of the International Solar Energy Society*, Orlando, Fla., June 6-10, 1977, p. 17-6.

⁹Sui Lin, "An Experimental Investigation of the Thermal Performance of a Two-Compartment Water Storage Tank," *Proceedings, the 1977 Annual Meeting of the American Section of the International Solar Energy Society (I SE S)*, Orlando, Fla., June 6-10, 1977, p. 17-1.

¹⁰D.L. Elwell, "Stability Criteria for Solar (Thermal-Saline) Ponds," *ISES*, p. 16-29.

Figure X -5.—Cost of Buried Tanks



SOURCE: Means Building Construction Cost Data, 1976, pages 18, 20, 22, 34, 184, 205-206, 258.

ing. Possibly the field is not sufficiently romantic.

It is possible to store water at temperatures above the boiling point if pressurized tanks are used. A number of such pressurized storage systems are available in European markets¹¹ and a device manufactured by the Megatherm Corporation of East Providence, R. I., is now available on the U.S. market. The Megatherm device, which is illustrated in figure XI-6, stores water at temperatures up to 280° F (138 °C).^{12, 13} The device is sold to institutions which can use interruptible electric service or take advantage of "time-of-day" rates (see chapter V).

Water storage is probably not an attractive option for storage above 1500 to 200°C (300 ° to 400° F) since the pressure required would greatly increase the cost and danger of operating such systems. Local ordinances frequently require all water tanks which operate at temperatures above 2000 F, contain more than 120 gallons, or require more than 2×10^5 Btu/hr inputs to comply with ASME low-pressure heating boiler codes.¹⁴ Pressure above 50 psia may require the presence of a trained operating engineer.

An EPRI study examined the feasibility of using steam accumulators to store heat for later use in a standard steam-electric generating plant and concluded that in this application, storage systems using fuel oil as the storage medium were less expensive.¹⁵

It may also be possible to store very large amounts of low-temperature thermal energy by pumping hot water into contained underground aquifers, as illustrated in figure XI-7.

If a deep aquifer is able to withstand high pressures, it may be possible to store fluids at temperatures as high as 200°C (392° F), but it is more likely that somewhat lower temperatures will be used.¹⁶

It should be possible to recover 70 to 90 percent of the energy injected and to maintain a reasonable thermal gradient across the aquifer (the warmest water will tend to float to the top of the structure).

Since the only investment required for such a storage device is a series of wells for injecting and withdrawing water, storage costs can be very low. There is some disagreement about the cost of constructing such systems, but costs could be as low as \$0.03/kWh¹⁷--with power costs in the range of \$5/kW.¹⁸ Pumping energy should be in the range of \$0.01/kWh (1970 dollars).

Aquifers adequate for thermal storage applications are found in wide areas of the country (see figure XI-8). It should be possible to use aquifers of brackish water as well as freshwater wells and, since there is little net consumption of water in the storage process, the technique will not deplete the water resources of a region or lower water tables. The environmental impact of these systems has, however, never been systematically addressed.

While a number of theoretical studies of aquifer storage systems have been undertaken, in 1976 there have been few field tests. One large-scale experiment has been under-

¹¹A. W. Goldstern, *Steam Storage Installations*, Pergamon Press, 1970.

¹²The Megatherm Corporation, East Providence, R.I., July 1976.

¹³*Thermal Energy Storage Materials and Devices*, OR NL-HUD-MIUS-23, August 1975, pp. 9-10.

¹⁴ASME, "Heating Boilers," *ASME Boiler and Pressure Vessel Code*, Section IV, New York, N. Y., 1968.

¹⁵*An Assessment of Energy Storage Systems Suitable for Use by Electric Utilities*, EM-264, EPRI Project 225, ERDA E (11-1) 2501, Final Report prepared by Public Service Electric and Gas Company, Newark, N. J., Vol. II, July 1976, pp. 4-45.

¹⁶W. Haur and C. F. Meyer, "Energy Conservation: Is the Heat Storage Well the Key," *Public Utilities Fortnightly*, Apr. 24, 1975.

¹⁷General Electric Corporation, *Heat Storage Wells Using Saline and Other Aquifers*, presentation to the U.S. Department of the Interior, Mar 5, 1976.

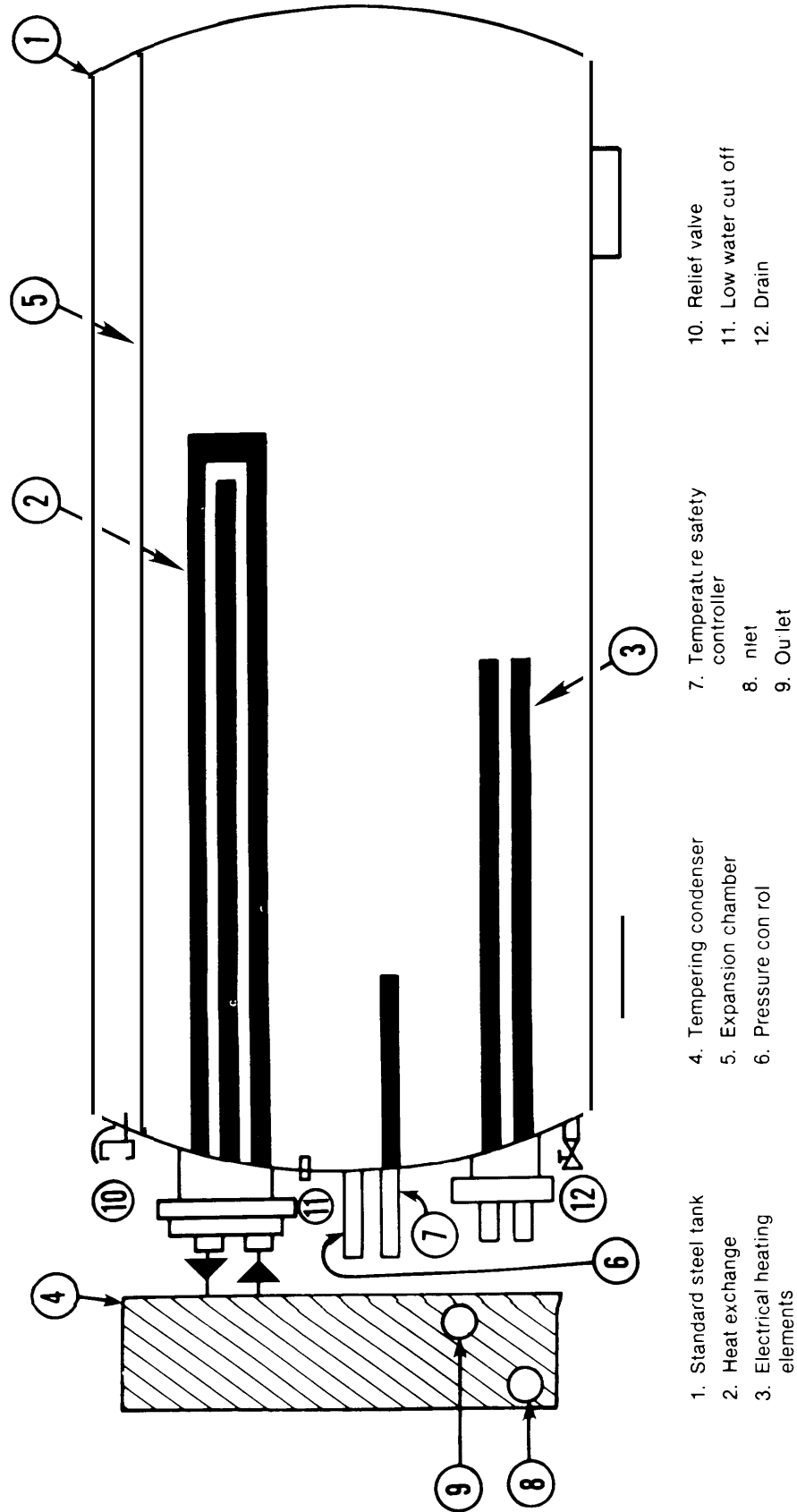
¹⁸General Electric Corporation, op.cit.

¹⁹C. F. Meyer and D. K. Todd, "Conserving Energy with Heat Storage Wells," *Environmental Science and Technology*, 7, p512,

²⁰C. F. Tsang, et al., *Numerical Modeling of Cycling Storage of Hot Water in Aquifers*, EOS, 57,918

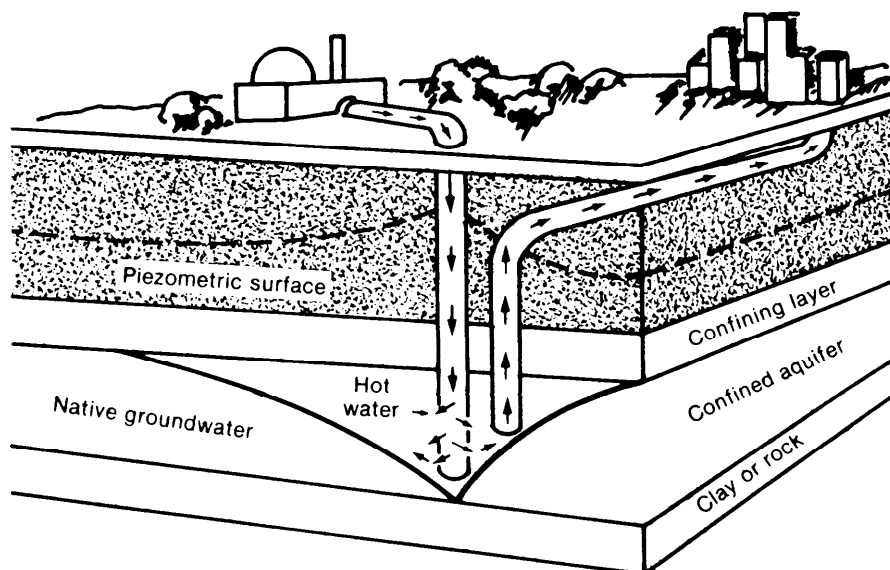
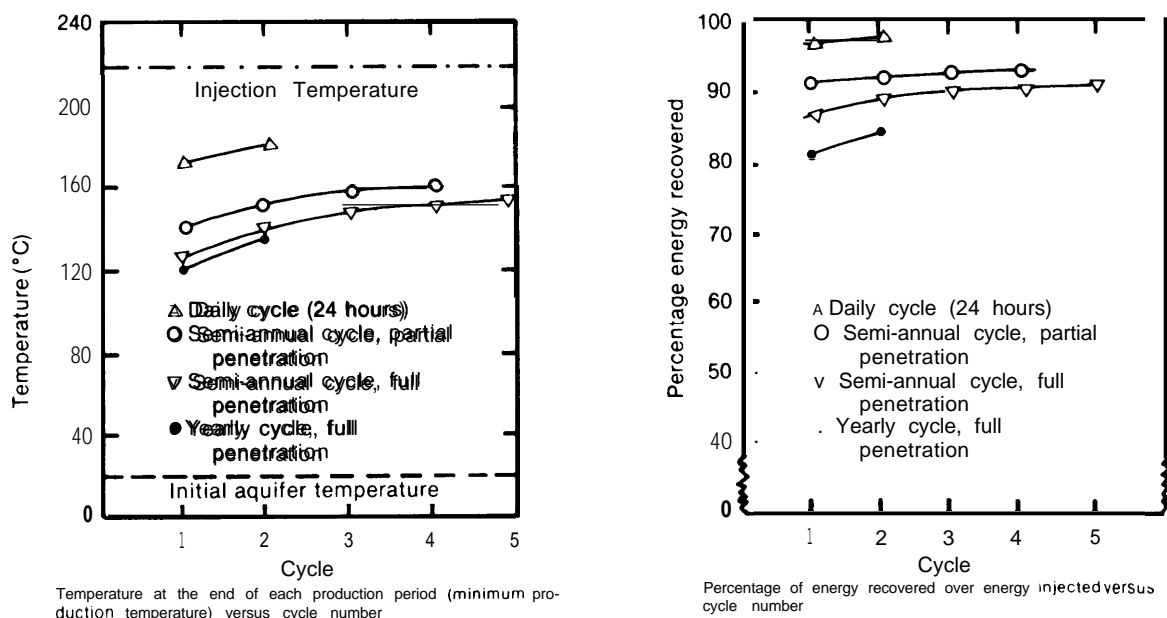
²¹C. F. Tsang, et al., "Modeling Underground Storage in Aquifers of Hot Water from Solar Power Systems," *Proceedings, the ISES 1977 Annual Meeting*, p. 16-20.

Figure X -6.— Megatherm Pressurized-Water Heat-Storage Tank



SOURCE: Megatherm

Figure XI-7.— Predicted Performance of an Aquifer Used for Thermal Storage



SOURCE: C.F. Tsang, et al., "Modeling Underground Storage in Aquifers of Hot Water from Solar Power Systems," *ISES Proceedings of the 1977 Annual Meeting*, page 16-20.

DRAWING FROM: Walter Hauz and Charles F. Meyer, "Energy Conservation: Is the Heat Storage Well the Key?," *Public Utilities Fortnightly*, Apr 24, 1975, p. 34.

**Figure XI-8. - Potential Sites for Aquifer Storage Systems
(Aquifers in the Shaded Areas Should Have Adequate Water Flow)**



SOURCE: Geraghty, et al., *Water Atlas of the United States*, Water Information Center, Port Washington, N. Y., 3rd Ed., 1973.

taken near Bucks, Ala. Approximately 2.4 million gallons of warm water were injected into an aquifer and stored at a temperature of 105° to 107° F (41 °C to 42 °C) and stored for 30 days. About 65 percent of the energy was recovered when the water was pumped out of the formation.²² Unfortunately, the water used in the test was taken from a local river and contained small clay particles which began to clog the aquifer after about 2 million gallons (7.6 million liters) of water had been injected. The test was stopped when injection pressures became excessive.

The experiment will be repeated using water from an aquifer in the same region which does not contain clay particles capable of plugging the aquifer. If all goes well, about 20 million gallons will be injected over a period of 2 months.

Swedish engineers have recently suggested that it may also be possible to store

large volumes of heated water in plastic bubbles suspended in a lake.

Sensible-Heat in Rocks

Energy can be stored at low and intermediate temperatures by heating rocks held in insulated containers. Rock storage is typically used with solar heating systems using air to transfer heat from collectors to storage since the rocks can be heated by simply blowing air through the spaces between the rocks. (If liquid is used in the collectors, a more elaborate heat-exchange mechanism is required.) Rock storage can be both simple and inexpensive, but designing an optimum system can be difficult since the performance is affected by the shape, size, density, specific heat, and other properties of the rocks used.²³

²²F. Molz, Department of Civil Engineering, Auburn University, private communication, November 1977

²³W. D. Eshleman, et al., *A Numerical Simulation of Heat Transfer in Rock Beds*, ISES, Proceedings of the 1977 Annual Meeting, p. 17-21.

It may also be possible to store large quantities of sensible thermal energy in underground rock formations using a technique which is essentially the solid-state equivalent of the aquifer storage discussed previously. A number of schemes have been proposed for storing energy in this way:^{24 25}

- Digging deep parallel trenches into dry earth (or land which is "dewatered" with a pumping well) and filling these trenches with crushed rock. The crushed rock would be heated from a series of distribution pipes buried with the crushed rock, and heat would be removed by blowing air through similar buried pipes.
- Excavating a large area in sandy soil, depositing a layer of material which can prevent ground water from entering the excavation, and filling part of the excavation with crushed rock. An insulating layer would be placed on top of the rock. (This scheme would lead to a significant change in local topography.) Hot air distribution pipes would be buried in the layer of crushed rock.
- Digging tunnels through layers of sandstone or other porous rock in naturally occurring formations. In one proposal, the rock is heated by sending hot air through pipes located in an intermediate plane in the rock formation. The air passes through the rock formation and is returned through a piping network on planes above and below the injection plane. Heat is removed in the same way when cold air is introduced in the intermediate plane.
- Caverns of crushed rock could be produced by drilling and blasting underground rock layers if the rock layers available were not suitably porous. Pre-

liminary calculations have indicated that performance of the storage bed would be optimum if the rock particles are about 0.3 cm (0.1 inch) in diameter.

It has been estimated that energy could be stored in these formations at temperatures up to 500°C (9320 F). The cost of the system will vary from site to site, but it may be possible to build devices for \$0.03 to \$0.09/kWh and \$150 to \$400/kW, if the storage cycle involves removing air at a temperature of 500°C above the temperature at which it was injected.²⁶ If a temperature swing of only 50°C is used, storage costs would be on the order of \$.30 to \$.90/kWh.

Latent Heat, Low-Temperature Storage

An enormous variety of phase-change materials have been examined for possible use in low-temperature storage systems.^{27 28 29 30} The properties of a selected set of these materials are summarized in table XI-2. Phase change materials used in low-temperature applications are of three basic types: inorganic salt compounds, complex organic chemicals (such as paraffins), and solutions of salts and acids. Water itself can be used as a latent-heat storage medium to store "coolness;" the latent heat of melting ice is 0.093 kWh/kg.

A successful latent-heat system must have the following properties:³¹

²⁴M P Hardy, et al, "Large Scale Thermal Storage in Rock Construction, Utilization and Economics," 12th IECEC Conference, p 583.

²⁵MRiaz, et al., "High Temperature Energy Storage in Native Rocks," *Proceedings, the ISES joint Conference Sharing the Sun—Solar Technology in the Seventies*, Volume 8, p 123 (1976) Pergamon Press

"Hardy, op. cit., p. 590.

²⁷Maria Telkes, *Thermal Energy Storage*, IECEC 1975 Record, p. 111

²⁸D. V. Hale, et al., *Phase Change Materials Handbook*, NASA-CR-61 36. Lockheed Missiles and Space Company, September 1971

²⁹C L Segaser, *MIUS Technology Evaluation: Thermal Energy Storage Materials and Devices* (ORN L-HUD-M IUS-23), August 1975, p. 28

³⁰OH C. Fisher, *Thermal Storage Applications of the IceMaker Heat Pump*, Oak Ridge National Laboratory, 9-30-76. (Paper prepared for presentation at Pennsylvania Electric Association, Harrisburg, Pa.)

³¹Harold Lorsch, *Conservation and Better Utilization of Electric Power by Means of Thermal Storage and Solar Heating — Final Summary Report*, NSF/RAN N/SE/G I27976/PR73/5, July 31, 1975 Some phrases taken verbatim.

Table X1-2.—Phase-Change TEC Materials in the Low-Temperature Regime With Melting Points Above 75°C [167°F]

TEC material	Class	Lab test*	Melting point °C	Melting point °F	Latent heat of phase change (Cal/G) (Btu/lb)	
Mg(N ₂ O ₃) ₂ · 6 H ₂ O	inorganic compound	S	89	192.2	NA	NA
Ba(OH) ₂ · 8H ₂ O	inorganic compound	G	82	179.6	63.5	114.3
N H ₄ Br(33.4%)						
CO(NH ₂) ₂	inorganic eutectic	G	76	168.8	NA	NA
Acetamide (C H ₃ C O N H ₂)	organic compound	s	82	179.6	NA	NA
Naphthalene (C ₁₀ H ₈)	organic compound	G	83	181.4	35.3	63.5
Propionamide (C ₂ H ₅ C O N H ₂)	organic compound	G	84	183.2	40.2	72.3
51.8% Benzamide (C ₆ H ₅ CONH ₂)	organic eutectic	G	83	181.4	30.4	54.7
48.2% Benzoic acid (C ₆ H ₅ COOH)						

NOTES NA — not available
 S — satisfactory performance
 G — good performance

SOURCE Hoffman (Oak Ridge National Laboratories), prepared for OTA, 1976.

- A melting point within the desired temperature range.
- A high heat of fusion (this reduces storage volume and material demands).
- Dependability of phase change (a melt should solidify predictably at the freezing point and should not supercool).
- Small volume change during phase transition (a volume change makes heat-exchange difficult, and can place stress on the storage containers; most materials increase in density when they freeze, but water and gallium alloys expand).
- Low-vapor pressure (some materials have high-vapor pressures near their melting points, placing stress on containers).
- If the latent-heat medium is a mixture, it must remain homogeneous; i.e., its parts should not settle out.

It has proven difficult to combine all of these properties in a single system.

