Chapter 5

ENERGY STORAGE

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I. THE USES OF ENERGY STORAGE

Energy storage is not a new branch of technology — indeed its roots reach back to antiquity. It is clear that several methods of mechanical energy storage were employed long before Newton formalized that subject in his treatise on the laws of motion. The flywheel, one of the devices to be considered in some detail here, plays an essential role in the potter's wheel which is mentioned in the Old Testament.

Thermal energy storage was also used long ago. Homes with thick adobe walls were constructed by the Pueblo Indians in the American Southwest. The walls would absorb energy during the hot days, and the interior would remain cool. The stored heat would warm the living quarters against the cold desert nights.

Due to the declining availability of inexpensive fossil fuels, energy storage is again assuming an important role. Whenever the availability of an energy resource and the load requirements do not match, it is necessary to store energy if the energy source is to service noncoincident portions of the load. The examples of the ancient flywheel and adobe walls provide just this ability to extend periods of energy excess into times of deficiency. Modern mechanical means include sophisticated flywheels, pumped hydroelectric, and compressed air storage; thermal energy may be accumulated as sensible heat changes, latent heat changes, or as changes in chemical bond energy. In addition, batteries and other electrochemical processes may be used to store electrical energy in chemical forms, and fuels such as hydrogen may be produced. Current applications for storage include solar energy processes, utility peak shaving, and electric load leveling. Storage may also become important in such areas as medium-to-light-weight vehicles and industrial waste heat utilization, although these applications will not be discussed here.

A. Energy Storage In Solar Applications

Since solar radiation is an inherently time dependent energy resource, storage of energy is essential if solar is to meet energy needs at night or during daytime periods of cloud cover and make a significant contribution to total energy needs. Since radiant energy can be converted into a variety of forms, energy may be stored as thermal, chemical, kinetic, or potential energy. Generally, the choice of the storage media is related to the end use of the energy and the process employed to meet that application. For thermal conversion processes, storage as thermal energy itself is often most cost-effective. For photochemical or photovoltaic processes, storage is more appropriate in chemical form. A device which produces mechanical energy directly stores energy easily as kinetic or potential energy.

The location and type of energy storage in the overall system is often not very well defined. For example, in a solar thermal electric plant, steam is produced by concentrating solar collectors and is used to run a turbine. The turbine powers a generator to produce electricity. As shown for this process in Figure 1, energy may be stored thermally between the collector and turbine, mechanically between the turbine and generator, or chemically by a battery between the generator and the user. Since the turbine and generator are not 100% efficient, more energy must be stored for a given final output of electricity the closer the storage is located to the solar source, assuming that the storage units are all of the same efficiency. On the other hand, locating storage near the source reduces the required capacity of all the subsequent units since they are used for longer periods of time; and better conversion efficiencies, lower capital costs, and higher utilization of equipment result. Ultimately the decision as to where to locate storage in the system depends on the cost of the energy delivered as well as the reliability of the device.

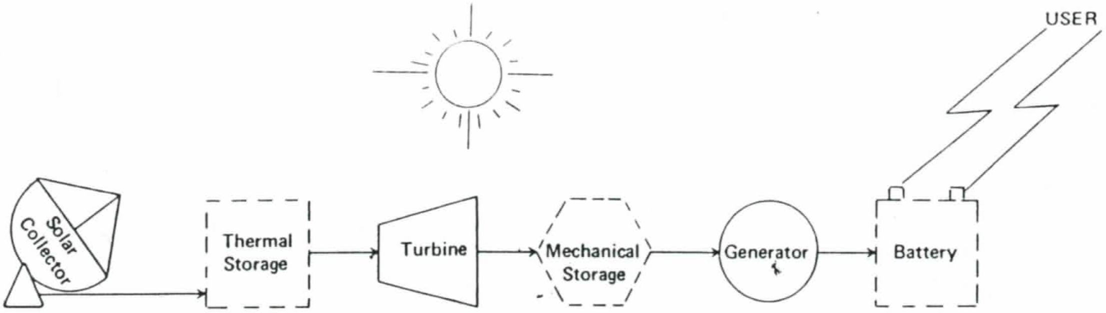


FIGURE 1. Possible locations for storage in a solar thermal electric plant.

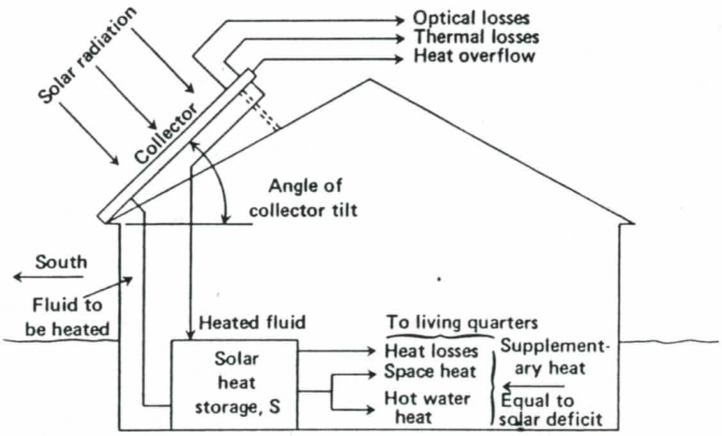


FIGURE 2. A residential solar heating system. (From Lof, G. O. G. and Tybout, R. A., *Sol. Energy*, 14, 253, 1973. With permission.)

The optimum capacity of the storage device for a given solar process depends on the time dependence of the solar availability, the nature of the load, the cost of auxiliary energy, and the price of the process components. These factors must all be weighed carefully for a particular application to arrive at the system design (including storage size) which minimizes the final cost of delivered energy. Such a cost optimization has been performed in a classic study of solar home heating by Löf and Tybout.[1,2] The following discussion will focus on some storage aspects of their work to illustrate the generally accepted role of storage current in solar home heating systems.

The system studied consists of flat-plate solar collectors tilted at some angle from the horizontal with necessary pumps or blowers to transfer heat from the collectors to storage. All the solar energy provided goes through the storage unit first as shown in Figure 2. Storage may be in a tank of water or a bin of dry crushed rock depending on whether water or air, respectively, is the heat transfer fluid. The stored energy could be used for both heating the living space and hot water. Since the storage unit is located inside the house, heat losses from storage are to the house itself and do not penalize the solar heating efficiency. A full sized backup heating unit is included since it is generally considered costly per unit of energy provided to meet the total heating demands by solar energy alone. Both the conventional heat source and the solar heating unit use the same heat distribution system to serve the house heating needs. (see Volume II, Chapter 8 for details.)

Relationships were incorporated into a computer program to describe the performance of the home heating system. To make the results adaptable to different system requirements, all the design equations were written on the basis of one square foot of collector area. The program requires that the collector temperature exceed the storage temperature by 6° C (10°F) before fluid is circulated between the storage device and the collectors to overcome heat losses in transfer and justify the electricity cost to operate the pump or blower. Since the collector temperature must exceed that in storage before fluid can be circulated profitably, it is more difficult for the collector to get to a high enough temperature to provide additional energy to a storage device which is already charged to high temperatures than to add heat to a discharged storage unit.

The objective is to find the solar system component sizes and the mixture of solar and conventional fuel which minimize the cost of delivered energy. At the time of the referenced study, commercial solar heating systems were not widely used; and the price information was somewhat sketchy. In addition, the costs employed in the analysis were for 1961 to 1962 and since they are no longer applicable, they will not be discussed in detail here. However, the authors found that changes in price levels did not significantly affect the conclusions of the study; and more recent work has substantiated the storage requirements.[3] Therefore, the findings of Löf and Tybout still have merit in matching storage requirements to home heating needs.

Weather data from eight different sites within the U.S. were employed in conjunction with the developed model to determine solar heating system performance. These locations, shown in Table 1, were judged representative of a range of world climates. Cities in parentheses in the table are locations where actual data was taken if the city identified in the analysis is different from the actual monitoring station by a few miles. A full year of hour-by-hour data of horizontal surface solar radiation, atmospheric temperature, cloud cover, and wind speed was selected for the year the Weather Bureau advised to be most typical for each location.

Each of the seven design and demand parameters was varied independently while maintaining all the others constant at levels believed to be nearest their optimum to keep the number of computer runs reasonable. Each variable was optimized for a 28.5 MJ per °C-day (15,000 Btu/°F day) and 47.5 MJ per °C-day (25,000 Btu/°F day) house. The influence of storage capacity on energy cost is shown in Figure 3 for three of the cities studied. The percent heating by solar energy with these designs is shown along the lines drawn. The absolute costs shown on the ordinate for fixed collector size do not represent general least cost values; but they were judged adequate for the relative comparison made in the study.

One observation from Figure 3 is the occurrence of the optimum at 0.2 to 0.3 MJ of storage capacity per °C temperature rise and m^2 of collector area (10 to 15 Btu/°F-ft^2) for each of the sites shown, with a range of 0.2 to 0.4 MJ/°C-m^2 (10 to 20 Btu/°F-ft^2) for all sites studied. Thus storage capacity varies quite closely with collector area. However, Lof and Tybout found that the optimum collector area changes significantly with sites (details are available in their references[1,2]). The somewhat fixed storage capacity to collector area ratio means that the larger collector areas required in colder climates must be accompanied by more storage to meet the higher fluctuation in solar insolation. Overall, the increase in both storage and collector capacities causes the energy delivery cost to be higher for colder cities such as Boston in Figure 3.

Another important conclusion from this study is the moderate storage capacity required. If the storage device could swing through the full 64°C (115°F) temperature range allowed between the low heating limit of 29°C (85°F) and ceiling for water of 93°C (200°F), only about one winter day's heat should be stored at Albuquerque in the optimum sized device. In Boston about 2 days heat should be stored in the optimum case. In practice, even less heat could be stored since a temperature swing of less than 64°C (115°F) is expected in the winter. In any event, storage durations on the order of one week are not currently considered cost-effective as shown in Figure 3 for the fixed collector size.

TABLE I

Eight Cities Used in Lŏf and Tybout Study

Year	Site	Climate classification (Trewartha, including alphabetic code)	
1955	Miami	Aw:	Tropical savannah
1959	Albuquerque	BS:	Tropical and subtropical steppe
1956	Phoenix	BW:	Tropical and subtropical desert
1955	Santa Maria	Cs:	Mediterranean or dry summer subtropical
1955	Charleston	Ca:	Humid subtropical
1960	Seattle-Tacoma	Cb:	Marine west coast
1959	Omaha (North Omaha)	Da:	Humid continental, warm summer
1958	Boston (Blue Hill)	Db:	Humid continental, cool summer

From Lŏf, G. O. G. and Tybout, R. A., *Solar Energy*, 14, 253, 1973. With permission.

B. Energy Storage In Central-Station Power Plants

Most electric utilities that serve the public experience a variable daily, weekly, and seasonal demand for their product — electric power.[4,5] Utilities are required by their charters to find economical ways to generate power over large swings of electric load; they must also have sufficient generating capacity to satisfy maximum demand plus, for reliability, a sizeable system reserve.

In order to satisfy these conflicting requirements, electric utilities use different kinds of generating equipment in their systems. So-called ''base-load plants'' are used to service that part ofthe system load that continues 24 hr a day every day of the year. Base-load plants are designed to operate with high efficiency on the least expensive fuels available. These two requirements generally lead to high plant capital or first costs, but the low fuel costs and high load factor more than compensate for the high initial cost and produce the lowest cost power in the system. Base-load plants today are primarily coal- or nuclear-powered. (Of course, if a utility has hydropower available, it will supply as much of its base-load power as water-level conditions would permit; hydropower has essentially zero fuel cost.)

The intermediate load which represents most of the daily demand swing is served by several different types of equipment. The equipment which is generally shut down at night is typically made up of older less efficient fossil fuel plants and, more recently, gas turbines. The peak load which may persist for only a few hours is usually met by the oldest fossil fuel equipment and gas turbine units.

Historically this generation mix has worked quite well for electric utilities, but as fossil fuel costs have steadily increased, the old mix has become more costly. At present, utilities must have considerable capacity that is used only a few hours a day to provide peaking- and intermediate-load power. However, if large-scale energy storage were available, relatively efficient and economical base-load power generation equipment could be employed at higher load factors with the excess over off-peak demand being used to charge the energy storage system. During periods of peak demand, the storage system would supply power, thereby reducing the need for fuel-burning peaking equipment and at the same time reducing expensive fuel consumption. Furthermore, the increased base-load capacity would replace a part of the intermediate generation, producing additional cost and fossil fuel savings, especially if the added base-load plants were to use nonfossil primary fuels. Currently, utilities which are located in favorable geographic regions handle peak loads and sometimes intermediate loads