The rate at which energy can be withdrawn from many phase-change storage sys-

tems is limited by the fact that the storage medium usually begins to solidify on the surface of heat exchangers; the layer of solid material acts as an insulator. Designs for increasing effective heat exchange areas have usually involved "microencapsulation" (in which the storage medium is separated into a number of small containers suspended in a heat exchange medium) or shallow trays.

The General Electric Company has recently proposed another approach. In their system, the phase-change materials is contained in a series of long, cylindrical containers which rotate (typically at 3 rpm) to keep the material mixed and to maintain a uniform temperature throughout the mixture. GE claims that with this approach, solidification begins at a number of nuclei distributed throughout the liquid and not on the walls of the cylinders,

INORGANIC SALT COMPOUNDS

Inexpensive salt mixtures have the potential of requiring up to 100 times less volume for low-temperature storage than a simple sensible-heat, water-storage system. The disadvantage of all such systems compared

with simple water storage is the need to use more complex heat exchangers, nucleating devices, and corrosion-resistant containers (if corrosive salts are used). The two categories of salt solutions which have received the most attention are inorganic salt hydrates and clathrate and semiclathrate hydrates.

If the concentrations of the components of a mixture are adjusted so that the mixture attains its lowest possible melting point, the mixture is termed "eutectic." In such a mixture, melting occurs at a constant temperature.³²

Inorganic salt hydrates are crystalline compounds of the general form $S \cdot nH_2O$, where S is an anhydrous salt. The hydrate dissolves when these compounds are heated, absorbing energy.

Clathrate and semiclathrate hydrates are compounds in which water molecules surround molecules of materials which do not strongly interact with water. These materials melt in the range of 00 to 30°C (30 to 860 F) and have heats of fusion which are in the range of 78-118 Btu/lb; most have not been studied in detail.³³ Materials suitable for use in connection with space heating (melting points in the range of 30° to 48°C (86° to 1180 F) and heats of fusion in the range of 66 to 120 Btu/lb.) include $Na_2SO_4 \cdot 10H_2O$ (Glauber's salts), $Na_2HPO_4 \cdot 12H_2O$, and $CaCl_2 \cdot 6H_2O$. Materials suitable for storing "coolness" (melting points in the range of 130 to 18°C (550 to 750 F) and heats of fusion in the range of 70 to 80 Btu/lb.) include eutectic salt mixtures such as mixtures of $Na_2SO_4/10H_2O/NaCl$, and $Na_2SO_4/10H_2O/KCl$.³⁴

³²See, for example, Walter J. Moore, *Physical Chemistry*, 3rd edition, Prentice-Hall, 1964, p. 148.

³³M. Altman, et al., *Conservation and Better Utilization of Electric Power by Means of Thermal Energy Storage and Solar Heating, Final Summary Report*, NSF/RANN/SEG127976/PR73/5, University of Pennsylvania, National Center for Energy Management and Power, July 31, 1973, pp. 6-51

³⁴Segaser, op. cit., p. 30.

³⁵St. E. Johnson, MIT, private communication, May 1978, R. Stepler, "Solar Lab Soaks Up Sunshine With Exotic New Materials," *Popular Science*, June 1978, pp. 96-98.

Many of the clathrates examined do not appear to melt in temperature regions useful for heating or cooling applications.

A technique for encapsulating a proprietary mixture of Glaubers salts, fumed silica, and other chemicals (melting temperature 730 F (230 C) in a polymer concrete shell has been developed by the Massachusetts Institute of Technology working in cooperation with The Architectural Research Corporation of Livonia, Mich., and the Cabot Corporation of Billerica, Mass. The storage elements are formed into units the size of standard ceiling tiles (2 ft x 2 ft x 1 in) and are designed to be installed as ceiling tiles in passively heated solar buildings. They store about 0.7 kWh/m² of ceiling area, and should sell wholesale for about \$32/m² in initial production (about 13 times the cost of standard acoustical ceiling tiles). The devices thus have an effective storage cost of \$39/kWh storage capacity. MIT does not expect prices to fall rapidly; apparently material costs already represent a large fraction of the cost of production. While the tiles can be hung on hangers similar to those now used for acoustical ceiling tiles, their greater weight, which is 54kg/m², requires the use of heavier gauge hangers.

The tiles, which will be marketed under the trade name "Sol-Ar-Tile," have been demonstrated in a 900 ft² passively heated solar house built by MIT's Architecture Department. Timothy E. Johnson, who heads the project, reported in May 1978 that tiles suffered no deterioration after accelerated lifetime testing, in which the tiles underwent 2,400 freeze-thaw cycles. The building uses specially designed window blinds which reflect sunlight from the southern windows to the ceiling. Johnson claims that the phase change medium is nontoxic.³⁵

ORGANIC COMPOUNDS

Organic compounds can also be used for storing energy as latent heat. These materials have the advantage of relatively high heats of fusion, and few of the materials examined present problems of supercooling or high vapor pressures. Unfortunately, some

of the most attractive organic materials under consideration (e. g., paraffins) have a relatively large volume change upon melting (nearly 10 percent in some cases), are flammable, and can cause stress cracking if the containment vessel is not constructed from a material as strong as steel. Experimental paraffin storage systems, however, have been operated successfully.³⁶

Materials suitable for heating include artificial spermaceti (manufactured by Lipo Chemicals) and paraffin wax (possibly mixed with carbon tetrachloride). These materials melt in the range of 350 to 50°C (95 °to 1220 F), and have heats of fusion on the order of 40 to 90 Btu/lb.³⁷ Materials such as Acetamide (CH_3CONH_2), Naphthalene (C_{10}H_8) and Propionamide ($\text{C}_2\text{H}_5\text{COHN}_2$) can be used to store energy at slightly higher temperatures, melting in the range of 820 to 83°C (180 °to 1830 F) and having heats of fusion in the range of 55 to 72 Btu/lb.³⁸ Materials suitable for storing coolness include paraffins and olefins with freezing points in the range of 30 to 80 C and heats of fusion in the range of 65 to 85 Btu/lb.³⁹

Concentrated Solutions

Concentrated solutions can also be used to store low-temperature energy without a phase change. It has been suggested, for example, that solutions of LiBr utilized in absorption air-conditioner systems could be used to store solar energy in the "generator" portion of an absorption unit.^{41 42} It has

³⁶A D Fong and C W Miller, "Efficiency of Paraffin Wax as a Thermal Energy Storage System," *Proceedings*, the 1977 Annual Meeting of I SE S, p 16-6,

³⁷Ibid, p 33

³⁸G A Lane, et al, *Solar Energy Subsystems Employing Isothermal Heat Storage Materials*, ERDA- 117, UC-94a May 1975

³⁹Segaser, op cit, p 33

⁴⁰J Baughn and A Jackman, *Solar Energy Storage Within the Absorption Cycle*. Paper delivered to the ASME meeting in New York, November 1974

⁴¹M Semmers, et al, *Liquid Refrigerant Storage in Absorption Air-Conditioning*. Paper delivered to ASME meeting in New York, November 1974

⁴²E H Perry, "The Theoretical Performance of the Lithium-Bromide-Water Intermittent Absorption Refrigeration Cycle," *Solar Energy* 17 (5), November 1975, p 321

also been proposed that a device similar in operation to an absorption air-conditioner could be used to provide heat from such storage, using an "absorption heat pump."⁴³ All such systems would require three storage tanks: one for the concentrated solution, one for water, and one for the dilute solution. The storage would not require insulation.

It is believed that approximately 65 Btu/pound of LiBr) could be stored in a system which uses sunlight to distill a solution of 66 percent LiBr to 54 percent.⁴⁴ A major drawback of using LiBr is the high cost of the material, but further study may reveal other less expensive salts with acceptable properties.

SALT STORAGE FOR OSMOTIC PRESSURE ENGINES

Energy can be generated from the osmotic pressure developed between salt solutions and freshwater. A system based on this principle is illustrated in figure XI-9. The concentrated saline solutions produced for use in such equipment can be stored in uninsulated tanks which can be quite inexpensive. A cubic meter of a salt solution comparable to water from the Dead Sea (27 percent salt by weight) can produce 1 to 2½ kWh in a reverse osmosis engine. " Figure XI-5 indicates that large tanks can be purchased for less than \$20/m³, and therefore brine storage can be achieved for about \$8 to \$20/kWh (or more if storage must also be provided for the freshwater distilled from solution). The use of covered ponds could result in substantially lower storage costs.

SALT SOLUTIONS FOR ENGINES USING LATENT HEAT OF MIXING

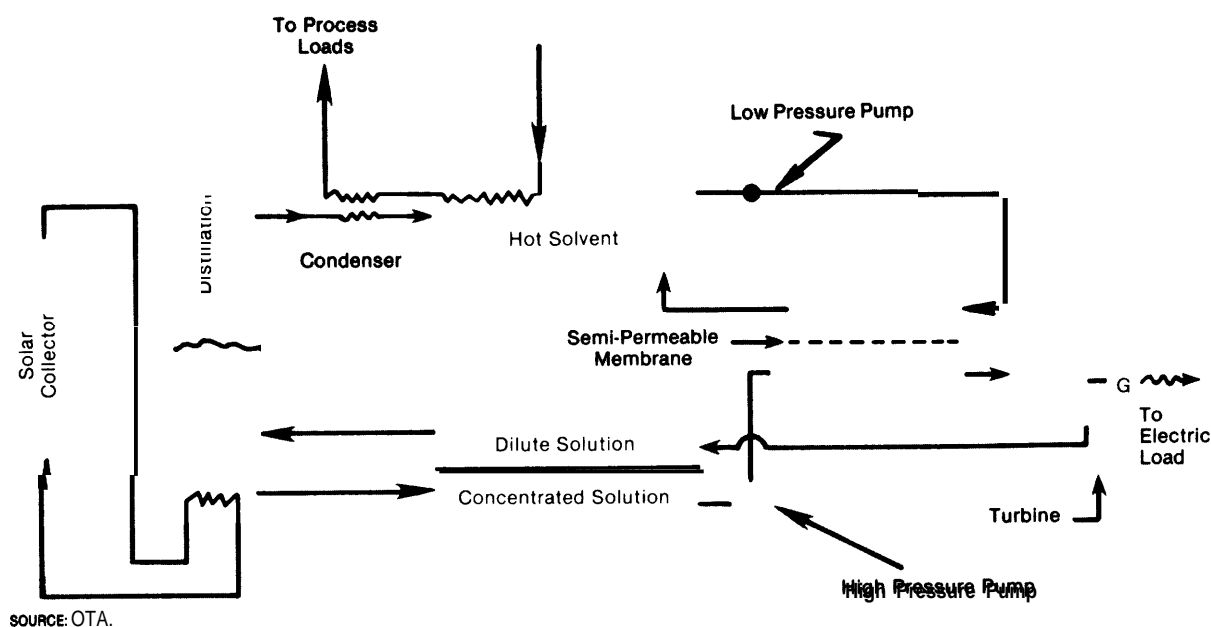
Engines can be operated from the latent heat released when concentrated solutions

⁴³Letter from Dr. Gary Vliet (University of Texas, Austin) to Dr Albert R Landgrebe (ERDA), Jan. 5, 1975

⁴⁴Gary Vliet, *ibid*,

⁴⁵S Loeb, et al., "Production of Energy from Concentrated Brines by Pressure Reduced Osmosis: I Experimental Results and Projected Energy Costs," *Journal of Membrane Science*, (1), p. 264(1 976)

Figure X1-9.—Osmotic Pressure Engine



of some types of salt are mixed with water (see figure XI-10). Energy is released when water is introduced and aqueous solutions are formed. A study of this effect has estimated that if energy is stored in the form of dry NaOH, the density of the energy stored is 135 kWh/m³, and if energy is stored in the form of dry ZnCl₂, CaCl₂, MgCl₂, LiBr, and LiCl, the energy storage density is about 80 kWh/m³.

CHEMICAL REACTIONS

There is growing interest in the possibility of storing energy for low-temperature applications in chemical form, but work is in a very preliminary stage and no practical systems have yet emerged. 46 A recent ex-

ploratory survey indicated that photochemical reactions can be competitive with other low-temperature thermal storage systems if they are capable of 25-percent conversion efficiency and energy storage at more than 158 Btu/lb. (88 cal/g), or 40-percent efficiency and 81 Btu/lb. (45 cal/g).

One of the few low-temperature reactions which has been studied involves the use of metal hydrides. The reactions are of the general form $M + (x/2)H_2 \rightleftharpoons MH_x$, where M is a metal or alloy such as LaNi₅, SmCo₅, or FeTi. These materials are capable of storing between 45 and 92 Btu per pound of hydride (0.029 to 0.059 kWh/kg), if storage temperature is held at 2000 F and initial hydride temperature is 700 °F.⁴⁹

Energy is stored when the hydride is heated, releasing the gas, and recovered when hydrogen recombines with the metal. Recent investigations at the Argonne Na-

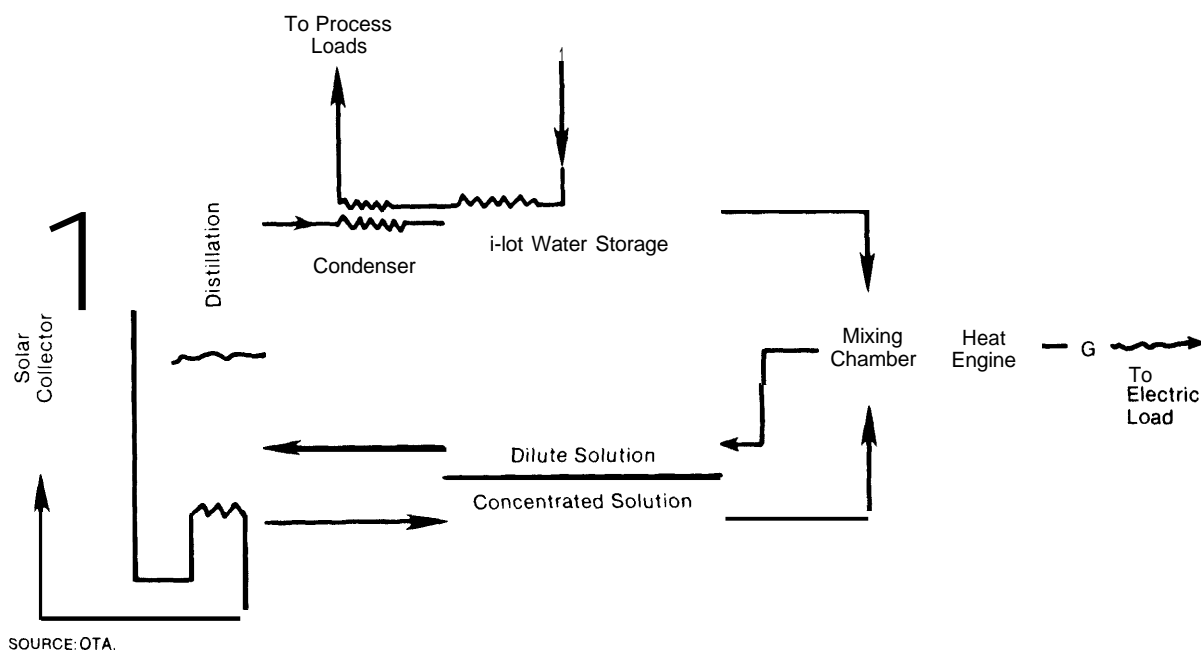
⁴⁶N. Isshiki, et al., "Energy Conversion and Storage by CDE (Concentration Difference Energy) Engine and System," Proceedings, the 12th Intersociety Energy Conversion Engineering Conference, Washington, D.C., Aug. 28-Sept. 2, 1977 (American Nuclear Society, La Grange Park, Ill.), page 1117.

⁴⁷G. S. Hammond, "High Energy Materials by Charge Transfer and Other Photochemical Reactions," ACS 122nd Meeting, San Francisco, Cal if., September 1976.

⁴⁸S. C. Talbert, et al., "Photochemical Solar Heating and Cooling," Chemtech, February 1976, p. 122.

⁴⁹G. G. Libowitz, "Metal Hydrides for Thermal Energy Storage," Proceedings, the 9th Intersociety Energy Conversion Engineering Conference, San Francisco, Cal if., Aug. 26-30, 1975, p. 324 (Quoted in Segaser, pp. 37-38.)

Figure XI-10.— Heat of Mixing Engine



tional Laboratory have demonstrated the feasibility of hydride storage for both heating and cooling applications ⁴⁰

The possible costs of several of the low-temperature thermal storage systems discussed in the previous sections are summarized in figure XI-11. The techniques used to compute these costs are explained in appendix XI-B,

THERMAL STORAGE AT INTERMEDIATE AND HIGH TEMPERATURES

Table XI-3 lists the properties of some of the materials which can be used to store thermal energy at high temperatures. Rock storage was treated in the previous section. The following discussion examines sensible heat storage in refractory bricks, iron ingots, and hot oils.

⁴⁰James H Swisher, Director of the Division of Energy Storage Systems, Office of Conservation, ERDA, letter to OTA dated Mar 30, 1977

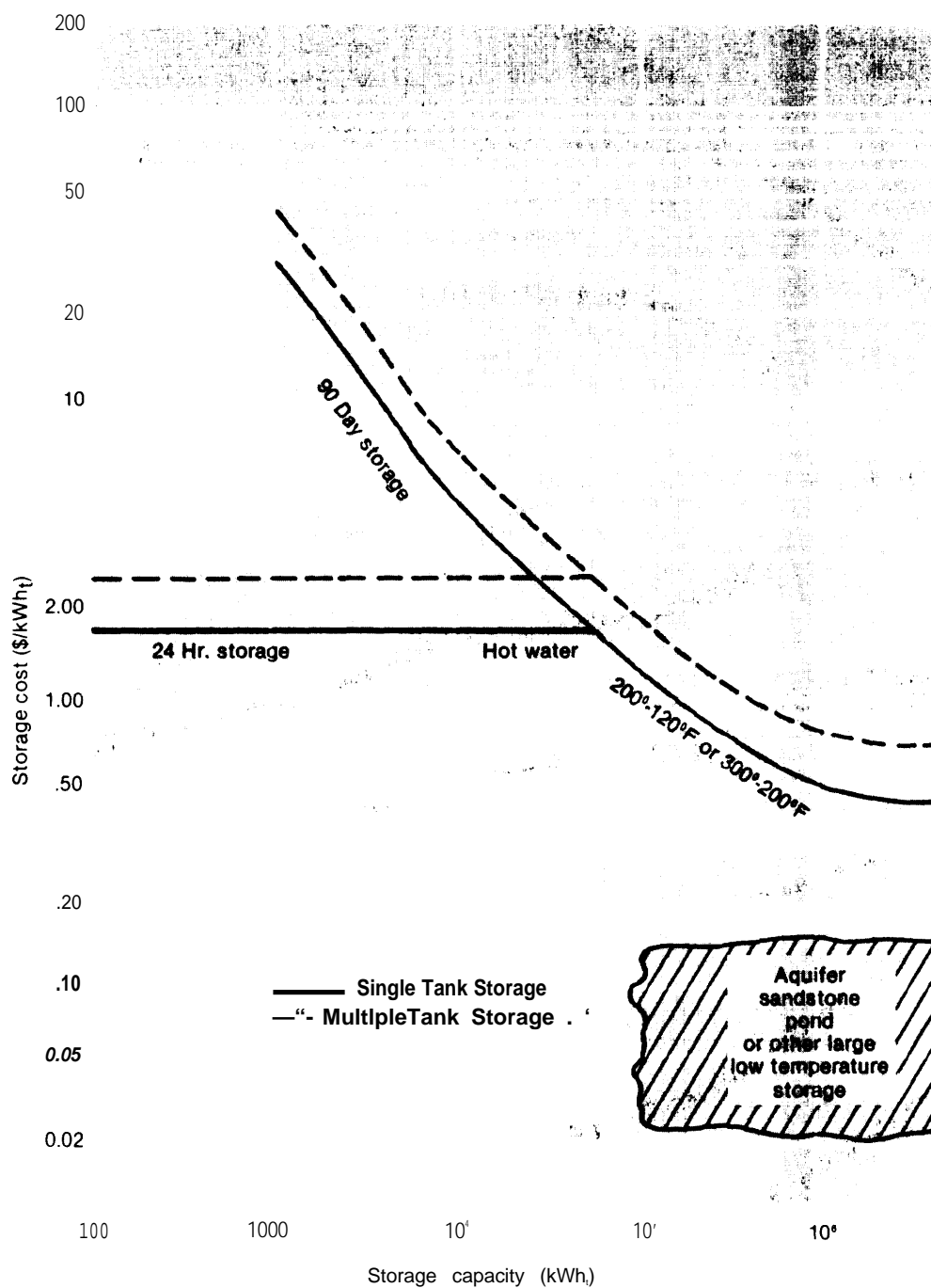
Refractory Bricks

Devices capable of storing energy in magnesium oxide bricks at temperatures up to 600 °C (1,120 F) have been commercially available in England and Western Europe for many years; the original patents date back to 1928. They are in buildings so that customers can charge the storage from the relatively inexpensive electricity available in these areas at night; during the day, homes and offices can be heated from the systems in the same way that a baseboard resistance heater would be used. In 1973, both Great Britain and West Germany had installed enough such devices to provide nearly 150,000 MWh of storage capacity^{51 52} for leveling the loads placed on their electric utilities. Devices such as the one shown in figure XI-12 are beginning to appear on the U.S. market in areas where *time-of-day*