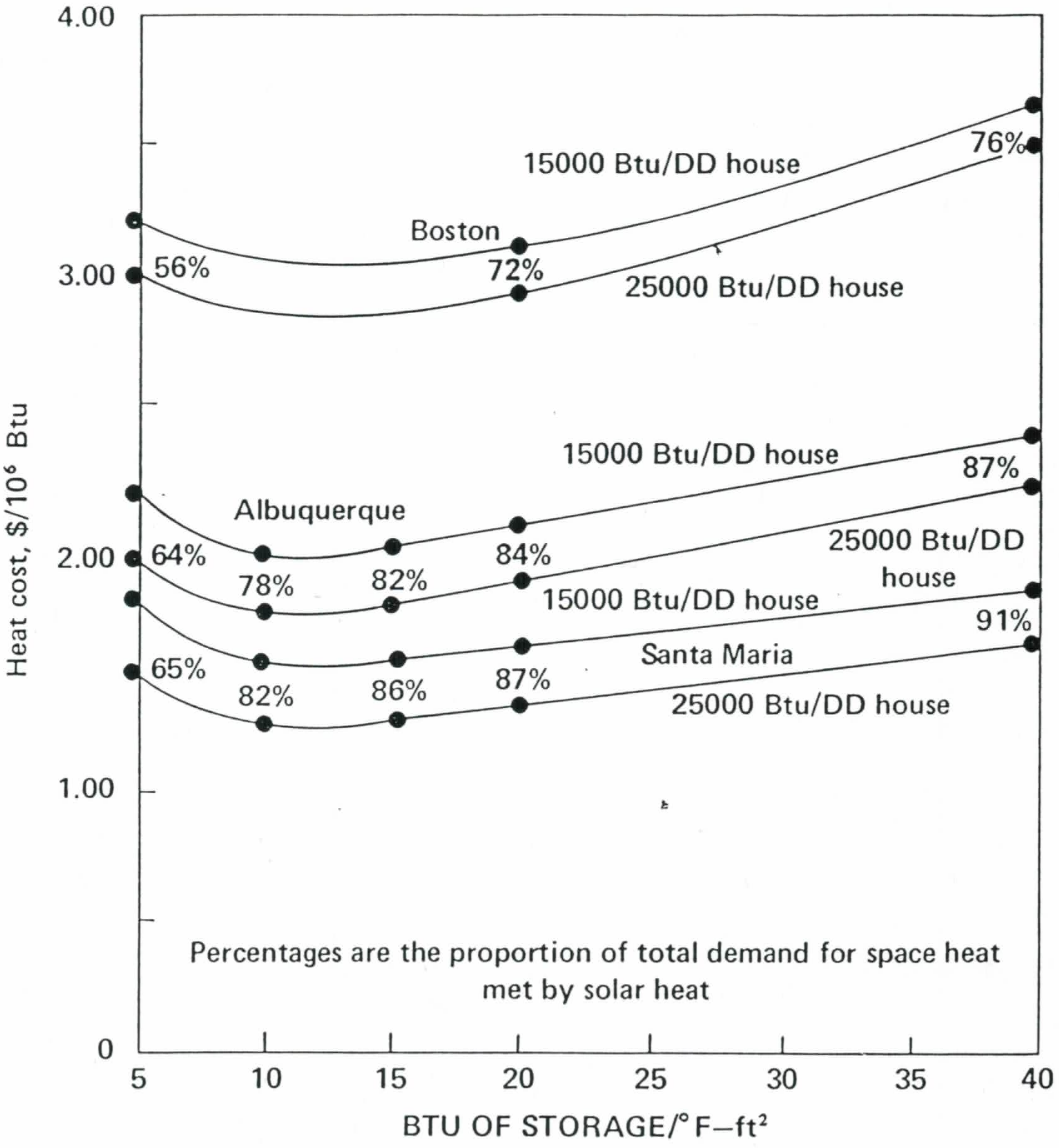


FIGURE 3. The influence of storage capacity on the cost of solar heat. (From Lof, G. O. G. and Tybout, R. A., *Sol. Energy*, 14, 253, 1973. With permission.)

with pumped storage units, if available. Using energy from a storage system to generate peaking power is termed "peak shaving;" the term "load leveling" describes the use of storage to eliminate conventional intermediate load cycling equipment.

It should be understood that the advantages of energy storage are not obtained without cost. The cost arises from the fact that it is impossible to get back every kilowatt-hour that is stored in the storage devices. Thus the real significance of energy storage is not a net saving of energy but a shifting of demand from inefficient units using costly fuels to more efficient primary units using less expensive fuels.

If storage technologies can be developed to meet the criteria for technical and economic feasibility that electric utilities demand, energy storage will certainly see widespread use in utility systems. Technical feasibility means that such systems must meet utility standards for operating life, reliability, safety, and compatibility with existing equipment. Economic feasibility implies that the total annual cost of electric energy delivered from energy storage systems must be equal to or less than the cost of energy from nonstorage equipment used for peaking and intermediate power generation.

The capital cost of an energy storage system is expressed to a first approximation as:

$$C_T = C_P + tC_S \qquad (1)$$

where C_T is the total capital cost in dollars per kilowatt, C_P is that portion of the capital cost proportional to the power rating, C_s is that portion of the capital cost proportional to the system's energy storage capacity in dollars per kilowatt-hour, and t is the number of hours per day during which energy can be delivered from storage. Thus the rate at which energy is delivered and the size of the storage device influence the total system cost.

Several preliminary analyses have been carried out with the goal of establishing probable ranges for technical and economic feasibility criteria. Table 2 gives the results of one such study.[5] In this analysis, distributed energy storage costs are assumed to include a credit of $60/kW to reflect the fact that transmission costs will be considerably less for distributed storage systems than for central storage systems.

Kalhammer and Zygielbaum[5] come to the following conclusions about energy storage systems:

1. Energy storage systems with what appear to be attainable technical and economic characteristics and charged with power from modern base-load plants, promise to be more economical than gas turbines and coal gas-fired combined-cycle machines for generation of peak and intermediate power up to approximately 2500 hr of annual operation.
2. For operating periods between about 3000 and 5000 hr per year, coal gas-fired combined cycle power plants promise to have more favorable economics than energy storage systems.
3. Those energy storage devices that are economical in relatively small sizes (such as batteries or flywheels) have particularly favorable economics for peak-power generation (less than 1000 hr of annual operation), because credits can be claimed for transmission and distribution capital cost savings as a result of siting close to the load, and capital costs are largely proportional to energy storage capacity and, thus, are low for short periods of daily operation.
4. Depending on annual operating time and local conditions, combinations of different energy storage methods might be used to achieve the lowest-cost peak- and intermediate-power generation in future electric utility systems.

Figure 4 summarizes these results.[5] Specific methods of storing energy and their usefulness to electric utilities will be cited in subsequent sections.

C. Energy Storage In Residences And Commercial Buildings

Base-load power plants can also be used to provide a larger fraction of the load if the electrical demand is nearly uniform over extended periods. If lower electricity rates are offered during periods of low demand, customers will tend to adjust their use pattern to take advantage of the savings. Thus electric clothes dryers, dishwashers, and other electrical appliances with sizeable electrical demands will be employed more often during the off-peak time periods. As a result, the peak demand will be lowered while the off-peak demand will rise.

TABLE 2

Feasibility Criteria for Utility Energy Storage

Energy storage application	Efficiency (%)	Life (Years)	Capital cost for central storage		Capital cost for distributed storage	
			C_p ($/kW)	C_s ($/kWhr)	C_p ($/kW)	C_s ($/kWhr)
Peak shaving	≥60	≥20	40—90	7—20	60—150	7—25
Load leveling	≥70	≥30	50—110	5—15	50—170	5—18

From Kalhammer, F. R. and Zygielbaum, P. S., Paper No. 74-WA/Ener-9, American Society of Mechanical Engineers, New York, 1974. With permission.

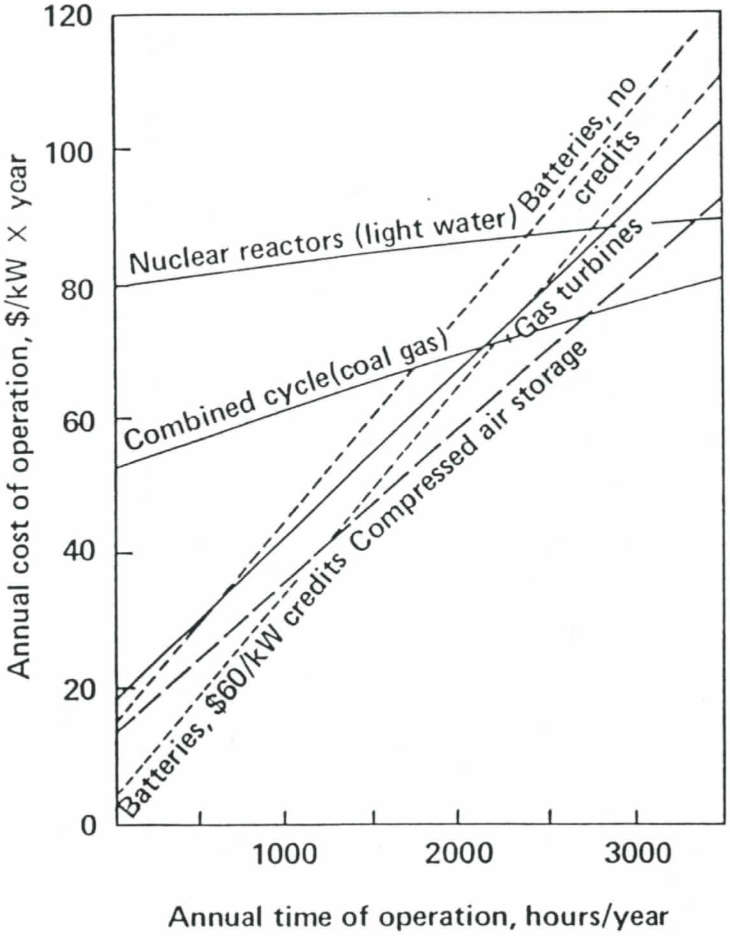


FIGURE 4. The economics of peak- and intermediate-cycling power generation as a function of annual hours of operation. The lower dashed line for batteries gives a $69/kW credit because of savings in transmission and distribution costs. (From Kalhammer, F. R. and Zygielbaum, P. S., Paper No. 74-WA/Ener 9, American Society of Mechanical Engineers, New York. With permission.)

Although many major electrical appliances can be used in the off-peak electrical periods, electrical home heating systems must be able to supply heat according to the demand. Since the latter is related to unpredictable weather patterns for reasonable comfort limits, it is not possible to shift the electrical requirement for conventional home heating systems. However, if a thermal storage medium is heated up electrically during off-peak hours, the energy can be released from storage during peak-load hours. Thus the daily load curve is smoothed, and the growth of winter peaks is retarded by displacing loads into the off-peak valley of the utility's load curve.

Utilities in the U.S. do not offer off-peak rates as a rule, and electric storage heating has consequently not been commercially successful. Utilities and their regulators apparently do not feel that electric storage heating is a cost-effective method of providing space heating in the U.S. On the other hand, favorable off-peak rate structures are offered in a number of European countries; and customer installation of storage heating systems has been successfully carried out in West Germany, Britain, Switzerland, Austria, Belgium, France, and Ireland. One of the major differences between the European and U.S. electric demand experience is that most U.S. utilities face peak demands in the summer while the Europeans see heavier loads in the winter. However, it is anticipated that the continuation of the current pace of electric heating system installation in the U.S. will shift the demand to winter peaking. Such is already the case for many northern states.[7]

Electric storage heating offers significant benefits for winter peaking utilities:[7]

- A slow down in the growth rate of winter peak loads with a consequent saving in transmission and generating capacity over that required otherwise
- Substitution of base-load generating plants for peaking and intermediate equipment due to the smoother daily demand curve
- A cost reduction in the electricity supplied enabling a greater market penetration for electricity

Of course, a favorable rate structure must be offered the customer to allow for a cost savings after the customer has paid for the purchase or rental of the storage equipment. Sufficiently large savings have been provided in the European countries previously mentioned to result in a significant penetration of storage heating systems. An example of the experience in England and Wales will be summarized in the following discussion based on Reference 6. More details on this example as well as the findings for West Germany can be found in that reference.

Under floor heating for air-raid shelters in World War II was the first important storage heater for Britain. Storage radiators such as in Figure 5 were introduced for the residential market in 1961 with later versions incorporating thermostatic and possibly weather-monitor controllers. A further refinement was the introduction of a fan into the unit to produce the storage fan heater shown in Figure 6. These latter two free standing concepts are used in existing housing in Britain, but the growth of fuel fired forced air systems in the 1960s led to the development of the central "Electricaire" heating system of Figure 7. The unit stores energy in a central unit of cast iron or refractory bricks with distribution throughout the building by warm air ducts. In 1971, a device was introduced called a "Centralac" unit which is similar to the Electricaire but uses an air-to-water heat exchanger to provide forced hot water heating. Electric domestic hot water storage units are also heated in off-peak hours to supply the daily needs of an average family.