⁵¹Gunter Mohr, *Electric Storage Heaters*, AE G-Telefunken Progress, (1970), 1, p 30-39

⁵²J G Ashbury and A. Kouvalis, *Electric Storage Heating: The Experience in England and Wales and in the Federal Republic of Germany*, ANL/E S-50(1976)

Figure XI-11.— Low-Temperature Thermal Storage Cost per kWh,
Versus Storage Capacity



NOTE:

The storage units would lose only about 5 percent of the energy stored in the interval indicated. This cost is based on precast concrete and coated steel, and excludes 25 percent O&P

Table XI-3.—Candidate High-Temperature Thermal-Energy Storage Materials Without Phase Change

Sensible-heat storage between 77° F and 900° F					
Material	Density (lb/ft ³)	Btu/lb	Btu/ft ³	Price (1971 \$) (\$/100 lb)	output (Btu/\$)
Al	168	200	34,000	29.00	690
A 1 ₂ (SO ₄) ₃ . . .	169	202	34,000	3.11	6,500
Al ₂ O ₃	250	200	50,000	2.20	9,100
CaCl ₂	135	135	18,000	2.20	6,000
MgO	223	208	46,000	2.80	7,400
KCl	124	140	17,400	1.65	8,500
K ₂ SO ₄	167	180	30,000	1.10	16,400
Na ₂ CO ₃	160	265	42,500	4.00	6,600
NaCl	136	180	24,500	1.33	13,500
Na ₂ SO ₄	168	247	41,500	1.50	16,400
Cast Iron	484	102	49,500	10.00	1,000
Rocks	140	160	22,500	1.00	16,000

SOURCE M. Altman, et al *Conservation and Better Utilization of Electric Power by Means of Thermal Energy Storage and Solar Heating, Phase I Summary Report*, NSF Grant 7976, University of Pennsylvania National Center for Energy Management and Power, Oct 1, 1971, pp. 2-10

rates have been introduced. The units typically sell for \$20 to \$40/kWh. ⁵³

Some thought has been given to using these bricks to provide high-temperature storage for a solar-powered gas turbine system. In one proposal, helium from a receiving tower would be passed through a pressure vessel containing refractory bricks, heating the bricks to about 530°C (986 °F). It is estimated that such a device could be constructed for \$11 to \$14/kWh. ⁵⁴

Steel Ingot Storage

A system for using steel or cast-iron ingots to store high-temperature energy for use in a steam electric-generating plant has been proposed by Jet Propulsion Laboratory (JPL). ^{55 56} This device, illustrated in figure XI-1 3, consists of an assembly of pipes with rectangular external cross sections. Super-

heated steam is passed through the pipes for charging and discharging. It should also be possible to maintain a significant temperature gradient along the length of the storage unit for several days (see appendix XI-B). The predicted performance of a large device is illustrated in figure XI-14. Like the MgO (magnesium-oxide) storage system, this device has the advantage of great simplicity, it has virtually nothing to wear out, no heat exchangers to clog, and no scarce or toxic materials are required. It has an advantage over the brick storage system in that a pressure vessel is not required to contain the heat-transfer fluid—the steel pipes provide the needed containment. For this reason, the cost should be slightly less expensive per unit of energy stored. ⁵⁷

It should be possible to build a steel ingot storage system with relatively little develop-

⁵³J. G. Ashbury, et al., "Commercial Feasibility of Thermal Storage in Buildings for Utility Load Leveling," presented to the American Power Conference, Apr. 18-20, 1977, Chicago, Ill.

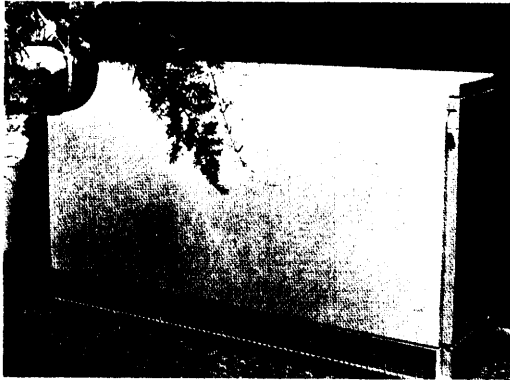
⁵⁴W. D. Beverly, et al., "Integration of High Temperature Thermal Energy Storage into a Solar Thermal Brayton Cycle Power Plant," 12 IECEC Conference, p. 1195

⁵⁵Beverly, op cit, p. 1199

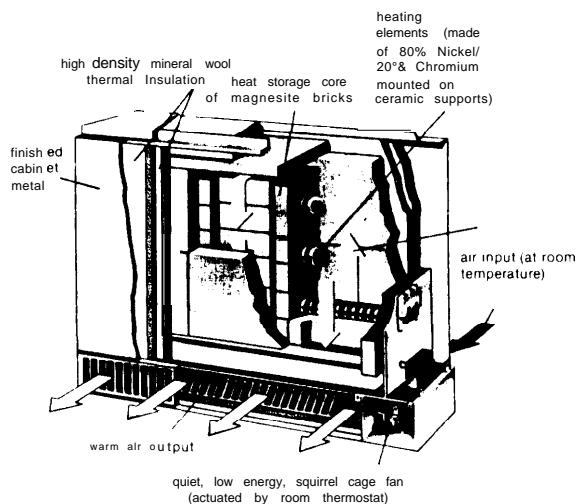
⁵⁶Program Review, Comparative Assessment of Orbital and Terrestrial/ Central Power Systems, October 1975- January 1976, JPL, p. 16

⁵⁷R. H. Turner, J. P. L., "Thermal Energy Storage Using Large Hollow Steel Ingots," *Sharing the Sun: Solar Technology in the Seventies*, joint Conference, American Section, International Solar Energy Society and Solar Energy Society of Canada, Inc., Winnipeg, Canada, Aug. 15-20, 1976, Vol. 8, pp. 155-162.

Figure XI-12.—A High-Temperature Thermal Storage Device Designed for Residential Use



A storage/heating unit installed in a home



An interior view of the unit showing the magnesium bricks, heating elements and air blower

SOURCE Control Electric Corporation Burlington, VT

ment work since most of the properties of the system can be computed with considerable precision. Since the system uses high-pressure steam, considerable care must be taken if it is used in onsite applications, but existing boiler codes should be able to ensure adequate safety. Lower pressures can be employed if the system uses a heat-transfer fluid other than steam.

Figure XI-13.—Steel-Ingot, Sensible-Heat Storage System

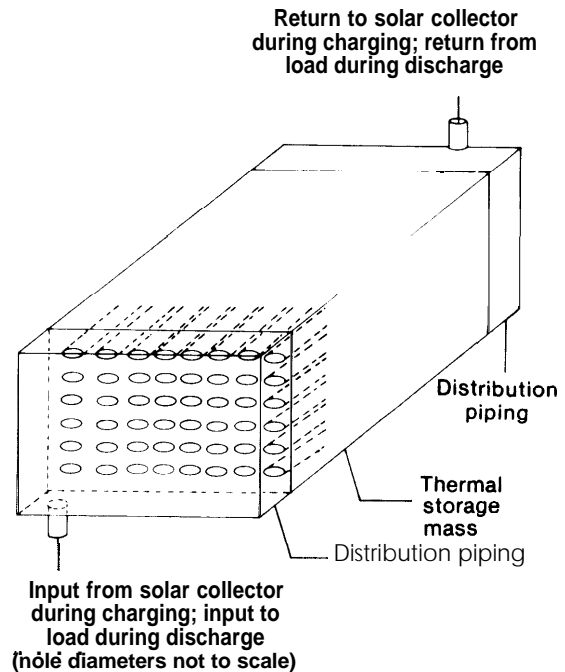
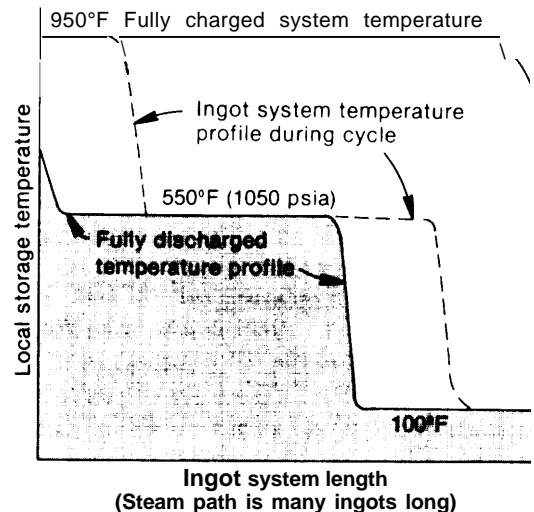


Figure XI-14.—Steel-Ingot Temperature Profiles at Various Times in a Typical Cycle



SOURCE:
R. H. Turner (JPL), "Thermal Energy Storage Using Large Hollow Steel Ingots," *Sharing the Sun: Solar Technology in the Seventies*.
Joint Conference, American Section, International Solar Energy Society and Solar Energy Society of Canada, Inc. Winnipeg, Canada, Aug. 15-20, 1976, Volume 8, page 160.

It may be possible to reduce the cost of the system by replacing some of the volume of metal with concrete. Concrete costs about a third as much as steel and could easily be formed around a matrix of separate steel pipes. The practical difficulties of constructing such a system have not been evaluated, however. The performance of the system could be degraded significantly if the concrete separated from the steel tubes; this may create problems even though concrete and steel have nearly the same coefficients of expansion. Another difficulty would be the relatively poor heat transfer between concrete and steel. Concrete itself has low conductivity, and cracks could further reduce its conductivity.

Heat-Transfer Oil Thermal Storage

Some of the sensible-heat storage systems utilize a mixture of rocks and a heat-transfer fluid such as Therminol. The properties of some common commercial heat-transfer liquids are listed in table XI-4. Sandia Laboratories in Albuquerque chose a system using Therminol-66 and rocks for storing energy in its total energy *system*. This system, shown in figure XI-1 5, has been operated successfully since early 1976. A mixture of Caloria HT43 and granite rock storage was chosen by McDonnell-Douglas for storing energy generated by their central receiver design. Martin-Marietta chose to use a sensible-heat storage system with two stages — a high-temperature stage for superheating, using HITEC as the storage medium, and a low-temperature stage using a heat-transfer oil. Each stage has two tanks for high performance.

All heat-transfer oils share a common set of problems. They all degrade with time, and their degradation is increased rapidly if they are operated above their recommended temperature limits for any length of time. This degradation requires a filtering system and means that the relatively expensive oils must be continually replaced. The oils also can present safety problems, since they can be ignited by open flames at temperatures in the range of 3000 F (fire point) and have a

high enough vapor pressure to sustain combustion at temperatures in the range of 600 ° to 1,000 F (ignition temperature). This means that great care must be taken to ensure that the material is not overheated. Dikes will be needed to prevent the material from spreading if a leak should occur. Some systems require an inert gas (such as nitrogen) over the liquids in the tanks to inhibit reactions which might degrade the storage material. The behavior of the rock-oil mixtures over long periods of time remains an open question, since little experimental evidence is available. The rocks may tend to crack, and the apertures between them may clog with degraded oil.

Refined Fuel Oil Thermal Storage

A thermal storage system proposed by EXXON eliminates the problems of degradation and clogging by using a relatively inexpensive fuel oil without rocks.⁵⁸ This system uses specially refined oil that does not degrade with time, but it can only be used at up to 530° F (277 °C). The oil is estimated to cost \$146/m³ (installed, excluding operations and maintenance) and, if necessary, can be used as fuel at any time.⁵⁹ Its specific heat is 0.795 kWh~Jm³°C.bo

An EPRI study estimates the installed cost of insulated tankage, including an inert gas system to exclude oxygen, to be \$91/m³ of oil for a two-tank system. Oil handling facilities, such as pumps, piping, and heat exchangers, are power related, rather than energy related, and cost \$288 per installed kW_m of capacity .61

⁵⁸An Assessment of Energy Storage Systems Suitable for Use by Electric Utilities, EM-264, EPRI Project 225. ERDA E (11-1) 2501, Final Report Prepared by Public Service Electric and Gas Company, Newark, NJ

⁵⁹Ibid , pp 4-40

⁶⁰Ibid , pp 3-48

⁶¹ Ibid , pp 4-41 Converted from \$144 kW_e using 0.4 kW_e kW_{th} and 1.25 O&P factor

Table XI-4.—Commercial Organic and Inorganic Heat-Transfer Agents

	Therminol- 55 ^a	Therminol- 66 ^a	Caloria-HT- 43 ^a	Dowtherm- A ^a	Humble- therm 500 ^a	HITEC ^a	Refined fuel oil ^b (see text)
Producer	Monsanto ^c	Monsanto ^c	EXXON ^c	Dow Chemical ^d	Humble Oil	E. I. Dupont	EXXON ^c
Highest usable temp (°C) = T_{max}	316	343	316	260	316	500	277
Lowest usable temp: (°F)	601	649	601	500	601	932	531
(°C)	-18	-4	—	-11	-21	142	—
(°F)						288	
Fire point (°C)	210	193	—	135	246	—	—
Autoignition temp(° C)	354	374	404	621	—	—	—
Specific heat (Btu/lb °F) ³ (or cal/gm°C) . .	0.72	0.655	—	0.537	0.7165	0.4	0.70
Viscosity (lb/ft-hr) ^e	1.1	0.649	—	0.65	1.01		—
Thermal conductivity (Btu/hr-ft° F °)	0.065	0.0612	—	0.0645	0.0655		0.68
Density (lb/ft ³)	43	50		53	41.3	112	—
Heat capacity (Btu/ ft ³ ° F) ^e	31	32.8		28.5	29.6	44.8	38.21
Cost (\$/lb)	0.38	0.81	0.26	0.71		0.25	
cost (\$/ft ³)	16.34	40.50		37.63		28.00g	4.13
Mills/Btu (assuming $\Delta T = T_{max} - 50^{\circ}\text{C}$ and perfect thermal gra- dient)	1.1	2.3	$S.2^f$	3.5		0.99	0.26
Mills/Btu (assuming complete mixing and allowing T_{max} to fall to $(T_{max}/2) + 25^{\circ}\text{C}$)	2.2	4.6	6.4	7.0		2.0^h	0.53

^a Compiled by Hoffman (ORNL) and Tas Bramlette (Sandia, Livermore)

^b Energy in 011," IEEE Power Engineering Society Summer Meeting, Portland, Oreg., July 1976

^c Requires nonoxidizing cover gas

^d Requires pressurization for temperatures above 260°C

^e Property at maximum usable temperature.

^f $\Delta T = T_{max} - 83^{\circ}\text{C}$

^g $\Delta T = T_{max} - 150^{\circ}\text{C}$

^h ΔT_{max} falls to $(T_{max}/2) + 75^{\circ}\text{C}$

At least one design for such a hot-oil energy storage system for use with a 1,000 MW nuclear powerplant has already been completed, and the EPRI study classifies this technique as "a near-term solution with certain economic advantages over other storage systems."⁶²

Latent-Heat Systems

Heat-of-fusion systems using inorganic salt mixtures have a distinct advantage for storing energy at high temperatures, since they can reduce storage volumes and provide more energy at constant temperatures. The major disadvantages have been the costs of the materials required and the problem of developing adequate heat transfer between the storage material and the working fluid. Two designs which have been used in devices designed to store energy for space conditioning are illustrated in figures XI-16 and XI-17. The Comstock and Wescott design uses relatively inexpensive materials: NaOH mixed with corrosion inhibitors. The unit shown consists of six modules containing sodium hydroxide which was heated with electricity. The unit has been redesigned to use steel pipes rather than the panels shown.^{63 64 65} A similar approach has been proposed by JPL for use in a central station powerplant. In their approach, a bundle of tubes is imbedded in a long cylindrical tank (in the central station design, the tanks were 60 feet long and 12 feet in diameter) filled with sodium hydroxide. The steam or other heat-transfer liquid is sent through the tubes to extract or to supply energy to the storage medium. The tubes

must be closely spaced to permit acceptable rates of heat transfer since sodium hydroxide has a relatively small heat conductivity. JPL estimated that such a system could store 52 MWh, if the temperature swing were between 6500 and 4000 F and would cost about \$13/kWh. A major problem with these systems is that the highly corrosive nature of NaOH (lye) demands expensive containment to prevent leaks.

The Philips Corporation has investigated a number of materials for possible use in a phase-change storage system. Lithium fluoride has received the most attention because of its extremely large latent heat of fusion, but other less expensive materials have also been examined for use in the Philips design.⁶⁶ Other fluoride compounds, for example, have extremely large latent heats.

The properties of a variety of salt compounds which might be considered for use in phase-change storage systems are illustrated in table XI-5 and their thermodynamic behavior is illustrated graphically in figure XI-18. It can be seen that the sodium hydroxide material appears to have an advantage in the temperature regime appropriate to conventional Rankine cycle systems, while fluoride compounds (such as the NaF/MgF₂ mixture) appear to have an advantage when used in connection with engines operating at very high temperatures such as Brayton or Stirling cycle devices.