In England and Wales, the Central Electricity Generating Board (CEGB) generates electricity and transmits it to 12 Area Boards who in turn distribute it to the customers. These Area Boards may set the retail rates for electricity within established guidelines. In the 1950s, the Area Boards began offering special off-peak rates to encourage use of floor warming in buildings; but not until the CEGB began basing capacity charges on contributions to the peak in the early 1960s and the storage radiator became avail-

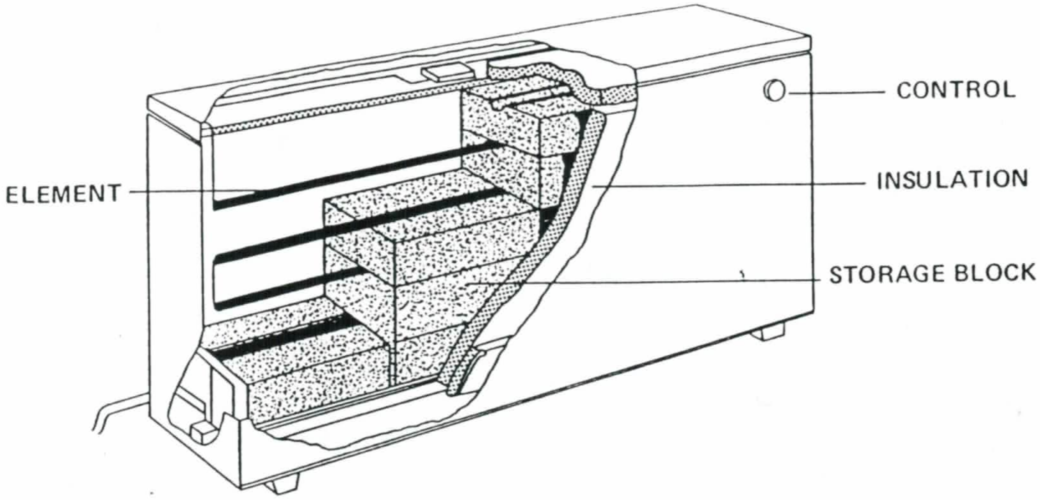


FIGURE 5. An electric storage radiator. (From Asbury, J. G. and Kouvalis, A., Rep. ANL/ES-50, Argonne National Laboratory, Argonne, Ill., May 1976.)

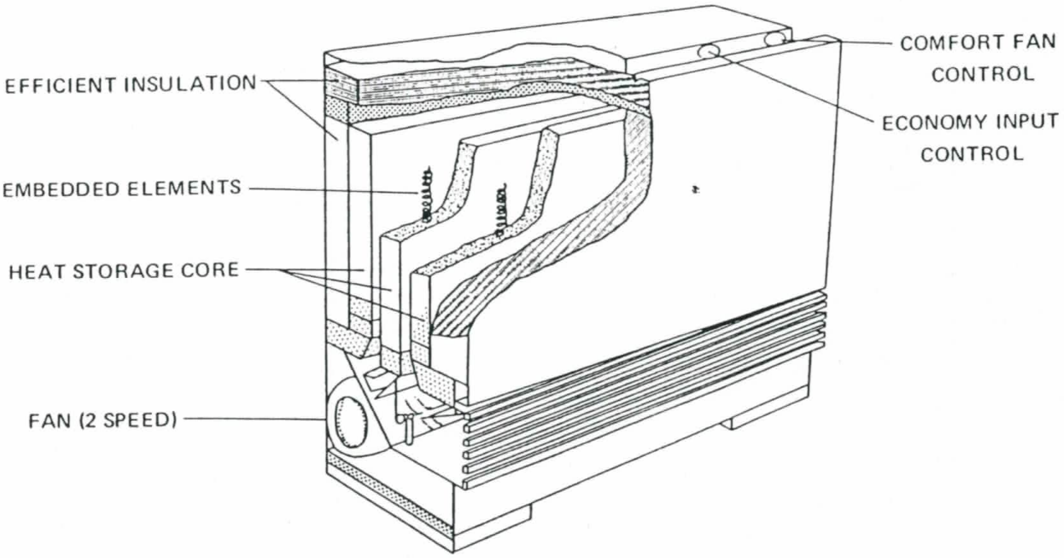


FIGURE 6. An electric storage fan heater. (From Asbury, J. G. and Kouvalis, A., Rep. ANL/ES-50, Argonne National Laboratory, Argonne, Ill., May 1976.)

able, did off-peak electricity rates become actively promoted. Representative rates for storage heaters and floor warmers are shown in Table 3 for the South Western Electricity Board (SWEB). The afternoon rate was required to boost the device since capacity was not enough to last the entire day.

In the period from 1962 to 1966, the rapid growth in storage heater installations and the low rate afternoon boost period caused a shift in the load curve from a midday valley to a midday peak. As a result, the off-peak tariffs for new customers were shifted to only the night period of generally eight hours at so-called White Meter rates by several Area Boards. This change allowed a daytime boost at regular rates if required, but the higher daytime rates encouraged night consumption of electricity if possible. Improvements in heater design and increases in storage capacity resulted in devices that could operate with only the nighttime charge. Figure 8 compares the

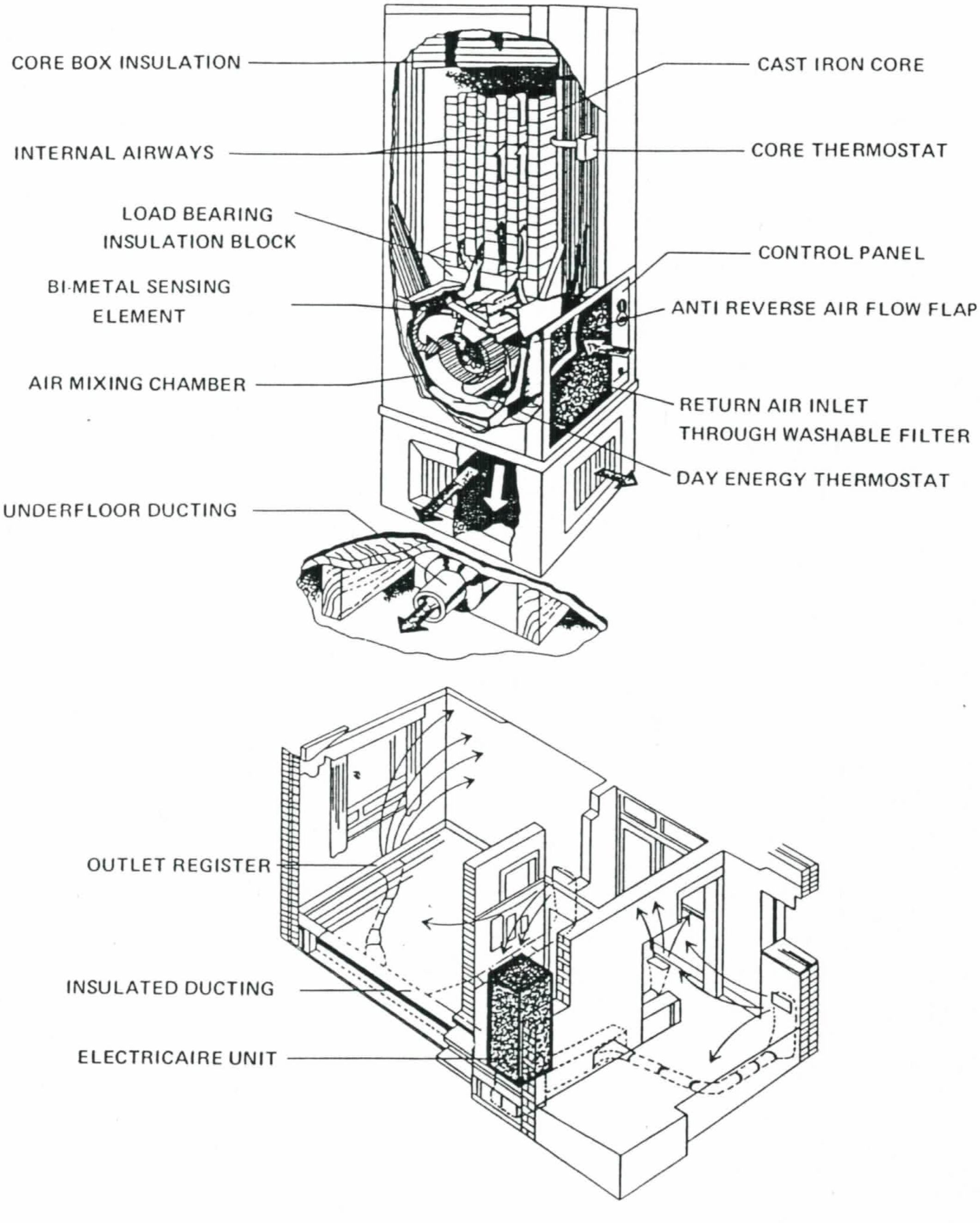


FIGURE 7. Electricaire storage heating system. (From Asbury, J. G. and Kouvalis, A., Rep. ANL/ES-50, Argonne National Laboratory, Argonne, Ill., May 1976.)

CEGB annual average daily load curve and the average weekday daily winter load curve for 1972/1973 with the 1960/1961 curves normalized to the same constant daily load line, and the effect of storage is obvious.

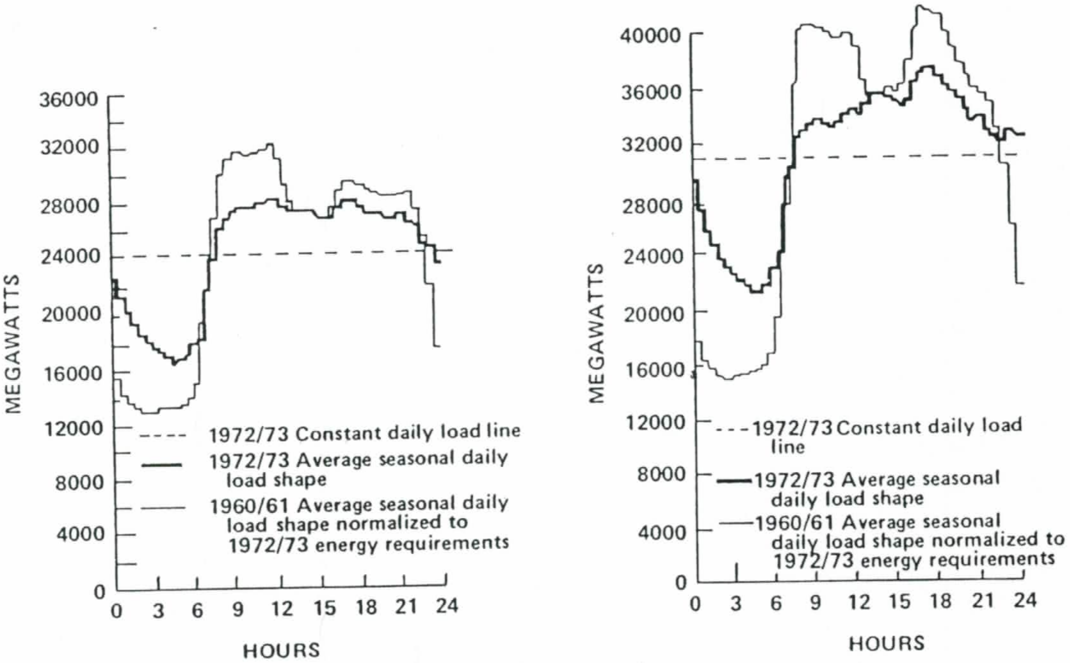
Table 4 summarizes the average electric rate structure used from 1973 to 1976 for England and Wales. Figure 9 presents the growth in the major types of storage heating units in Great Britain over the period in which off-peak rates were introduced. About 20% of the electricity for residential use in England and Wales was sold under off-peak or White Meter night rates in 1975.

TABLE 3

SWEB 1962 Off-peak Electricity Rates

Rate	Hours of availability	Total hours	Rate, pence/kWh	Ratio to normal domestic rate
A	23:00—07:30 and 11:00—16:00	11	0.85	0.62
B	19:00—07:30 and 13:00—16:00	15.5	1.0	0.73

From Asbury, J. G. and Kouvalis, A., Rep. ANL/ES-50, Argonne National Laboratory, Argonne, Ill., May 1976.



Annual-average Daily Load Curve

Winter-average Weekday Load Curve

FIGURE 8. The 1972/1973 CEGB daily load curves versus those of 1960/1961. (From Asbury, J. G. and Kouvalis, A., Rep. ANL/ES-50, Argonne National Laboratory, Argonne, Ill., May 1976.)

II. ENERGY STORAGE IN BATTERIES

There is now renewed interest in the possible use of rechargeable batteries for bulk energy storage in utility systems and in vehicles because of: (1) the specific advantages of batteries (which include distributed storage of energy for central station plants with its significant economic and siting benefits, as well as the rapid installation and demand-responsive capacity for growth of essentially modular storage units); and (2) the emergence of new battery concepts for both central station and transportation applications that appear to offer promise of meeting the stringent cost and life requirements of these applications of energy storage.