In general, the nitrates and nitrites are relatively inexpensive and do not corrode their containment vessels, but they tend to decompose at temperatures above 4000 to 500 °C. The hydroxide eutectics can operate at high temperatures, but become corrosive and thus require corrosion-resistant alloys. Carbonates have good thermophysical properties, but also decompose at high temperatures unless a cover gas of CO₂ is used in the tanks. Chlorides and fluorides have high specific heats, conductivities, and latent heats,

⁶²Ibid, pp 3-51 The completed study is referenced as R P Cahn and E W Nicholson, *Storage of Off-Peak Thermal Energy In Oil*, Approved by I E E Power General Committee, Paper No A76 326-9 Summer 1976

⁶³Comstock and Wescott, Inc., "First Step of Heat Storage Research Activity of Heat Storage Systems," *EEIBull.*, June 1959

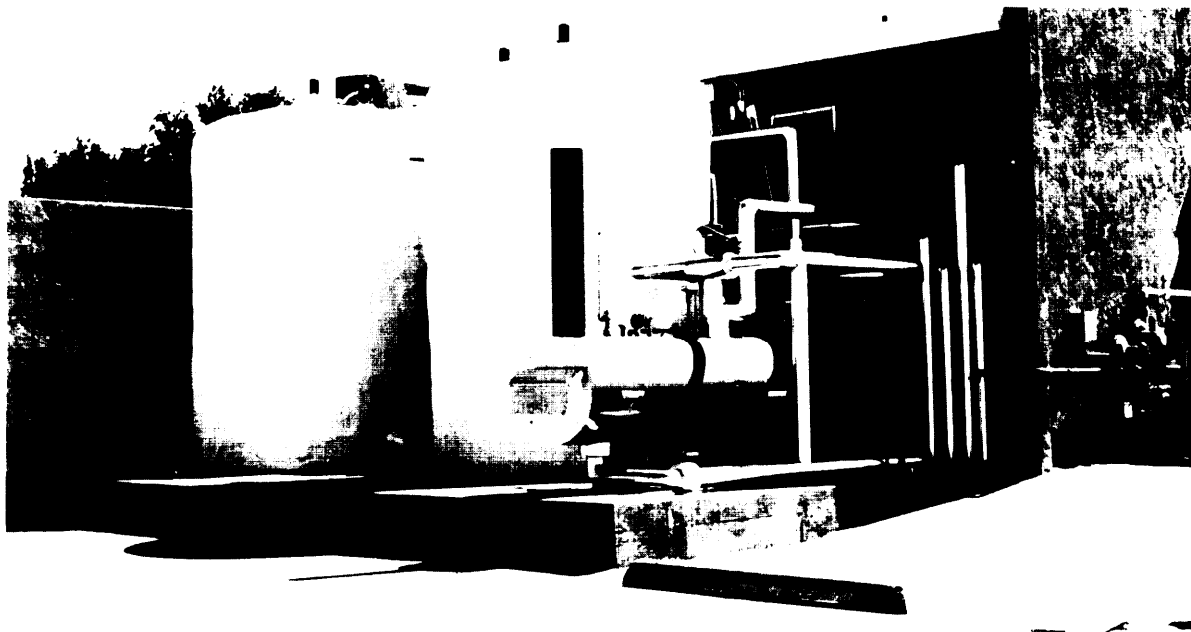
⁶⁴Comstock and Wescott, Inc., "Promising Heat Storage Material Found Through Research," *EEIBull.*, February 1962, p 49

⁶⁵R H Turner (J PL), private communication, June 9, 1976

⁶⁶R H Turner (J PL), private communication, June 9, 1976

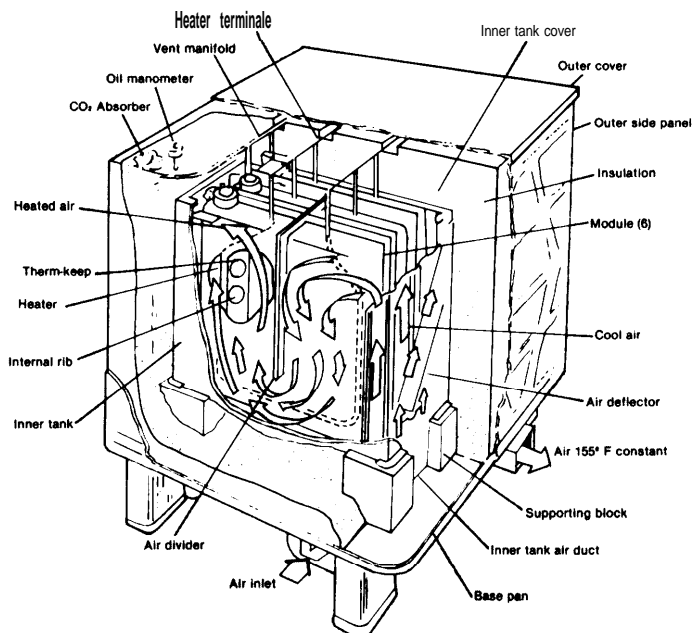
⁶⁷J Schroder (N.V Philips Aachen Lab), *Thermal Energy Storage*, N V Philips publication

Figure XI-15.— The High-Temperature Heat Storage System at the Sandia Total Energy Experiment



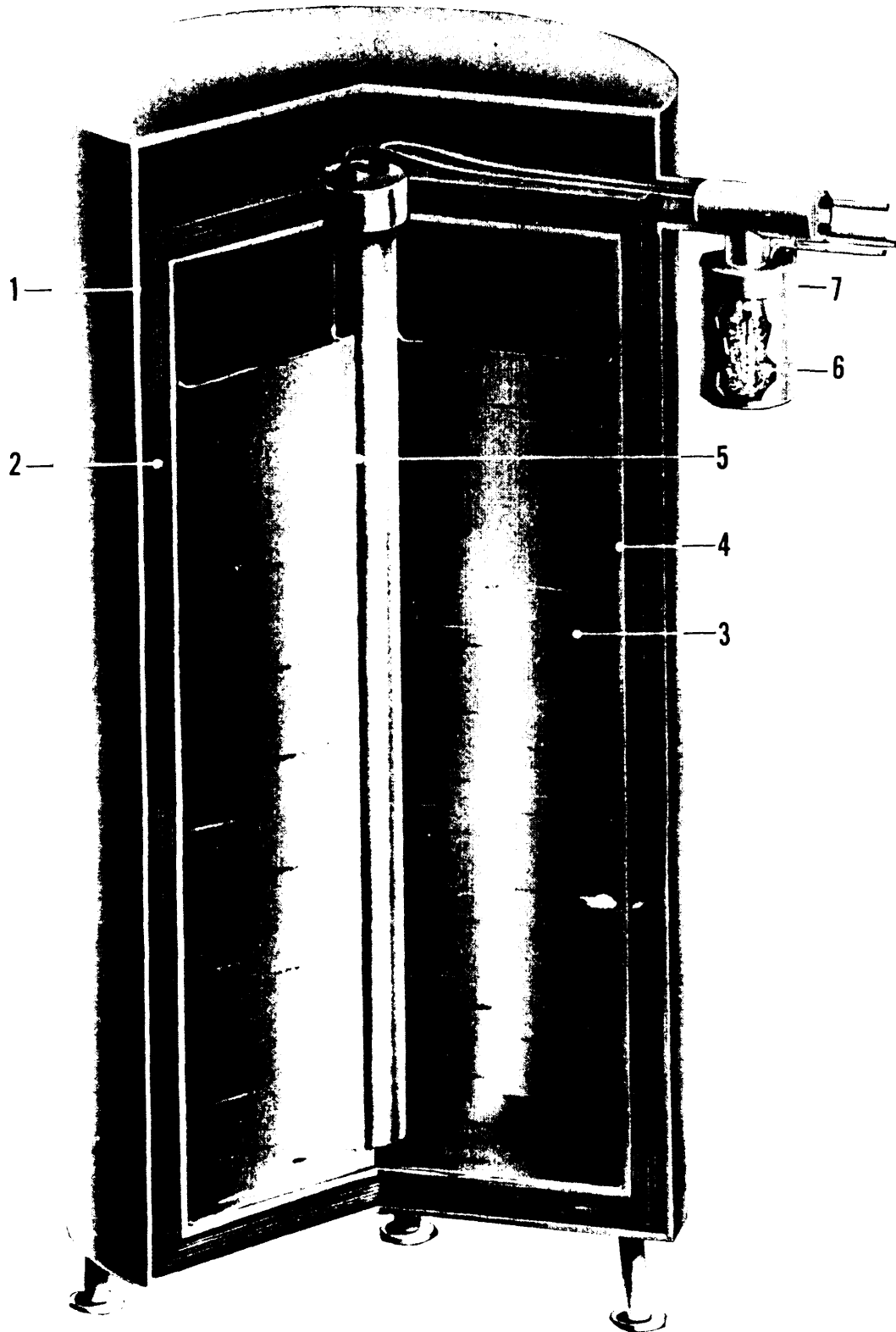
photograph by John Furber

Figure XI-16.— Design of "Therm-Bank" Space Heater



SOURCE
R E Rice, *Thermal Storage Application to Energy Conservation* Comstock and Wescott, Inc April, 1975 Reprinted in
Bramlette, et al. SAND75-8083 page 42

Figure XI-17.— Philips Latent-Heat Storage System With Vacuum Multifoil Insulation



SOURCE N.V. Philips

Table XI.5.—Properties of Latent-Heat Thermal Storage Materials

Storage material (mole %)	NaOH	NaF/MgF ₂ (75/25)	B ₂ O ₃	LiF/NaF/MgF ₂ 46/ 44/ 10	NaN ₃	LiF
Melting point °C.	320a	832b	450c	632d	310c	845c
°F.	608	1530	842	1170	590	1553
Density at m.p. (kg/m ³) .	1784	2190b	1571 c	2105d	1916c	1829c
(most bulky phase)*	(liq)	(liq)	(liq)	(liq)	(liq)	(liq)
Heat of fusion (ΔH _{pc}) .	0.0442c	0.174b	0.092d	0.226	0.0481	0.290
(kWh/kg)	0.0442**			(e)	(c)	(c)
Specific heat at m. p.	5.89 x 10 ⁻⁴ a	4.1 x 10 ⁻⁴ **	4.48 x 10 ⁻⁴ d	4.88 X 10 ⁻⁴	5.06 X 10 ⁻⁴	6.69 X 10 ⁻⁴
solid (C _p) (kWh / kg°C)	(below 295° C)					
	5.97 x 10 ⁻⁴ (a)			(e)	•••	(d)
	(above 295° C)					
Specific heat at m. p., liquid (C _p) (kWh /kg° C)	5.75 x 10 ⁻⁴ c	4.07 x 10 ⁻⁴ e	5.09 x 10 ⁻⁴ d	4.88X 10 ⁻⁴ ••	5.058 X 10 ⁻⁴	6.94 X 10 ⁻⁴
					(c)	(c)
Heat capacity (m. p.-50° C to m.p. + 50° C) (kWh/ m ³)	262	471	205	578	189	655
Present price (\$/kg)	0.55f	1,10-0.55g	0.20	2.20	0.57	5.56h
(\$/m ³)*	983	2400-1200	312	4641	1098	10,161
Material cost (\$/ kWh ca- pacity) (m. p. -50° C to m.p. + 50° C)	3.75	5.10-2.55	1.52	8.02	5.81	1551

* Volume of storage container must be large enough to accommodate most bulky phase

.. Solid/solid phase change at 295° C (563° F)

... Estimate based on specific heat of other phase

aKubaschewski, O., et al (National Physical Laboratory, Middlesex), *Metallurgical Thermochemistry* Fourth Ed Pergamon Press Ltd., 1967bSchroder, J (N V Philips Aachen Lab), "Thermal Energy Storage Using Fluorides of Alkali and Alkaline Earth Metals," *Proceedings of the Symposium on Energy Storage* The Electrochemical Society, Inc., 1976cJanz, G J (Rensselaer Polytechnic Institute), *Molten Salts Handbook* Academic Press Inc., 1967dWicks, c E and F E Block (U S Bureau of Mines), *Thermodynamic Properties of 65 Elements — Their Oxides, Halides, Carbides and Nitrides* Bulletin 605, Bureau of Mines, 1963

eSchroder, J (N v Philips Aachen Lab), private communication, Jan 13, 1977.

f*Chemical Marketing Reporter* Vol 210, No 10, Sept 6, 1976 100 lb drums of U S Pharmacopia NaOH in truckload quantities

g\$0.55/kg is a cost estimate made by N V Philips, based on the use of waste materials from fertilizer manufacturing Present cost is \$110/kg

hLithium Corporation of America quotation, Sept 15, 1976, for 99.5% LiF in lots greater than 5 tons This material is proposed for use in Philips space heat storage system

m.p. — melting point

(liq)—liquid phase

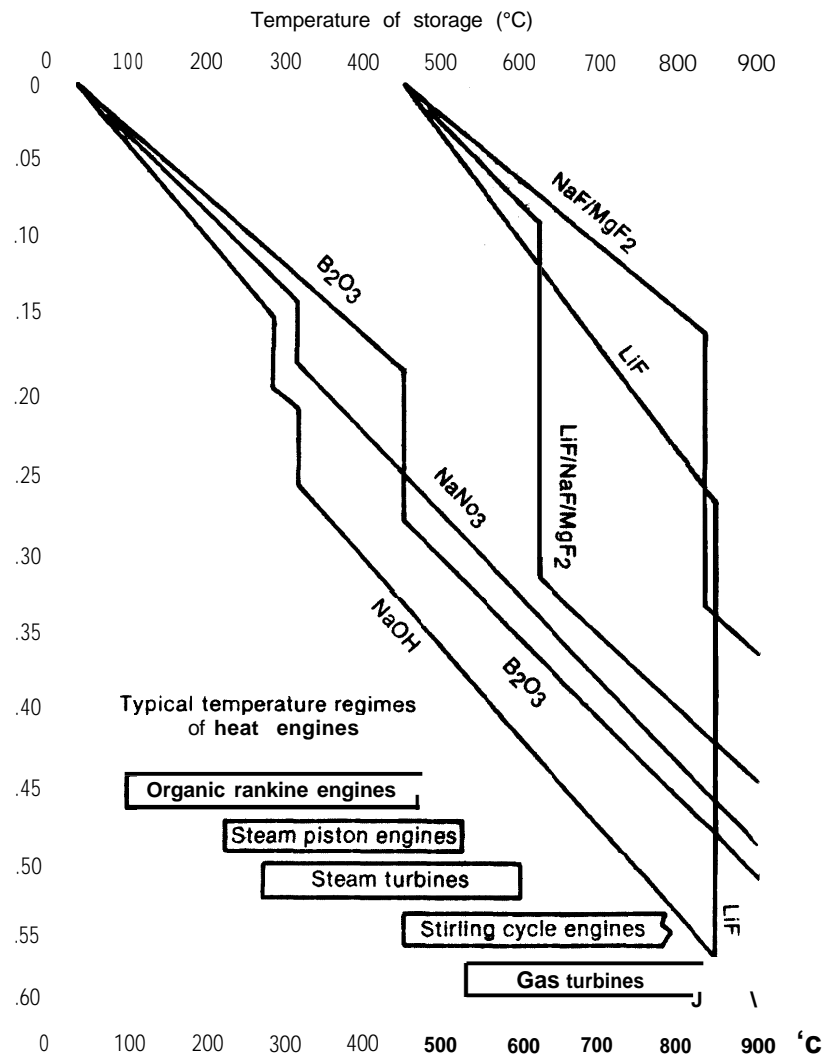
but tend to be higher in cost and can have corrosive properties. Phosphates and sulfates are very corrosive.

If the latent-heat storage system can be located very close to the collectors, it may be possible to use a heat-pipe system to convey the energy from a collector to storage. Extensive surfaces would have to be affixed to the heat pipes to produce sufficient heat-transfer surface area in the storage medium. This may be feasible since the latent-heat

systems are capable of storing a large amount of energy per unit weight. The storage could be mounted directly on a tracking dish, or it could be physically close to an engine mounted at the top of a tower.

Heat pipes operate most effectively if their working fluids have pressures in the range of 1 to 10 atmospheres. Both sodium and potassium have these pressures in temperature ranges of 600 to 1,000 °C. The technology of sodium-vapor heat pipes has

Figure XI-18.—Thermodynamic Behavior of Candidate Latent-Heat Storage Salts



SOURCE Table XI 7

been thoroughly investigated, and pipes made of relatively low-cost "type-304" stainless steel are predicted to have lifetimes of 10,000 hours.¹⁹ This lifetime corresponds to only a little more than a year of continuous operation for a generating system, and further improvements are needed if an ac-

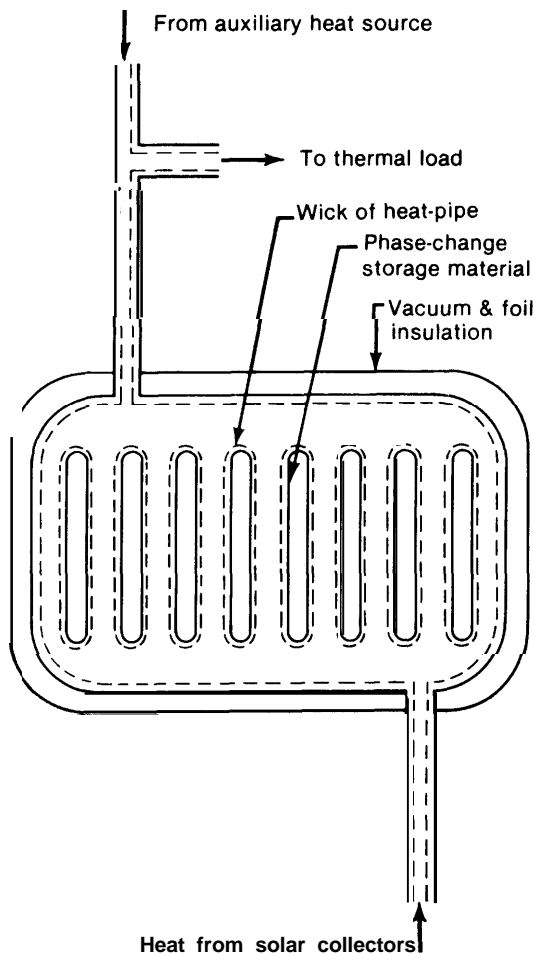
ceptable generating system is to be designed. Such improvements are expected, but design research and much more operating experience is needed.

A Philips design employing a heat-pipe and a phase-change storage system is illustrated in figure XI-19. When the storage is being "charged," the liquid sodium flows to the collector where it is vaporized and returns as a gas to the storage vessels. (Electric pumps for moving sodium without moving

¹⁹G A A Asselman, et al., "Heat Pipes," *Philips Tech. Review*, Vol 33, No 4 (1970), p 104

²⁰C A A Asselman, et al., "Heat Pipes," *Philips Tech Review*, Vol 33, No 5 (1970), p 168

Figure XI-19.—Use of a Sodium Heat Pipe With a Latent-Heat High-Temperature Thermal Storage System



SOURCE: Drawn by OTA using N. V. Philips concept.

parts have been developed by the breeder reactor program.) The vapor condenses on the storage containers, giving the energy of vaporization gained at the collector and the cycle begins again. When the system is being discharged, the vapor is generated by the storage vessels and condensed in a heat exchanger sending energy to a heat engine. If auxiliary power is needed to supplement the solar energy, a separate heat exchanger can be built into the heat-pipe loop to permit running the engine from fossil fuels.

If these low-pressure sodium or potassium heat-pipe systems could be developed, they would be very attractive. They should not require extensive maintenance or a trained

operator, and they do not appear to present any serious safety problems. Release of the sodium from the system could be hazardous, but only very small amounts of sodium are required in the system per-unit-of-power output.

Unfortunately, there remains a substantial amount of disagreement about the performance capabilities of phase-change systems. N.V. Philips and others feel that while a substantial amount of design engineering needs to be performed, most of the major development problems associated with heat exchangers, average cycle efficiency corrosion resistance, and development of low-cost materials have been resolved.⁷⁰ On the other hand, others are still having substantial development problems and feel that a considerable amount of fundamental development work is needed. Only more research and the fabrication and testing of real devices will resolve these debates.

Environmental Concerns

The environmental problems associated with the use of high-temperature thermal storage devices have not been explored in detail, although a preliminary survey of the issues has been conducted.⁷¹

Some of the oils proposed for use as heat transfer fluids or as storage materials can be explosive. Care will have to be exercised in the construction and operation of these systems, particularly if they are integrated into systems close to populated areas. Most oil storage tanks must be covered with an inert gas such as nitrogen to minimize the risk of explosion when the oil is heated. Leaking tanks could result in fires; earthen dikes or dams would be required around large tanks built above the ground. The risk would be reduced if underground storage were used. Care would also be essential when the ther-

70). Schroder (N V Philips Aachen Lab), private communication, Jan 13, 1977

71) John G. Holmes, "Environmental and Safety Implications of Solar Technologies" *Proceedings*, the 1977 annual meeting of the American Section of the International Solar Energy Society, p. 28-5

ma storage materials are discarded after a system is dismantled or when fluids are replaced if they have been damaged or degraded with repeated thermal cycles. The oils would typically be dumped into city sewage systems.

THERMOCHEMICAL STORAGE

Background

Recent interest in thermochemical reactions for storing energy has been motivated primarily by a desire to find a way to store and transport energy generated by nuclear plants.^{72, 73} Like the heat of fusion storage systems, chemical storage has the advantage of being able to produce heat at constant temperature. It has the additional advantage of not requiring insulated storage tanks. Some chemical systems could allow storage densities many times higher than any other types of thermal storage. A variety of reactions have been examined, and there appears to be no technical barriers to using a number of them in connection with solar collectors.

The problems remaining involve both the need to understand much more about the fundamental chemistry of some simple reactions which have never been examined in detail, and the engineering details of converting laboratory reactions into reliable commercial products. It is also possible to use the energy stored in chemical reactions to transport energy from collectors to a storage vessel. The "Solchem" process, for example, being examined by the Naval Research Laboratory, uses the SO_3/SO_2 reac-

tion to transfer heat to a latent-heat storage system.⁷⁴

Developing procedures which will be useful for onsite applications may be difficult, since many of the reactions being examined are quite complex. Frequently, the reaction in the collector is simpler to control than the reverse reaction. In this case, a series of distributed onsite collectors could be used to feed a common collection pipe network which operates an electric-generating device at a central facility. If hydrogen or other easily reacted materials are produced, the storage products could be used easily in onsite facilities without trained operators.