The major challenge in battery energy storage systems for either central station power or transportation use is to develop a battery that has a significant cycle life and can be mass produced at very low cost. Several different approaches toward these goals

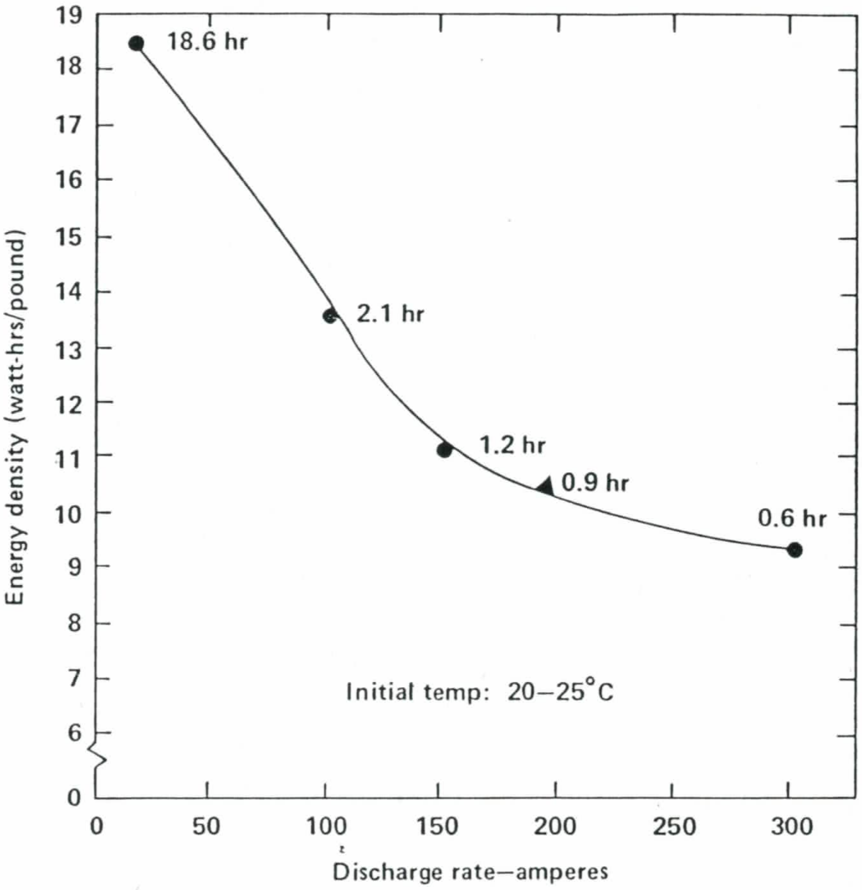


FIGURE 10. The effect of discharge rate and time of discharge on energy density. (From Gross, S., Proc. Battery Council Int. Golden Anniversary Symp., London, May 1974. With permission.)

The nickel-hydrogen cell is a relatively recent development in the area of alkaline storage batteries. This system combines the best electrode from the nickel-cadmium system with the best electrode from the hydrogen-oxygen fuel cell system. The system has an open circuit potential of 1.358 V and a theoretical energy density of 390 Wh/kg. An energy density of 55 Wh/kg has been achieved on prototype cells, and design studies reveal that 88 Wh/kg should be attainable. Power densities of 88 W/kg have been realized, and it is believed that the power density might be raised to 440 W/kg in an optimized design. A possible improvement to the nickel-hydrogen battery would be the development of a means to store hydrogen in a solid — perhaps as a metal hydride.

The zinc-chlorine battery is potentially an important system even though it is the most complex because of the use of a flowing electrolyte and the external storage of chlorine. The couple has an operating potential of 1.9 V and a theoretical energy density of more than 440 Wh/kg. The system has an edge in development and has already performed well in sizes larger than any other advanced battery that has been built. Because the battery uses two relatively cheap materials, it could offer relatively inexpensive storage after development.

B. Metal-Air Batteries

In this battery system, a metal forms the negative electrode, and a gas electrode using oxygen from the air is the positive electrode. Such systems are potentially very flexible, but practical problems such as the development of improved high-rate air electrodes with nonnoble metal catalysts remain to be solved. High energy density metal-air batteries have severe thermal problems, as well: they can overheat, or for high temperature design, the problem of initial heating arises.[7]

The zinc-air system has received the most attention. It has a theoretical energy density of 1350 Wh/kg and an open circuit potential of 1.65 V. Primary batteries have demonstrated energy densities of 330 Wh/kg. However, some investigators believe that the problems encountered in zinc-air batteries are so basic that they will not likely yield with additional development.[7] Such problems include the difficulty of producing a compact enough zinc deposit during charge to avoid interelectrode shorting, achieving a good air electrode capable of high current densities at low gas pressure, and loss of water in the air exhausted from the air electrodes.

The aluminum-air battery appears to be an attractive battery from both a weight and cost standpoint. It has been used successfully as a primary battery but shows little promise as a secondary (rechargeable) material in aqueous electrolytes. Aluminum apparently can be cycled in nonaqueous electrolytes, but with reduced energy density. One aluminum-air battery under development is a two-kilowatt system that is mechanically recharged by replacing the aluminum and alkaline electrolyte. The air cathode uses platinum catalyst, though it is believed that nonnoble metals could be substituted in commercial applications.

Considerable development has been done in Sweden on iron-air batteries where an experimental 30 kWh battery has been built and used to power a small truck achieving 66 Wh/kg with an energy density of 99 Wh/kg expected in production models. It is estimated that these batteries will have a lifetime of about 500 cycles, limited by the cathode.

C. High Temperature Batteries

These batteries are potentially attractive for both traction applications and central-station work. High power capability is achieved by use of low resistance electrolyte materials such as fused salts and by operating at elevated temperatures to increase the charge current density. The benefits of high temperature operation are not achieved without cost — especially troublesome are material and seal problems. The large increase in solute (up to 25%) when electrolyte salts melt poses a design problem. On the other hand, high temperature cells use electrode materials in a liquid state, thus avoiding morphological changes that occur with solid electrodes and thereby offering at least the promise of long life.

The sodium-sulfur cell has received the most publicity of all the high temperature battery systems. It has a theoretical energy density of 790 Wh/kg and an open circuit potential of about 1.8 V, depending on state of charge. The operating temperature of this cell is approximately 300 to 350°C with all reactants and products in the liquid state. Standby temperatures cannot be lower than 230°C. The use of sodium-sulfur cells for bulk energy storage in central-station power plants along with test results on a series of tubular cells is presented by Mitoff and Bush.[10]

The lithium-metal sulfide ($LiSi/FeS_2$) design has a theoretical energy density of 950 Wh/kg. The operating potential is around 1.4 V with an operating temperature of 400 to 450°C. These cells have a very high specific energy but show a rapid degradation of capacity with time. The high operating temperature of the lithium-metal sulfide battery raises serious problems of lifetime. The question of lithium availability also must be answered. Nevertheless, this battery has demonstrated an ability to be cycled.

A lithium tellurium tetrachloride system has achieved the elusive goal of a cycle life in excess of 2000 cycles without lithium dendrites forming or other problems.[7] An open circuit potential of 3.1 V and a theoretical energy density of 1120 Wh/kg are possible. The electrolyte is a molten eutectic of lithium chloride and potassium chloride operating at about 400°C. The active lithium negative materials, rather than being liquid, are alloyed with aluminum to form a solid and then encapsulated in a screen. This system has attained an energy density of 84 Wh/kg and a projected level of 130 Wh/kg.