The basic chemical cycle employed is shown in figure XI-20. A chemical (labeled "A" in the diagram) is preheated in a counterflow heat exchanger and sent into the collector where it is separated into products ("B" and "C" in the diagram) through a chemical reaction. The heated-reaction products are cooled to ambient temperatures in the heat exchanger. If the reaction requires a catalyst in the solar collector, it may be possible to store the products at ambient temperatures. If no catalyst is needed, it may be necessary to store each reaction product separately. The stored products can then be piped to other sites where energy is needed. When energy is to be extracted from the system, the reaction simply proceeds backward at a lower temperature (Le Chatelier's principle). In the diagram, "B" and "C" recombine to form "A". If the original chemical ("A") is valuable, it must then be piped back to the collector. In some cases, the reaction must proceed through numerous intermediate steps (i.e., $A \rightarrow A' \rightarrow A'' \rightarrow B + C$).

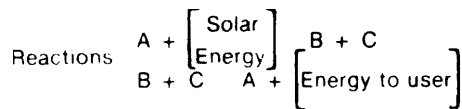
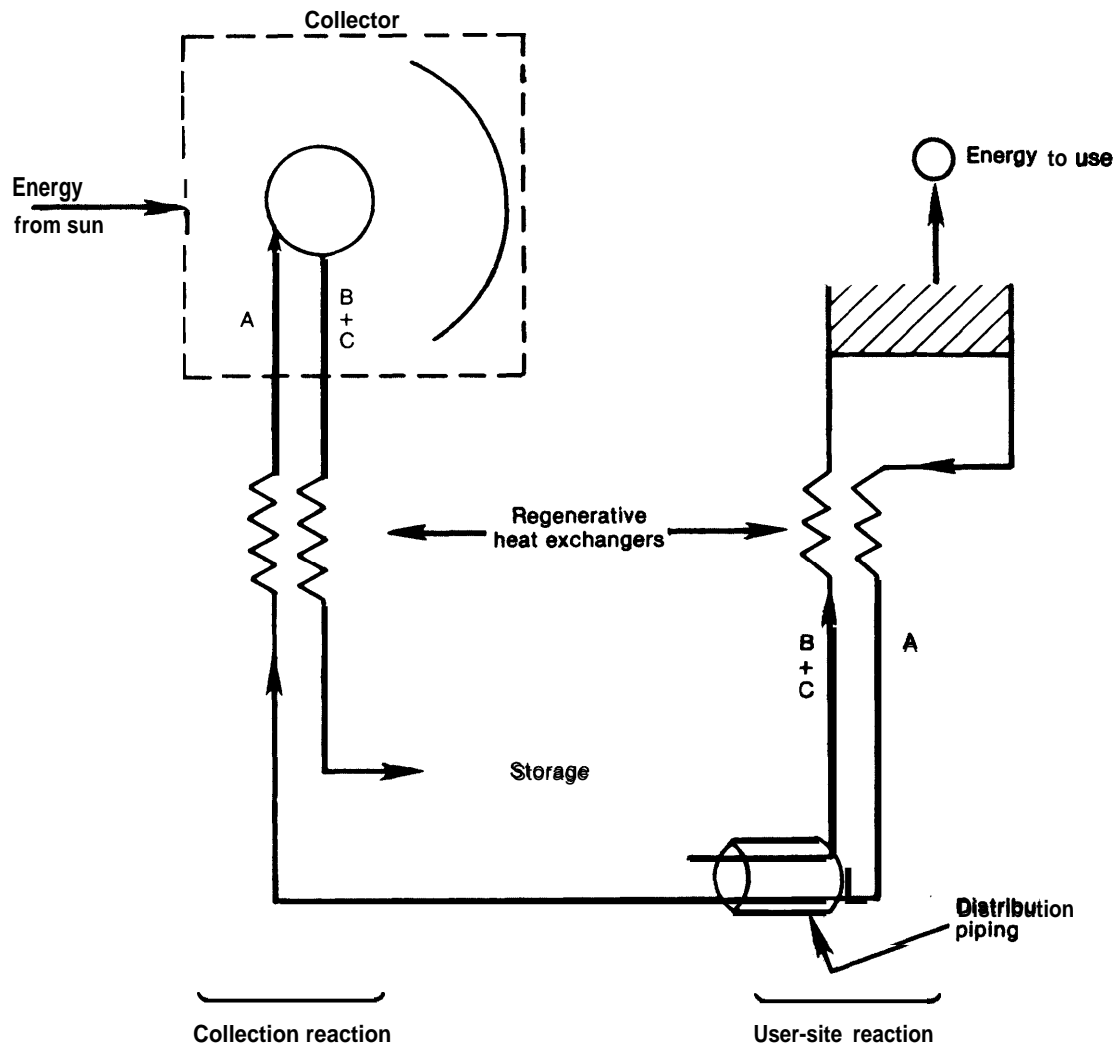
In a recent paper, W. E. Wentworth and E. Chen presented an elegant approach for evaluating and comparing thermochemical

⁷²RSchulten, et al., *The Concept of Nuclear Hydrogen Production and Progress of Work in the Nuclear Research Center Juelich*, paper presented at the 1st World Hydrogen Conference, Miami Beach, Fla., Mar 1-3, 1976

⁷³Jon B Pangborn, "Hydrogen Energy Technology-Update 1976," in *Energy Technology III* proceedings of the third energy technology conference, Washington, D C, 1976, p 1972

⁷⁴T A Chubb, "A Chemical Approach to Solar Energy," to be published in *Chemtech*, 6, p 654, (October 1976)

Figure XI-20.—Typical Thermochemical Storage Technique.



reactions. Their work provides the basis for the analysis which follows. 75

The basic measures of merit for a thermochemical reaction are: 76

⁷⁵W.E. Wentworth and E. Chen, "Simple Thermal Decomposition Reactions for Storage of Solar Thermal Energy," *Solar Energy* 18(3), 1976, p. 205.

⁷⁶Ibid., p. 208,

- 1 The reaction should be nearly complete within the temperature range of available collectors. (In practical terms, it would be desirable to have 95 percent completeness at temperatures below 1,000°C.)
2. The reverse reaction should be nearly complete at the temperature at which useful energy is to be extracted. (If the reaction is to be used in connection

- with a conventional powerplant, this temperature would be approximately 500 °C; if a Stirling cycle or Brayton cycle device were to be used, the temperature should be closer to 800 °C.).
- 3 The reversible reaction should be able to release energy for the user at temperatures close to those supplied by the collector. (The collector temperature should be as low as possible to minimize material problems and to maximize collection efficiency— in the following discussion, it will be seen that this requirement will be met by reactions which involve large changes in entropy.)
 4. The energy absorbed per-unit-volume of the products stored should be as large as possible to minimize the volume of storage. It would be most desirable to be able to store the reaction products in liquid form. This would both reduce storage costs and the energy losses in pumping the stored material.
 5. The reaction should be completely reversible and no side reactions should occur to produce contaminants in a closed-cycle system. These side reactions would tend to create products which would accumulate and eventually poison the system.
 6. Reactions should be fast.
 - 7, None of the reactions involved should require extensive development of new chemical techniques. They should not require expensive or elaborate equipment. This is of paramount importance for onsite equipment not operated by trained personnel.
 - 8 The reaction products should not react strongly with water or oxygen, since it would be difficult to seal the system against these materials.
 - 9 The materials used should be inexpensive and should not require chemicals for which shortages are likely to develop.

Design Alternatives

Most of the thermochemical reactions which are now being examined for use in connection with high-temperature storage systems require fairly sophisticated reaction apparatus which must be maintained by trained personnel. As a result, these thermochemical systems will be limited to relatively large onsite systems, such as shopping centers, industries, and communities. Research may develop reactions which do not require such attention and the equipment needed for existing systems may be simplified, but much more development work is needed before assessment of this issue can be made.

METHANE-STEAM

A variety of reactions have been proposed for use in larger systems, and some of them are summarized in table XI-6. The reaction which has probably received the most recent attention is the methane/syn-gas reaction. The methane reaction probably requires the least development since the technology required for each step of the storage process is commercially available and the chemistry is well understood.

The Ralph M. Parsons Company, for example, has operated a device for converting hydrogen and carbon monoxide to methane for 3 years, producing nearly a million ft³/day of methane. The equipment was designed as a part of a synthetic fuel plant, where the first step would be partial combustion of coal to produce the "syn-gas" combination of H₂ and CO, and the second phase would use the Parsons' "methanation" process.⁷⁷

One potential difficulty of the methane/steam process for onsite application is the difficulty of controlling the reaction. The thermal output from the reaction which generates heat can be throttled down to about 50-percent peak capacity without major dif-

⁷⁷Charles Luttman (Ralph M Parsons Co.), private communication, Aug. 6, 1976.

Table X1-6.—Candidate Chemical-Energy Storage Reactions

Reaction	Temperature of reaction in collector •		Temperature of user reaction •		Energy stored per unit mass (vol.) of storage material		Cost of storage material		Comments
	°C	°F	°C	°F	Btu/lb	kcal/liter	\$/kWh		
$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	780	1,440	0.94	610	1,130	2,792	50		Products of the storage reaction are gases and thus volume is large. Gas must be stored under pressure. Reactions are well known. Nickel catalyst required. $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ is a methanation reaction.
$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$	619	1,090	0.92	589	1,150		60		Products stored as gas
$\text{SO}_3 \rightleftharpoons \text{XO}_2 + \frac{1}{2}\text{O}_2$	1,025	1,880	0.95	590	1,090	532	110	0.16	Cost includes system cost SO_2 stored as liquid, O_2 as gas,
$\text{NH}_4\text{HSO}_4 \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O} + \text{SO}_3$	498	930	0.90	435	850		512	1.1	Products stored as liquids. $\Delta H = 60$ kcal for liquid storage experiments in progress
$\text{Mg}(\text{OH})_2 \rightleftharpoons \text{MgO} + \text{H}_2\text{O}$	199	390	0.67	335	635	446	740	0.62	H_2O stored as liquid ($\Delta H = 9.6$ kcal). Laboratory scale experiments.
$\text{Ca}(\text{OH})_2 \rightleftharpoons \text{CaO} + \text{H}_2\text{O}$. .	595	1,100	0.92	390	740	567	470	0.07	Experiments have been made. H_2O stored as liquid ($\Delta H = 16.4$ kcal).

. See text for explanation of terms. In the analysis of "temperature efficiency" $T_c = 100^\circ \text{F}$ has been used.

SOURCES W. E. Wentworth and E. Chen, "Simple Thermal Decomposition Reactions for Storage of Solar Thermal Energy," *Solar Energy* 18(3), 1976.

T. T. Bramlette (Sandia Laboratories, Livermore), *Survey of High-Temperature Thermal Energy Storage*, SAND D75-8063, March 1976, pp. 83-94.

R. S. Hockett and R. W. Serth, "High Temperature Thermal Energy Storage System," *12th IECEC Conference*, (1977), p. 510.

facility, but control beyond the 50-percent reduction becomes difficult. Another major problem is the relatively low-energy density of the gas which must be stored. The H_2 + CO mixture holds approximately 60 Btu/ft³ at atmospheric pressure, and methane holds approximately 240 Btu/ft³. The price of tanks for storing the coal and gas mixture will dominate the cost of this type of storage. If large amounts of gas are to be stored and underground caverns or abandoned gas fields are available, underground storage is clearly the most inexpensive approach. A recent JPL study estimated that hydrogen could be stored in depleted gas fields and aquifers for about \$1/1,000 SCF,* in dis-

solved salt caverns constructed for this purpose for about \$3/1,000 SCF, and in mined caverns for about \$5.6/1,000 SCF.⁷⁸ The energy storage costs would thus range from about \$17/10⁶ Btu (\$0.057/kWh) of storage capacity for gas field storage to about \$93/10⁶ Btu (\$0.32/kWh) for mined caverns.

These underground storage systems would not be available in many sites. They could probably be used only in connection with a very large plant, and then only if appropriate geology could be located. With current technology, it would be necessary to store the gas in pressurized tanks. In the future, it may be possible to store hydrogen

*The abbreviation "SCF" stands for standard cubic feet. If the gas is stored under pressure, the volume would be less than the "SCF."

⁷⁸Toshio Fujita (JPL), *Underground Energy Storage for Electric Utilities Emphasizing Hydrogen Energy Systems*, June 1976, p. viii.

in solid hydrides.⁷⁹ A recent EPRI study indicated that hydrogen could be stored at 88 atmospheres for about \$0.50/SCF⁸⁰ (or \$28/kWh) in the syn-fuel storage system.

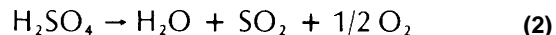
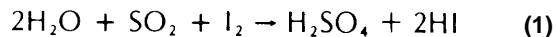
Major development problems which must be overcome for the methane/steam cycle include the design of high-temperature receivers using nickel-base catalysts. The receivers must be capable of operating for extended periods with minimal maintenance. Another unresolved issue is the question of the extent to which the system will be stable when the load or solar influx changes suddenly. There may also be difficulties with side reactions which would lead to the accumulation of reaction products that would poison the system. The seriousness of these difficulties and the cost of overcoming them cannot be determined without operational testing.

MULTISTAGE PROCESSES FOR GENERATING HYDROGEN

A number of multistage processes have been suggested for generating hydrogen, but most are cumbersome for onsite applications and involve several different reactions, some of which require the addition of low-temperature "process heat" in addition to the high-temperature processes. Two advantages of these multistage processes over single-stage hydrogen production are that lower temperatures can be used and that the two gases are released separately at different stages.

General Atomic Company, which in 1973 developed a computer program to find the best combination of chemical reactions that could form closed hydrogen-producing cy -

cles, reported to ERDA last fall that it found the following cycle the most promising:



Two other high-temperature chemical storage cycles are being studied by Westinghouse in the United States and KFA in West Germany. In all three cycles, the primary heat storage occurs in the dehydration and pyrolysis of H_2SO_4 .⁸² Several reactions have also been proposed by Debini and Marchetti (using CaBr_2 and HgBr_2), Westinghouse (using a hybrid sulfuric acid process), General Atomics (using an iodine-sulfur dioxide cycle), Schulten (using a methanol-sulfuric acid process), the Lawrence Livermore Laboratory (using a zinc-selenium cycle), the Institute of Gas Technology (using iron chloride), and others.⁸³ A major problem with all of the reactions examined is low efficiencies (typically 20 to 40 percent). In many cases, the basic chemistry of the processes has not been well established.

In addition to the calcium-bromide process described above, reactions using cesium, tin, iodine-vanadium chloride, and iron chloride-oxide have been proposed. The calcium-bromide reaction appears to be the most efficient. All require three or more processes and considerable quantities of process heat.⁸⁴ The cost of such systems is extremely difficult to estimate at present. One preliminary study showed that a 47-percent efficient thermochemical-process plant for converting solar-supplied heat into hydrogen would cost \$25 per kW of thermal in-

⁷⁹G Strickland and J J Reilly, *Operating Manual for the PSE&G Hydrogen Reservoir Containing Titanium Hydride*, Brookhaven National Lab, February 1974

⁸⁰Utilization of Off-Peak Power to Produce Industrial Hydrogen, EPRI 320-1, Final Report, prepared by Institute of Gas Technology, August 1975

⁸¹M M Eisenstadt and K E Cox, "Hydrogen Production From Solar Energy," *Solar Energy*, 17(1), 1975, p 59

⁸²Data provided by ERDA, Office of Conservation

⁸³Eisenstadt and Cox, op cit, *A Technoeconomic Analysis of Large-Scale Thermochemical Production of Hydrogen*, (EPRI EM-287), December 1976, Preliminary Assessment of Economics of Hydrogen Production From Lawrence Livermore Laboratory, ZnSe Thermochemical Cycle, United Engineers, September 1976

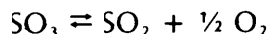
⁸⁴R F Chao and K E Cox, "An Analysis of Hydrogen Production via Closed Cycle Schemes," *Proceedings, THEME Conference*, Miami Beach, Fla., S13 1-S1 32 (March 1974), cited in Eisenstadt and Cox

⁸⁵Pangborn, op cit, p 174

put capacity .8' Converting this to 1976 dollars and removing the contractors overhead and profit, which will be added in later, this cost is \$26 per kW of thermal input capacity, or \$57 per kW of hydrogen- production capacity. This cost does not include the cost of hydrogen storage tanks, which would cost a great deal. A big central system could pipe the hydrogen to gas customers in natural gas pipelines, or store it in depleted natural gas wells, but these options may not be available to the small onsite units. In addition, much work remains to be done on the systems, however, and it seems that the chemistry required will be too complex for any but the largest "onsite" facilities being examined in this study.

SULPHUR DIOXIDE/SULPHUR TRIOXIDE

Some of these difficulties associated with the methane system can be avoided in the other simple chemical system which has received major interest—the



reaction. Its major advantage is that only the oxygen cannot be stored as a liquid at ambient pressure and temperatures; this results in a very substantial saving in the cost of storing the material. The system has no side reactions, and it requires relatively small catalyst volumes.

Since the sulfur trioxide reaction reaches completion at temperatures nearly 2000 F higher than the methane/steam system, a receiver and reaction chamber must be made out of ceramics or other material capable of

withstanding high temperatures. The development of such a receiver presents a major problem. The system would also require relatively large heat exchangers at both the collector site and in the system for reacting the sulfur dioxide to generate heat. This results from the high molecular weight of the materials used and the necessity of condensing the products in the heat exchangers. The sulfur system could also present corrosion problems since corrosive acids would form if any water entered the system; the safety problems associated with piping the materials must also be examined.

Examining the chemicals in table XI-6, it appears that one of the most attractive materials for high-temperature storage would be NH_4HSO_4 , since all of its reaction products can be stored as liquids at ambient temperature and since its reaction temperatures are not as high as those required for the SO_3 system.⁸⁷ Work has begun on this and a variety of other reactions, and it is clear that not all possibilities have been explored.

The sulphur compounds used in this storage system could create environmental hazards if the equipment leaks or is not properly maintained. Accumulations of sulfur-based gasses can be highly toxic and may be explosive under the right conditions.

Summary

The costs of several of the high-temperature thermal storage systems discussed in this section are summarized in figure XI-21.

ELECTRIC STORAGE

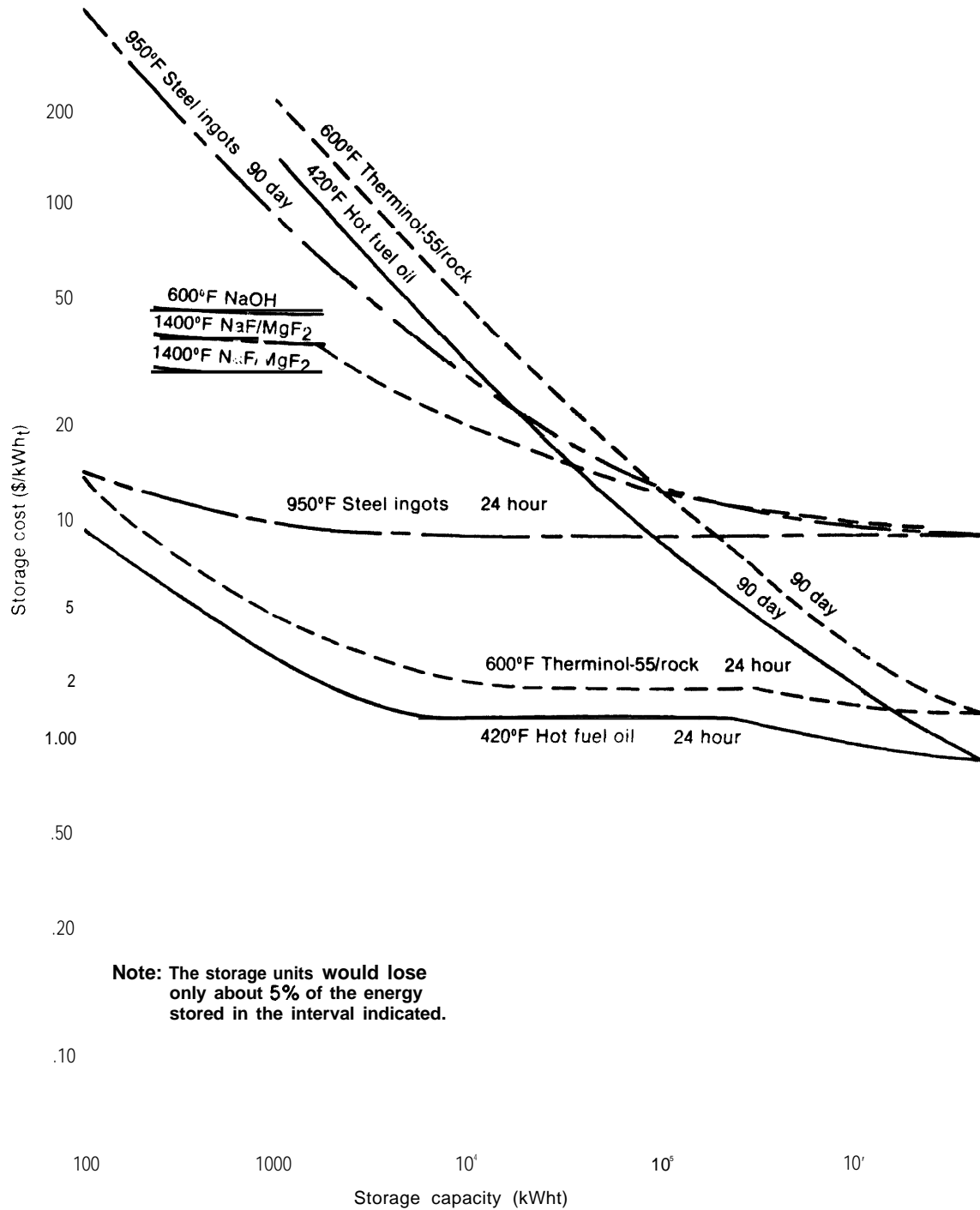
All of the storage devices examined thus far are designed to deliver heat which can be either used directly to heat a building or for some other purpose or to operate a heat

engine. It is also possible to store the electricity produced by heat-engine generators or photovoltaic devices. Electricity can be "stored" directly in a loop of superconducting (zero-resistance) wire, and although research is being conducted on such devices,

⁸⁶W. Haug et al., Publication 72 TM P-1 5, General Electric-TEMPO, Santa Barbara, Calif., April 1972, cited in Eisenstadt and Cox.

⁸⁷Wentworth and Chen, op. cit.

Figure XI-21 .— High-Temperature Thermal Storage Cost per kWh_t Versus Storage Capacity



they are unlikely to play a significant role in energy storage for some time. All other forms of electric "storage" convert the electricity into mechanical or chemical energy in such a way that electricity can be easily removed.

MECHANICAL STORAGE DEVICES

The only large-scale electric storage systems in use today are pumped hydroelectric storage facilities. A conventional installation consists of two lakes connected with a device which is a combination pump and turbine generator. Water is pumped into the upper lake when energy is available to charge the storage and is discharged through the turbine generator when the system is discharged. Standard hydroelectric facilities can provide storage since the flow of water through turbines can be restricted during periods of low demand, in effect storing water in the dam's lake for later use.

Hydroelectric storage facilities are likely to continue to be one of the least expensive techniques for storing electricity, even if advanced electric storage systems of other types are developed. Unfortunately, the United States has already exploited a significant fraction of the most attractive sites for hydroelectric facilities, and attempts to develop many of the remaining sites are likely to face determined opposition on environmental grounds. A number of potential sites are protected under the "Wild and Scenic Rivers Act" and other legislation. A pumped hydroelectric facility is particularly unattractive from an environmental standpoint, and the lakes created are difficult to use for recreation. This is because the water levels in lakes created in a pumped hydroelectric system change significantly throughout the day and the pumping continuously mixes water from different parts of the lake.

It may be possible to greatly expand the number of potential sites for pumped hydroelectric facilities by placing one of the stor-

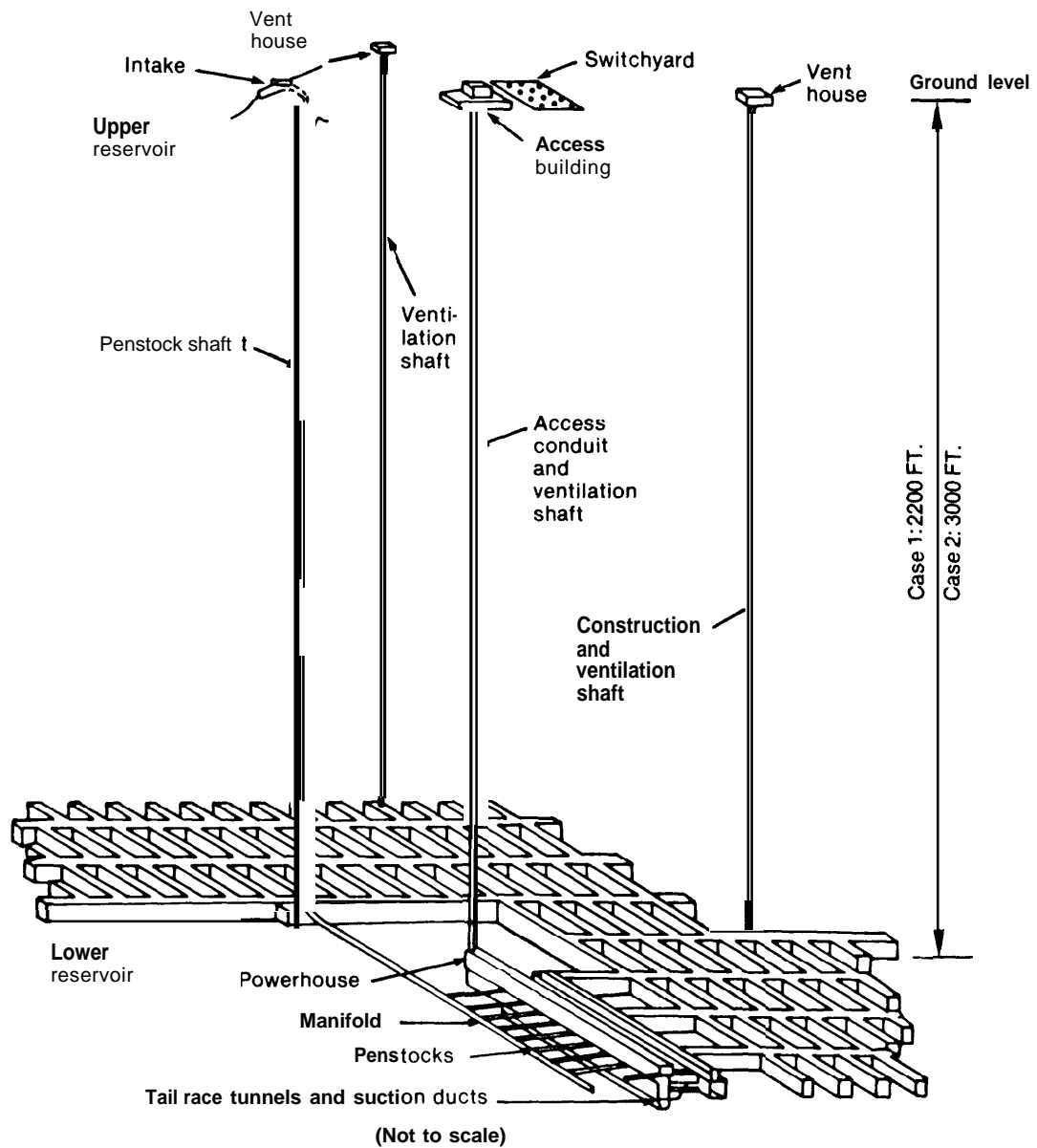
age reservoirs deep underground as illustrated in figure XI-22. Such a facility could be located wherever minable rock exists at the required depths, but would cost considerably more than a standard hydroelectric facility. Recent estimates of the cost of a pumped hydroelectric facility capable of producing 2,000 MWe for 10 hours range from \$270 to \$350/kW.⁸⁸

Looking in another direction, it has been found that a very large amount of potential hydroelectric capacity can be found in the numerous small dams which already exist around the United States. The generating capacity of existing small hydroelectric sites could be expanded, and generators could be added to a number of dams which currently are used exclusively for other purposes. The results of a preliminary survey of the opportunities presented by existing dams are summarized in figure XI-23 and table XI-7. The survey discovered that a generating capacity of 26.6 GWe could be installed at small dams (dams capable of producing less than 5 MWe of power) and that these small facilities could provide 159 billion kWh annually. This represented approximately half of the new capacity identified. The extent to which such dams could be used for power and storage cannot be determined without a more detailed examination of the issue.

It must also be recognized that solar energy systems will not be able to benefit directly from most of the added hydroelectric capacity, since utilities will want to take maximum advantage of new and existing hydroelectric facilities for storage and for meeting peak demands. Solar equipment could benefit indirectly to the extent that the new facilities improve the ability of utilities to meet fluctuating demands. Mechanical storage of electricity can also be accomplished with flywheels by compressing gas in underground caverns for use in Braxton cycle engines, and in other ways. These techniques have been adequately reviewed elsewhere.

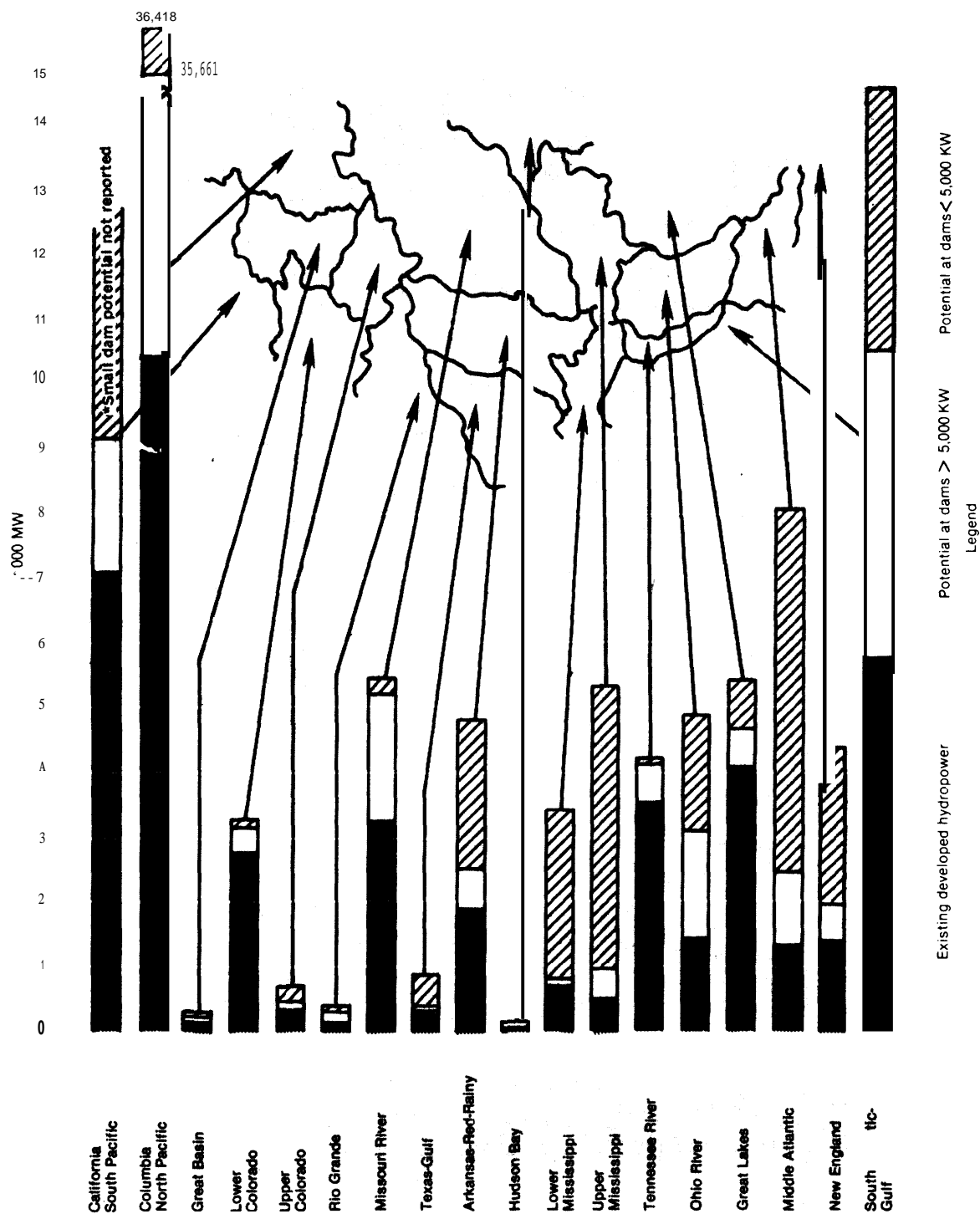
⁸⁸Frank M. Scott, "Underground Hydroelectric Pumped Storage. A Practical Option," *Energy*, Fall 1977, p 20.

Figure XI-22.— An Isometric View of an Underground Pumped Storage Plant



SOURCE: Scott, Frank M. "Underground Hydroelectric Pumped Storage: A Practical Option" *Energy* Fall/1977 p. 20

Figure XI-23.—Conventional Hydroelectric Capacity Potential at Existing Dams



SOURCE: McDonald, R. J. Principal Investigator (U.S. Army Corps of Engineers).
 "Estimate of National Hydroelectric Power Potential at Existing Dams," July 20, 1977.

Table XI-7.-Conventional Hydroelectric Capacity Constructed and Potential at Existing Dams

	Capacity (millions of kW)	Generation (billions of kWh)
Developed	57.0	271.0
Under construction	8.2	16.8
Total installed	65.2	287.8
Potential rehabilitation of existing hydrodams	5.1	24.4
Potential expansion of existing hydrodams	15.9	29.8
Potential at existing non- hydro dams greater than 5,000 kW	7.0	20.4
Potential at existing non- hydro dams less than 5,000 kW	26.6	84.7
Total potential	54.6	159.3
Total (developed and undeveloped).	119.8	447.1

SOURCE: McDonald, R. J. Principal Investigator (U.S. Army Corps of Engineers Institute for Water Resources), "Estimate of National Hydroelectric Power Potential at Existing Dams," July 20, 1977

BATTERY STORAGE

Batteries are able to store electrical energy by using a variety of different reversible electro-chemical reactions. The electrical energy must be introduced and withdrawn from batteries as direct current, however, and a "power-conditioning" device must be included in any battery system which receives and produces alternating current. Within large bounds, the cost of batteries per unit of storage capacity is independent of the size of the system since most batteries are built by combining a large number of individual reacting cells. Larger systems may benefit from some economies of scale because of savings due to more efficient packing, lower building costs, and possibly lower costs of power conditioning for larger systems, but a separate anal-

ysis on this point must be performed for each type of battery. It is likely that there will be an optimum size for each device.

Lead-acid batteries are the only devices currently mass produced for storing large amounts of electrical energy using electro-chemical reactions. Systems as large as 5,000 kWh are currently used in diesel submarines. Batteries now on the market which can be deeply discharged often enough to be attractive for onsite or utility storage applications, however, are too expensive for economic use by electric utilities. Extensive work is being done to determine whether it is possible to develop batteries suitable for use in utility systems. Work is being done on advanced lead-acid battery designs and on several types of advanced batteries which it is hoped will be less expensive than lead-

acid batteries in the long term. This work has been thoroughly reviewed in several recent papers.^{89 90 91 92}

Lead-Acid Batteries

When voltage is applied to a lead-acid battery, energy is stored by converting the lead sulfate (PbSO_4) on the battery electrodes into a mixture of pure lead (Pb), lead dioxide (PbO_2), and sulphuric acid (H_2SO_4); the reaction is reversed when the battery is discharged.

The current market for lead-acid batteries capable of multiple deep cycles is very limited and prices are high. (Automobile batteries cannot be used in power applications since the full charge in such batteries cannot be withdrawn repeatedly without damaging the battery.) "Houselighting battery sets" are being manufactured for use with windmills and remote generating plants. Units capable of 2,000 deep cycles cost approximately \$385/kWh.⁹³ 94 Golf cart batteries sell for as little as \$40/kWh, but are only capable of about 350 cycles. Industrial traction batteries, used in fork-lift trucks and the like, have lifetimes of nearly 2,000 cycles and are available for as little as \$80/kWh.

⁸⁹An Assessment of Energy Storage Systems Suitable for Use by Electric Utilities, Public Service Electric and Gas Company under E P R I Project 225 and ERDA Contract No E (11-1)-2501, Vols. I & II, July 1976.

⁹⁰Near-Term Energy Storage Technologies: The Lead-Acid Battery, a compilation of papers presented at the ERDA-E P R I-ILERO Workshop, Dec. 18-19, 1975, EPRI SR-33

⁹¹J.R. Birk, *The Lead-Acid Battery for Electric Utilities: A Review and Analysis*, presented at ERDA-E P R I Lead-Acid Battery Workshop 11, Dec. 9, 1976

⁹²Ralph Whitaker and Jim Birk, "Storage Batter[ies]: The Case and the Candidates," *EPR/ Journal*, October 1976, pp 6-13

⁹³Prices quoted by Solar Wind Company, North Orland, Maine. The batteries are of Austrian manufacture and come in a clear polystyrene case with built-in pilot-ball charge indicators in each cell.

⁹⁴All prices quoted are based on the battery capacity when discharged to rated depth-of-discharge. Unless otherwise stated, it is assumed that batteries operate with 80-percent discharge in a typical cycle.

The Department of Energy asked several battery manufacturers to estimate how much it would cost to manufacture a battery capable of storing 5 megawatt-hours, discharging in 10 hours, and lasting 500 to 1,000 cycles, using essentially off-the-shelf components. The manufacturers' responses averaged about \$93/kWh, but responses varied from \$41 to \$138/kWh.⁹⁵ This spread reflects a range of battery capabilities. An independent survey conducted by the Bechtel Corporation resulted in an estimate of about \$63/kWh.⁹⁶

The industrial battery price of \$80/kWh will be used in further analysis to represent "current" battery prices for community systems.

While the range of prices encountered for near-term batteries reflects the differing specifications, production rates, etc., there is rather remarkable agreement about what batteries will cost in the intermediate term when comparable assumptions are used. Table XI-8 shows recent estimates of the price and specifications of load-leveling batteries, assuming a production rate of 1,000 MWh/yr in a dedicated production facility. These estimates reflect a relatively rapid writeoff of plant costs. Westinghouse has estimated⁹⁷ a selling price of \$41.68/kWh by assuming vertical integration of lead production and battery manufacture, present battery technology, and more optimistic assumptions about writeoff.

A major disadvantage of contemporary lead-acid battery designs is their relatively low storage capacity per unit weight. This is due largely to the amount of lead used. Lead-acid batteries have a theoretical "energy density" of about 0.175 kWh/kg, and

⁹⁵"A National Battery Energy Storage Test (BEST) Facility Conceptual Design and Design and Cost Estimate," BEST Facility Study Project Team, EPRI 255, ERDA 31-109-38-2962, Technical Report 1, August 1975, p 11-11

⁹⁶Bechtel Corporation, op cit

⁹⁷*Study of the Manufacturing Costs of Lead-Acid Batteries for Peaking Power*, Final Report, Westinghouse Electric Corp., ERDA Contract No. E(40-18)-21 14, December 1976,

Table X1.8.—Economic Specifications (5-hr Battery)

Specification	C & D ^a	ESB	Globe-Union	Gould	Westing - house ^b
Price (\$/kWh) ^c	55	56	58	54 ^d	49
Life (cycles at 77° F), ., . .	2,000	2,000	2,000	2,000	1,750 (95° F)
Price/cycle, .,	2.7	2.8	2.9	2.7	2.8
Efficiency (%) ^e	73	76	72	70	68
Replacement price (\$/kWhr)	40	32	38	25	34
O&M cost (mills/ kWhr)	0.28	0.18	—	—	—

^aBased upon 85% depth of discharge to achieve 2,000 cycles. Instead of 85% of discharge to achieve 1,250 cycles at a price of \$49/ kWhr (to be discussed)

^bDoes not reflect raw materials integration and market optimism included by Westinghouse (to be discussed)

^cAssumes 25c / lb lead

^dInstalled cost

^eIncludes Conversion efficiency of 90%

SOURCE James R Birk, "The Lead-Acid Battery for Electric Utilities A Review and Analysis "presented at the ERDA / EPRI Lead-Acid Battery Workshop 11, Dec 9, 1976

thus a perfect battery would weigh about 12.6 pounds per kWh. Commercial batteries weigh more than this because of design inefficiencies and the need to provide packaging for the active materials. Commercial lead-acid systems weigh about 100 pounds per kWh of storage capacity, of which 60 to 80 pounds is lead. The cost of this rather substantial quantity of lead imposes a practical lower limit on the price of lead-acid batteries.

In 1975, when ERDA asked three of the largest battery manufacturers in the United States to design the lowest cost battery for utility applications, the estimates of material costs ranged from \$24 to \$34/kWh.⁹⁸ (The range is much smaller if allowance is made for the differing lifetimes of the designs.) Very high production volumes would be required before the price of the complete battery would approach this minimum material cost.

The Axel Johnson Institute for industrial Research in Sweden has proposed a novel technique for reducing lead requirements by

using aluminum electrodes covered with a lead coating. The device is currently being tested by EPRI.⁹⁹

The current U.S. production rate of lead could support all foreseeable needs of on-site electric systems and should be able to support the development of a nationwide battery system used for utility peak shaving (although the price of lead would undoubtedly increase if a very large demand developed). Present U.S. domestic lead consumption is about 600,000 tons per year, and our reserves are estimated at 40 million tons (World production is approximately 3.6 million tons and world reserves 141 million tons.)¹⁰⁰ Thus, at present energy densities, current production rates could provide 15 to 20 million kWh of storage per year or enough to provide 4,000 to 5,000 MWe for 4 hours every day. At this rate of production, therefore, it would take 10 years to develop a battery system capable of meeting 10 percent of U.S. electricity demand for 4 hours.

⁹⁸J. R. Birk, "Technical Analysis," in *Near-Term Energy Storage Technologies: The Lead-Acid Battery*, EPRI SR-33, March 1976, p. 185.

⁹⁹AC Simon and S. M. Cauldar, "The Lead-Acid Battery," *Proceedings, Symposium and Workshop on Advanced Battery Research and Design*, Argonne National Laboratory (AN L-76-8), March 1976.

¹⁰⁰OM/ner.21\ Yearbook, U. S. Department of the Interior, Bureau of Mines, 1973.

per day. The lead used in the batteries is not consumed in the storage process, and after the initial investment is made, the material can be recycled indefinitely.

An ordinary automobile battery will last 3 to 5 years, undergoing extremely shallow cycles several times a day, but would be capable of only 150 to 250 deep discharges. The electrodes in batteries used in golf carts, industrial forklifts, etc., are usually 2 or 3 times as thick as those used in car batteries and are typically capable of 300 to 500 deep cycles. Batteries capable of discharging 2,000 times are currently available and this has become a design objective for utility storage batteries.

A practical limit to the depth of discharge which can be obtained from a given battery design can be obtained by watching the battery's voltage. This voltage drops slowly during discharge and then begins to fall sharply. If the battery is discharged beyond this point, its life is shortened substantially.

ENVIRONMENTAL AND SAFETY PROBLEMS

Lead-acid batteries produce potentially hazardous gasses, such as hydrogen, arsine (AsH_3), and stibine (SbH_3) when they are cycled. Hydrogen released in the atmosphere has no effect on air quality or human health, but is highly flammable and explosive in concentrations above 3 percent. This danger can be eliminated by placing batteries in well-ventilated compartments.

Arsine and stibine are toxic, colorless, gaseous compounds which form during the required, periodic, high-voltage charging of lead-acid batteries. For example, the recommended threshold limit values for arsine and stibine in workroom air are 0.05 ppm (0.2 mg/m^3) and 0.1 ppm (0.5 mg/m^3), respectively.¹⁰¹ Whether these levels will be exceeded when charging lead-acid batteries for home

energy storage is presently unknown. The recognition of the possible adverse environmental impact of arsine and stibine and implementation of appropriate safeguards—proper battery placement and ventilation—reduces the risk of harm from these gasses.

Advanced Batteries

Three basic categories of advanced systems are under examination:

1. Aqueous or water-based systems which operate with electrodes surrounded by a liquid electrolyte, as do lead-acid systems.
2. Nonaqueous high-temperature systems, which use a nonaqueous material to conduct ions needed to complete the electrochemical reaction.
3. "RED OX" (reduction/oxidation) devices which reduce aqueous solutions to store energy. (REDOX batteries are "aqueous," but they are usually considered separately.)

Table XI-9 summarizes the characteristics of several advanced battery designs.

AQUEOUS BATTERIES

Zinc Chloride

Zinc-chloride batteries are aqueous devices which can store electrical energy in aqueous chemical solutions at ambient temperature. Research on this battery is underway in a joint venture of Gulf Western Industries and the Occidental Petroleum Corporation. Small (50 kWh) units have been tested at Argonne National Laboratory, and it is expected that a 10 MWh battery will be tested in a realistic utility environment by 1980.

The small experimental batteries now being produced cost approximately \$2000 a kilowatt hour, but when the system reaches production stages, cost is expected to be reduced to \$40 to \$50. This is more expensive than projections for lithium or sodium battery systems, but this cost is offset to

¹⁰¹ "Report on an Engineering Study of a 20 MWh Lead-Acid Battery Energy Storage Demonstration Plant," for Argonne National Laboratory under Contract No. 31-109-38-2962, by Bechtel Corporation, October 1975, p. 5-5.

Table X1.9.—Load-Leveling Batteries: Candidates and Characteristics; Developers and Demonstration Dates

	Operating temperature (°C)	Theoretical cell energy density (Wh/lb)	Design cell energy density (Wh/lb)	Design modular volumetric energy density (Wh/in ³)	Depth of discharge ^a (%)	Density 10 hr rate (mA/cm ²)	Active materials cost (\$/kWh)	Demonstrated cell size (kWh)	Demonstrated cell life (cycles)	Critical materials	Major developers	BEST facility test (5-10 MWh)	Demonstration station	Commercial introduction
Lead acid (Pb/PbO ₂)	2030	110	11	075	25	10-15	850	>20	2,000	Lead	Gould Inc Batteries Inc.; K.W. Battery Co	1979	1981-83	
Sodium-sulfur (Na/S)	300-350	360	70	2.5	85	75	0.49	0.5	400		General Electric Co Chemical Co; Ford Motor Co	1981-82		
Sodium-antimony trichloride (Na/SbCl ₃)	200	350	50	20	80-90	25	235	0.02	175	Antimony	ESB Inc	1981-82		
Lithium-metal sulfide (Li/Si/FeS ₂)	400-450	430	85	35	80	30	4.27	1.0	1000	Lithium	Atomics International Div Rockwell International Corp.; Argonne National Laboratory	1980		
Zinc-chlorine (Zn/Cl ₂)	50	210	45	1.0	100	40-50 ^b	Theor - 0.59c Practical - 0.84	1.7		Ruthenium (catalyst)	Energy Development As- sociates	1980		
Zinc-bromine (Zn/Br ₂)	30-60	195	40	15	90	30	Theor - 1.56 Practical - 1.65	0.1	2,000	None	Exxon; Gould; GE	1983	—	Post 1985
Hydrogen-chlorine (H ₂ /Cl ₂)	30-60	450	50	0.3	95	300	20	0.01	50	Platinum Ruthenium (catalyst)	GE, BNL	1983	.	Post 1983
REDOX	ambient	—	40 ^d	—	90	40-60	\$3-\$10	0.05	200	None	NASA-Lewis	1984	1986	1988
Iron-REDOX	ambient	—	38	2.6			\$1	~1	>1,000	None	G E L		1980	

^aAlso known as utilization of active materials^b5 hr rate^cGE calculation for (Zn/Cl₂)^dWeighted of solution

SOURCES: EPRI Journal and Kuratowski (under Battery Branch Office of Conservation EROA)

some extent by the fact that zinc-chloride batteries produce a constant voltage and equipment necessary to convert the current to a.c. is cheaper than other systems, resulting in an overall competitive price. Zinc-chloride batteries are capable of operating at ambient temperatures, but require a complex plumbing system for circulating the electrolyte and controlling the temperature of the system.^{102 103} The presence of chlorine gases could create an environmental problem if used in onsite systems.

Zinc Bromide

The zinc-bromide battery is another aqueous device being developed primarily for utility load leveling and electric automobiles. Early work on these batteries was done by the G.E.L. Corporation of Durham, N.C. Devices developed by the General Electric Corporation have operated for more than 2,000 cycles of 2.5 hours discharges.¹⁰⁴

Researchers at G.E. believe that batteries based on this concept, capable of 65 to 80 percent efficiencies, should cost no more than \$17 to \$26/kWh (excluding the cost of pumps, controls, and marketing). The major problem is the development of a low-cost and reliable membrane. Imperfect membranes lead to a "self-discharge." In the most recent G. E. designs, the cell discharges at about 0.1 percent per hour.

One potentially serious problem with zinc bromide is the caustic nature of the bromine solution. Containment of this material can be expensive and great care must be taken to ensure that this powerful chemical is properly contained.

HIGH-TEMPERATURE BATTERIES

Sodium/Sulfur

Sodium/sulfur batteries, under developments by the Ford Motor Company, use ac-

¹⁰²N Yao and J.R Birk, op cit.

¹⁰³Bechtel Corp., op cit.

¹⁰⁴F G Will, "The Zinc-Bromide Battery: Possible Candidate for Electric Vehicles and Load Leveling," Proceedings, 12th IECEC Conference, 1977, p 250.

tive materials which are inexpensive and widely available. Most of the development work on this battery has centered on a solid electrolyte material called "beta-alumina" (an alloy made of sodium, aluminum, and oxygen),¹⁰⁵ and the electrolyte costs considerably more than the active materials today.¹⁰⁶ Small 10-to-15 watt sodium/sulfur cells are now being run in excess of 3,000 cycles, and Ford hopes to test a 5-to-10 MWh battery in late 1981. A second sodium/sulfur concept is being developed by Dow Chemical, and is about 2 years behind the Ford research. Both systems still cost some \$3,000 a kilowatt hour, but projections are that the Ford system will be reduced to \$30 by 1985-87, while Dow suggests that a \$24.50 cost can be attained perhaps a year later from its system. G.E. and EPRI spent about \$3.5 million developing this system between 1967 and 1976, and expect to spend about \$3.5 million in FY 78.

Systems have been demonstrated which are capable of 90-percent discharge and 77 percent-efficiencies.¹⁰⁷ The major development problem remains the beta-alumina electrolyte. Poor quality material tends to crack and degrade and seals have been unreliable. Another issue, identified as a problem by G.E., is the difficulty which may be encountered in scaling the units up to a size where they can be used in large central utility applications. It is expected that large batteries will be constructed from units of 10 to 100 kWh.¹⁰⁸

Lithium-Metal Sulfides

Lithium-metal sulfide batteries are being examined primarily by Argonne National Laboratories under a DOE contract. Argonne is now making 150 W/h cells capable

¹⁰⁵N Yao and J R Birk, op cit, p 1107.

¹⁰⁶Arthur L Robinson, "Advanced Storage Batteries Progress But Not Electrifying," Science, May 7, 1976, p 543

¹⁰⁷S. P Mitoff, et al., "Recent Progress in the Development of SodiumSulphur Battery for Utility Applications," Proceedings, 12th IECEC Conference, 1977

¹⁰⁸S P Mitoff, Op. cit

of 500 deep cycles. In 1982, a 5-to-10 MWh cell module is scheduled to be tested in Argonne's Battery Energy Storage Test (BEST) facility. Argonne foresees a cost of \$29.16 per kWh at full production in 1985-87. Like sodium/sulfur batteries, lithium-metal sulfide devices now cost about \$3,000 a kWh to produce experimentally and in small working applications.

Both the sodium/sulfur and the lithium-metal sulfide batteries operate at temperatures above 300 °C, and the combination of high temperatures and reactive materials requires hermetic sealing.¹⁰⁹ There are accompanying seal problems. Questions have been raised about the safety of using the sodium/sulfur system in large numbers unless stringent precautions are taken to protect against a rupture of the containment vessel. Since the lithium battery uses two metals, the chemical reaction caused by a rupture would not be as serious as it would in a sodium cell, which uses two liquids.

Both lithium and sodium are flammable and, under some conditions, explosive.¹¹⁰ The use of lithium and sodium batteries, therefore, must include careful provision for fire and explosion containment.

REDOX BATTERIES

The REDOX battery presents a tantalizing opportunity for electric storage since devices based on the design may be able to store energy in tanks of inexpensive chemicals; storage costs could be \$10/kWh or less. The problem which has plagued the development of these systems for many years is the need for a semipermeable membrane with some rather remarkable properties. The need for a sophisticated membrane could be eliminated, however, if an iron-REDOX design is perfected.

¹⁰⁹ Herbert P. Silverman, Lynn S. Marcoux, and Ed die T. See, TRW, Inc., "Development Program for Solid Electrolyte Batteries," Final Report for EPRI, EM-226, September 1976

¹¹⁰ Chemical Rubber Company, *Handbook of Chemistry and Physics*, 54th Edition, 1973-74, pp B-19, B-31

In a standard REDOX battery, the two storage tanks (called the "catholyte reservoir" and the "anolyte reservoir" in the diagram) contain different chemicals. In one design which has received recent attention, the tank connected to the positive terminal contains a solution of Fe^{+2} and Fe^{+3} ions, and the tank connected to the negative terminal contains a solution of Ti^{+3} and Ti^{+4} ions. When the battery is completely discharged, the one tank is filled with FeCl_2 and the other with TiCl_4 . When the battery is being charged, negatively charged chlorine ions drift across the semipermeable membrane and combine with FeCl_2 , producing FeCl_3 and giving up the extra negative charge to the positive terminal. On the other side of the membrane, chlorine ions are released when TiCl_4 forms TiCl_3 , taking an electron from the negative electrode. The electric current from the positive to the negative electrode is matched by the flow of chlorine ions across the membrane. It is important that the membrane be able to pass chlorine ions with minimal resistance, but not allow either the iron or the titanium to pass. If iron or titanium leaks through the membrane, the performance of the device is gradually degraded. NASA-Lewis has been working on systems based on this design for a number of years, and it is hoped that a battery suitable for demonstration in utility applications will be available by 1985.

Iron REDOX

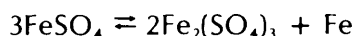
The iron-REDOX battery being developed by the G.E.L. Corporation operates on much the same principle as the REDOX system just described, but uses the same chemical at both electrodes, thereby greatly simplifying the requirements placed on the membrane.¹¹² The basic components of an iron-REDOX battery system are illustrated in figure XI-24.

When the iron-REDOX system is completely discharged, the storage tanks are

¹¹¹ K. W. Klunder, Office of Conservation, ERDA, private communication

¹¹² The G.E.L. Corporation, Durham, N.C., *Performance Status*, January 1977

both filled with iron sulfate $\text{Fe}_2(\text{SO}_4)_3$. Charging occurs when an atom of iron is deposited on the negative electrode and two electrons removed from this electrode produce a SO_4^{-2} ion. These SO_4^{-2} ions drift across the membrane and combine with FeSO_4 to form $\text{Fe}_2(\text{SO}_4)_3$, giving up two electrons to the positive terminal in the process. The net reaction is:



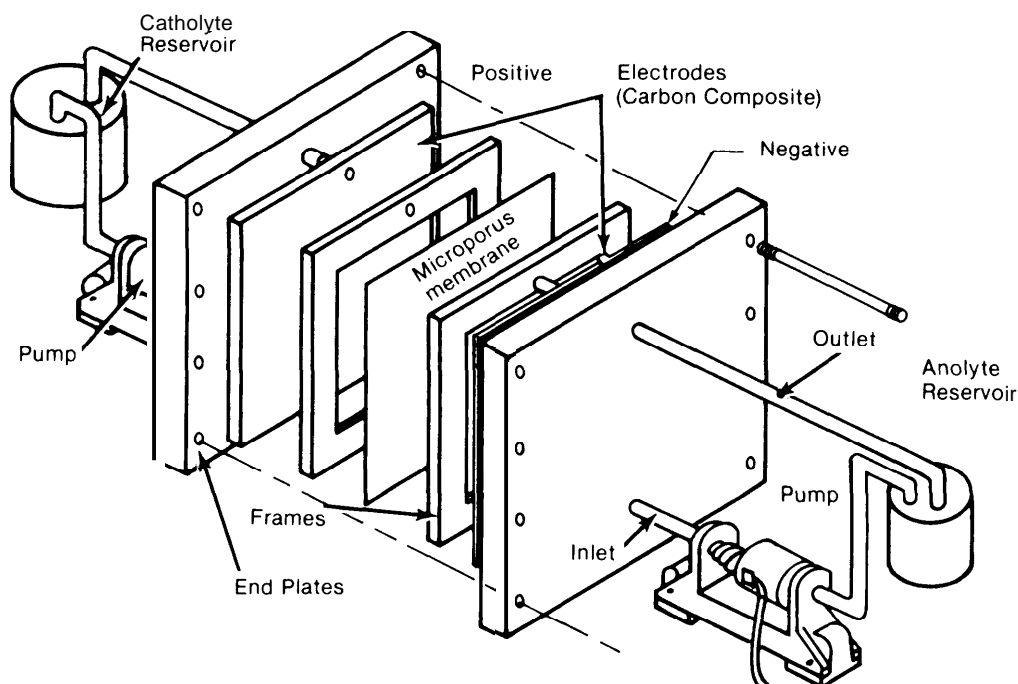
All that the membrane must do is insure that the flow of SO_4^{-2} ions between the cathode and anode reaction chambers exceeds the drift of Fe^{+3} ions. Systems have survived more than 1,000 cycles with no observed degradation in performance, and overall efficiencies are in the order of 65 to 75 percent.¹¹³ The sources of these losses are tabulated in table XI-10. It can be seen that rapid discharge rates increase losses largely

¹¹³ "Dr. R Zito, President, the G.E. L. Corporation, private communication, September 1977.

by resistive heating. With design improvements it may be possible to achieve overall efficiencies of 80 to 85 percent with moderate discharge rates. The system is not damaged by deep discharges.

The reaction chamber with its membrane will account for the bulk of the cost of the iron-REDOX system – the chemicals and the tanks needed to store them will probably cost less than \$2/kWh. The cost of this reaction chamber is a direct function of the area of membrane required. G. E. L. estimates that the graphite electrodes they are now using can store about 1 amp-hour per square inch of electrode surface. After this thickness has been deposited, the deposited iron becomes uneven and physically unstable. If a large area is allowed per unit of power delivered, the system is more efficient but costs per kilowatt increase. The cost of reactors capable of delivering different amounts of power per unit of membrane surface is shown in table XI-10. An electric storage system de-

Figure XI-24.—Iron"REDOX Battery Structure and Plumbing Diagram



SOURCE: GEL, Inc., Durham, N.C.

Table XI-10.— Loss Mechanisms of iron-REDOX Batteries

Loss mechanisms	Loss factors	
	Percent at 0.10 A / in ²	Percent at 0.4 A / in ²
H ₂ evolution	1-2	2-3
pH regeneration	1-2	2-3
Fe + 3 membrane diffusion .	2-3	0.5-2
Joule heating		
—electrolyte	2-4	6-14
—thru membrane	- 0	- 0
Polarization effects	14-20	14-20
Fluid pumping,	'1	- 1
Fluid manifold conduction	-1-2	-1-2
Total loss.	22-34	26.5-45
Reactor cost	\$68/ kW	\$18/kW

SOURCE The G E L Corporation, Durham, N C., September 1977

signed for use in a solar energy application may require a device capable of storing a large amount of energy for periods of 10 to 20 days, but there would be no need to discharge the entire device over a short period. The REDOX device would appear to be well suited for such an application.

The devices will probably not show significant economies of scale until systems of more than a few hundred kwh of storage capacity are constructed.

G.E.L. is presently constructing a 2.2 MWh iron-REDOX battery system with a peak output of 250 kW for use in the Mississippi County Community College total solar energy system. This DOE-sponsored project should be operating by late 1979. The storage system will consist of 24 reactor modules rated at 11 kW. Each module will contain 130 to 150 bipolar electrodes and will measure approximately 120 x 60 x 240 cm (2' x 4' x 8'). The entire system will require 60,000 to 80,000 liters (15,000 to 20,000 gallons) of electrolyte. A model of the system is shown in figure XI-25. Electrodes and membranes for the system have been developed for reproduction with acceptable electrical and mechanical characteristics, but improvements can be expected as the design

matures. To date, no chemical or mechanical problems have been encountered which would cast doubt on the ultimate practicality of the device. However, firm conclusions are not possible until information becomes available from a demonstration of the full-scale system.

POWER CONDITIONERS

Design Alternatives

Most battery storage systems will require some kind of "power-conditioning" system to supervise their connection with sources of charging energy and with the loads met while discharging.

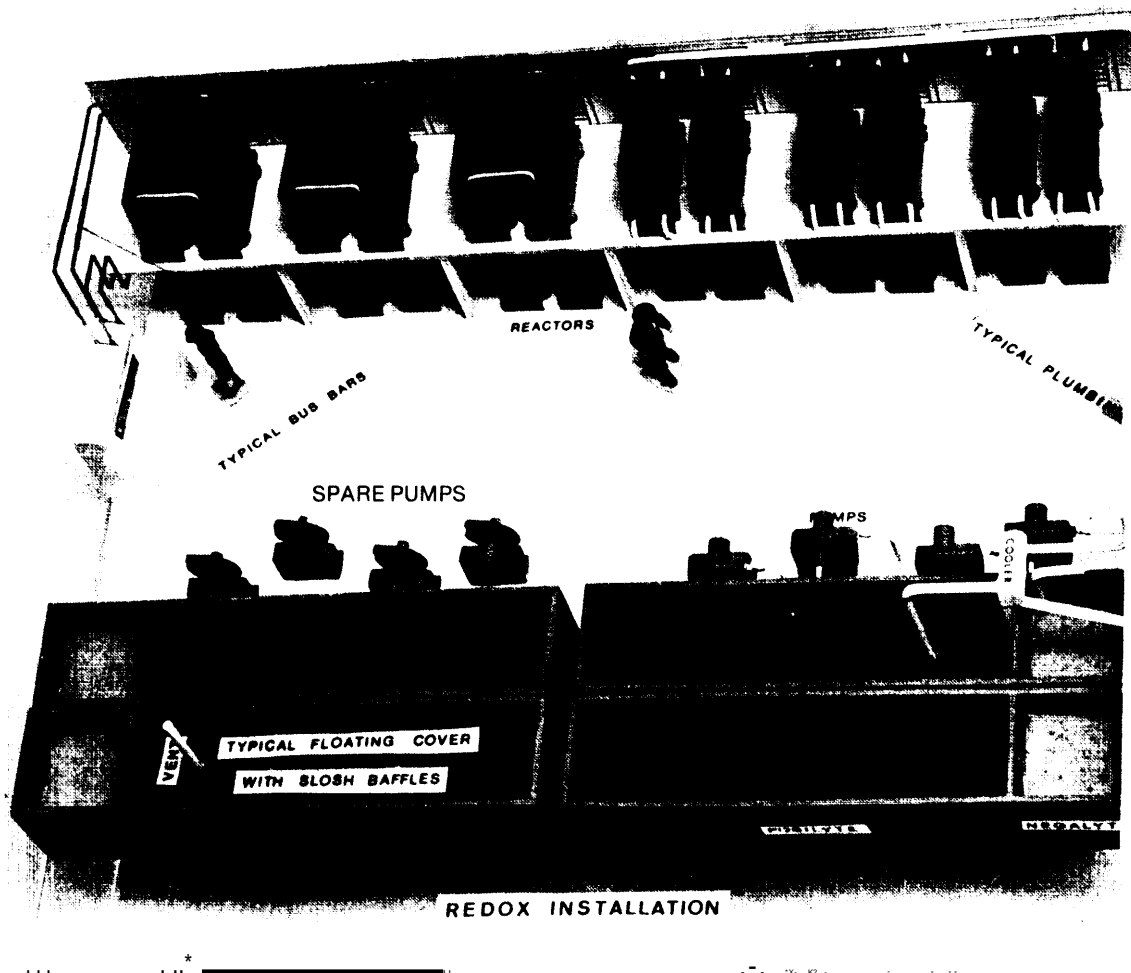
This equipment can serve four functions:

- 1 Regulate the rate at which a battery is charged and discharged to protect the battery and extend its useful life;
- 2 Serve as a switching system, and determine whether the loads will be met directly from the onsite generating system, from storage, from the utility, or from some combination of these (in some cases it can also allow the storage to be charged from the utility);
- 3 Rectify alternating current received from the onsite generator or from the utility so that this energy can be used to charge the battery; and
- 4 Invert the direct current produced by the battery or by the onsite generating equipment, creating alternating current whose voltage and frequency meet acceptable standards of uniformity.

A system which can perform all of these functions is illustrated in figure XI-26. Not all devices will be as complex as the one shown, and designs will differ greatly from one application to another.

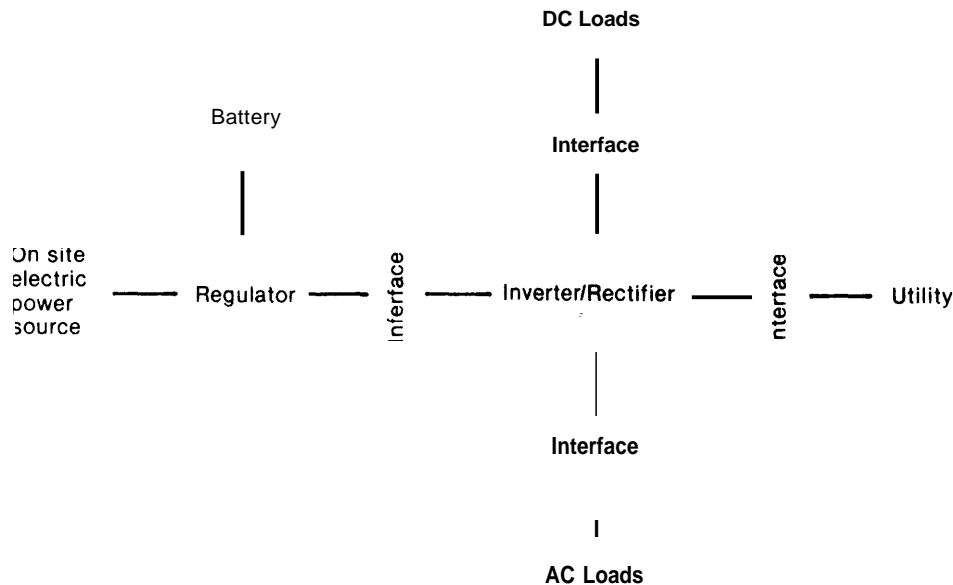
The most important design decision is whether to use an inverter. These devices are by far the most complex elements of a power-conditioning system and represent 85 to 95 percent of the cost of a typical power conditioner. Inverters would not be needed

Figure XI-25.— Model of iron-REDOX Battery Facility



SOURCE: G. E. L. Inc

Figure XI-26.—The Elements of a Power Conditioning System



if local loads could be met by direct current, but these savings could be largely offset by the costs of converting a residence or industry to d.c. operation. A quantitative assessment of this issue is beyond the scope of the current study, but it is possible to outline the major factors which must be considered if conversion to a d.c. system is contemplated:

- Over two-thirds of the power required in a typical residence is used in equipment which could easily be converted to d.c. operation. Incandescent lights, heaters, stoves, heating elements in driers, etc., could all operate with direct current without major difficulty.
- The only devices requiring a.c. are fluorescent lights, systems with electric motors, and electronic devices such as televisions, radios, and the like. Most of these appliances are currently available in d.c. versions, however, although some are more costly than their a.c. equivalents. A complete line of residential d.c. appliances is available for mobile homes.

- Direct current systems would require more expensive switches and fuses. The cost of wiring would be higher if low-voltage d.c. were used,

It should also be recognized that a d.c. system which relies on the utility grid to provide backup will need a rectifier. (Most inverters can rectify as well as invert and so would not require separate rectifying equipment.) Rectifiers tend to cost about 30 percent as much as inverters of equivalent power ratings.

A typical inverter can provide some kind of fault or short-circuit protection and can provide a.c. synchronized with the utility grid. The cost, design, and performance of inverters vary greatly and are strongly dependent on the quality of the a.c. current required. Systems using grid backup will clearly be required to provide a well-filtered output which matches the grid in frequency and

¹Facility Systems Engineering Corporation, Shopping Center Application of Photovoltaic Solar Power Systems, ERDA Contract (1-1-77) 2748, 1976

phase. Performance is usually specified in terms of the voltage control, and the harmonic content of the voltage produced.

Older units frequently were nothing more than a d.c. motor which drove an a.c. generator, but most modern devices use solid-state components based on silicon-controlled rectifiers. The solid-state devices are usually more reliable and require less maintenance. Most of these systems are "line commutated" in that they rely on utility power to establish the phase and frequency of their a.c. generation. Devices operating independently of grid power (self-commutated systems) are also available, but are more expensive.

Interest in developing inverters of various sizes has come from a variety of places. Small inverters have been developed for military applications, for small onsite generating plants (using windmills and conventional power sources), etc. Larger devices are available from suppliers of interruptible

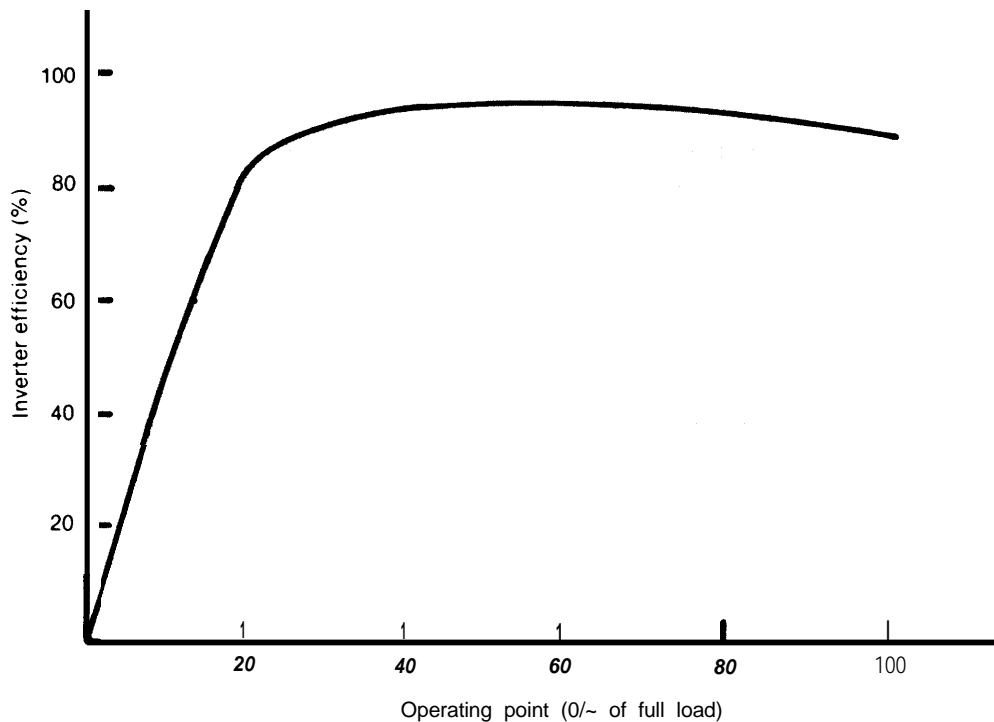
power supplies which are used in hospitals, computer centers, and other installations which cannot afford to lose power when grid electricity is unavailable. Much larger units are in use and being developed for d.c. transmission lines.

The design of interface and regulator systems is quite straightforward and systems are available in a variety of sizes. The complexity and cost of the system will depend strongly on the speed with which the system must shift from one power source to another, and on the system design.

System Performance

The efficiency of modern solid-state inverters is in the range of 92 to 95 percent when the devices are operating at more than about 25 percent of peak capacity. Below this point, the efficiency falls off quite sharply since a fixed amount of energy is required even at zero loads. Figure XI-27 illustrates the part-load efficiency of a typical

Figure XI-27.— Efficiency of a Solid-State Inverter as a Function of Load



SOURCE: MERADCOM, DoD

sol id-state inverter. The mechanical inverter systems mentioned earlier are typically less efficient than the sol id-state units.

The overall operating efficiency of inverters in small systems will probably be lower than the efficiency of inverters in large systems because there is less load diversity in the smaller systems. This can be expected to result in more operation at partial load.

Voltage regulators are quite efficient at all power levels; typical systems are 98-percent efficient.¹¹⁵

BATTERY SYSTEM COSTS

Since there is considerable disagreement about the future price of batteries and supporting equipment for onsite storage systems, cost estimates for battery storage systems will be given in four categories:

1. A near-term price, reflecting the costs of devices which could be purchased in 1976.

¹¹⁵Bechtel Corporation, *Energy Storage and Power Conditioning Aspects of Photovoltaic Solar Power Systems*, prepared for Spectrolab, Inc., under Sub-contract No 66725, October 1975.

- 2 An estimate based on present estimates of the cost of lead-acid batteries and inverters produced in large numbers (1,000 MWh/yr) for distributed storage applications.

- 3 An advanced-concept estimate of future prices which assumes that inexpensive, advanced battery systems such as sodium/sulfur or lithium-metal sulfide are successfully developed. This price could also apply to very large contract or Government purchases, where sales overhead could be reduced.

4. A very low-cost estimate which assumes that low-cost advanced-concept systems such as iron-REDOX are successfully developed.

The results of these estimates are summarized in table XI-11 and figure XI-28.

The cost of a battery storage system consists of three major components: the cost of the battery itself; the cost of the power-conditioning system; and the remaining cost which includes installation and the space required to house the system. The cost of each component is treated separately,

**Table XI-1 1.—System Cost Estimates for Near-, Intermediate-, and Long-Term
(Including 25-Percent Off)**

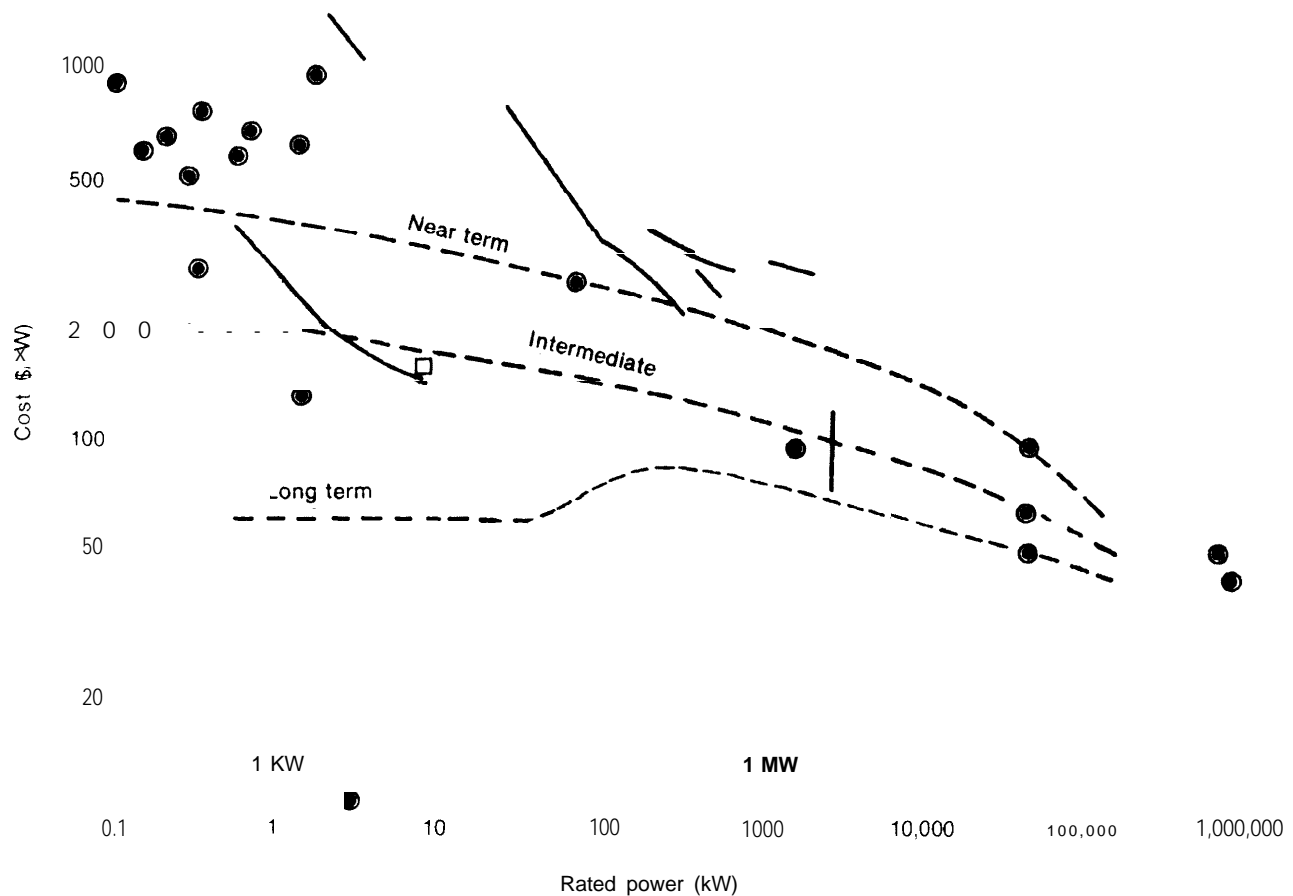
	Present market prices	Present technology with mass production	Advanced concept or advanced lead-acid tech- nology with large firm con- tracts (e.g., GSA) 1990-2000	Long-term iron-REDOX
Lifetime (deep cycles)	2000	2000	2000	2000
O & M cost (mills/kWh discharged)	028	028	(0.287)	(c)
Replacement cost (% of original)	85	60	100	100
Assumed discharge time (hours)	5	5	5	10
First costs				
(1) Commercial and multifamily residential systems				
Battery cost (\$/ kWh)	88	60	33	11.7
Building and other costs ^a (\$/kWh)	20-3 log ₁₀ C	13.7-1.8 log ₁₀ C	5.7-0.7 log ₁₀ C	5.7-0.7 log ₁₀ C
Power-conditioning costs ^b (\$/kW)	400-67 log ₁₀ P	200-29 log ₁₀ P	80	80
(2) Home systems				
Battery costs (\$/kWh)	96	66	36	
Building and other costs ^a (\$/kWh)	20-3 log ₁₀ C	13.7-1.8 log ₁₀ C	5.7-0.7 log ₁₀ C	
Power-conditioning costs ^b (\$/kW)	400-67 log ₁₀ P	200-29 log ₁₀ P	60	

^aC is the capacity of the storage system in kWh. The dependence on capacity is assumed related to inverter cost for a 5-hour system as described in the text.

^bP is the rated power of the inverter in kW.

^cAnnual O&M assumed to be 1 percent of original cost.

Figure XI-28.— Power-Conditioning Cost Versus Power



Bechtel Corp., op. cit. This data represents prices for *single units*.

Below 10kW this data represents catalog prices and quotes for commercially available units

The unit at \$10/kW (3kW) provides square wave output. The prices between 10 kW and 25 MW are prices for uninterruptible power supplies less batteries which are generally more sophisticated than will be required for onsite electric systems

The data for higher power levels represent projected prices for utility load-leveling systems

—The solid line segments represent prices for a single manufacturer as a function of size
 = "Gemini Synchronous 8 kW Inserter," Windworks, P O Box 329, Mukwango, Wis

x Prices for current-fed inverter systems from Peter Wood. AC/DC power Conditioning and Control for Advanced Conversion and Storage Technology EPRI 390-1-1 (1975) The lower price is for a line commutated system higher price is for a comparable Isolated system