Another high temperature battery which might find application in central-station plants and for motive uses is the aluminum-chlorine battery which has a theoretical energy density of 1430 Wh/kg and an open circuit potential of 2.1 V. The electrolyte in this system is molten $AlCl_3$-KCl-NaCl, the latter two constituents being a binary eutectic and the amount of $AlCl_3$ varying with cell state of charge. It has been found that the electrolyte can melt as low as 70°C, but a realistic operating temperature is 150 to 250°C. It is believed that operating above 200°C and the use of ceramic separators would help to solve problems of aluminum dendrite formation and excessive blockage of the aluminum by the $AlCl_3$ discharge product. Since overall electrical efficiencies of 87% have been observed with these cells, they should appear especially attractive as storage units in central-station power systems.

A battery with an operating temperature near that of the aluminum-chlorine battery uses sodium-antimony trichloride (Na/$SbCl_3$). It has a theoretical energy density of 770 Wh/kg and an operating potential near 2.6 V. However, the current density per unit area of electrolyte is about one third that of the sodium-sulfur battery. The cost and availability of antimony raise questions about large-scale use of this battery.

D. Organic Electrolyte Batteries

Much effort has been expended on cells that use lithium as a high energy negative electrode in organic electrolyte batteries. Such systems typically suffer from low discharge rates and low charge rates; nevertheless they do appear to hold some promise because they possess wide operating temperature ranges.

One cell that has received some attention is the lithium-sulfur dioxide battery which has a theoretical energy density of 1090 Wh/kg and open circuit potential of 2.95 V. A small primary cell has delivered 265 Wh/kg. This particular system seems to be capable of operating at high discharge rates. At present, this system is used in a primary battery; but it is capable of being produced as a secondary battery.

Another lithium-based battery is the lithium-lamellar dichalcogenide battery which is a new class of rechargeable lithium systems utilizing lamellar transition metal dichalcogenides such as niobium diselenide as host structures for cathodic nonmetals such as iodine and sulfur. Open circuit potentials of three volts have been achieved. Batteries have operated for more than 1100 cycles at low current densities and ambient temperature. Propylene carbonate was the electrolyte.[7]

Another cell utilizing propylene carbonate as the electrolyte is the lithium-bromine battery which has an open circuit potential of 4.05 V and a theoretical energy density of 1110 Wh/kg. An experimental cell was cycled 1785 times, although current densities were only 30% of the initial value at the end of cycling. It appears that the long life of this system is due in part to a bromine shuttle mechanism which limits self-discharge.[11] This system with further development might find application where high energy density is required.

E. Evaluation of Selected Candidate Secondary Batteries

The characteristics required of a battery to be used in central-station work or for motive power are in some ways different. However, both applications will require that the battery be manufactured at low cost. Long battery life is important, but there is a limit to the increase in first cost that will be acceptable in order to achieve long-lived systems. Table 5 lists five promising battery candidates for load-leveling purposes and their characteristics.

TABLE 5

Load-leveling Batteries: Candidates and Characteristics

	Operating temperature (°C)	Theoretical cell energy density (Wh/kg)	Design cell energy density (Wh/kg)	Design modular volumetric energy density (Wh/in^3)	Depth of discharge (%)	Density—10-hr rate (mA/cm^2)	Active material cost ($/kWh)	Operating potential (V)	Demonstrated cell size (kWh)	Demonstrated cell life (cycles)	Critical materials
Lead-acid (Pb/PbO_2)	20—30	240	20	0.75	25	10—15	8.50	1.9	>20	>2000	Lead
Sodium-sulfur (Na/S)	300—350	790	150	2.5	85	75	0.49	1.8	0.5	400	None
Sodium-antimony trichloride ($Na/SbCl_3$)	200	770	110	2.0	80—90	25	2.35	2.6	0.02	175	Antimony
Lithium-metal sulfide ($LiSi/FeS_2$)	400—450	950	190	3.5	80	30	4.27	1.4	1.0	1000	Lithium
Zinc-chlorine (Zn/Cl_2)	50	460	55	0.7	100	40—50	0.74	1.9	1.7	100	Ruthernium (catalyst)

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III. THERMAL STORAGE OF ENERGY

A. Sensible Heat Storage

Energy is stored as sensible heat by raising the temperature of a solid or liquid. This is the simplest way to store thermal energy, and current technology is generally adequate for good system design. Most thermal storage devices now in operation, including those for electrical storage heating or solar heating discussed in the examples, utilize sensible heat storage. The amount of energy stored, Q, is equal to the integral of the specific heat, C_p, between the peak and minimum temperatures (temperature swing) experienced by the storage medium:

$$Q = \int_{T_1}^{T_2} C_p \, dT \tag{2}$$

The temperatures T_1 and T_2 can be any values useful for the application provided the properties of the medium are not altered over the storage temperature range. This latter condition, however, requires that the material chosen must be thermally stable and undergo no phase change between the temperature extremes. To be economically attractive, the substances should also be inexpensive, have a high heat capacity, high density, and acceptably low vapor pressure.

The energy storage capacities of a number of liquids suitable for sensible heat storage are shown in Figure 11 as a function of the temperature swing of the storage media. A constant specific heat has been used to plot the data. Figure 12 shows the storage capacity per 1975 dollar of storage material cost on the same basis. Water appears to be the best sensible heat storage liquid since it is inexpensive and has a high specific heat. However, an antifreeze must be added to water if the fluid temperature can drop below 0°C, and this adds significantly to the system costs. In addition, above 100°C, the storage tank must be able to contain the vapor pressure of water; and the storage tank cost rises sharply with temperature beyond this point. From this viewpoint, organic oils, molten salts, and liquid metals are more desirable for high temperature operation since they circumvent the vapor pressure problems; but significant limitations in handling, containment, storage capacities, cost, and useful temperature range are evident for each as shown in Table 6.[13,14,15]

The vapor pressure difficulties associated with water can also be avoided by storing thermal energy as sensible heat in solids. In addition, many inorganic solids are chemically inert even at high temperatures. To store the same quantity of energy, larger storage vessels are needed than for water since the heat capacity of the solids is less (Figure 13). The amount of energy stored per 1975 dollar invested in storage media only, although not as high as water, is still acceptable as shown in Figure 14. In fact, the cost of water and many solids is so low that the storage costs are influenced more by the price of containers and heat exchangers than by the storage materials. Direct contact between the solid storage medium and a heat transfer fluid is vital to minimize the cost of heat exchange in a solid storage medium, and the storage volume must be increased by up to 50% to allow for fluid passage. While air is generally acceptable as a heat transfer fluid for low temperature home heating systems, other fluids such as high pressure helium or heat transfer oils are generally required in high temperature installations to provide adequate heat transfer capability.[15,16] The heat transfer fluid must be carefully chosen to be compatible with the solids as well. The problems asso-

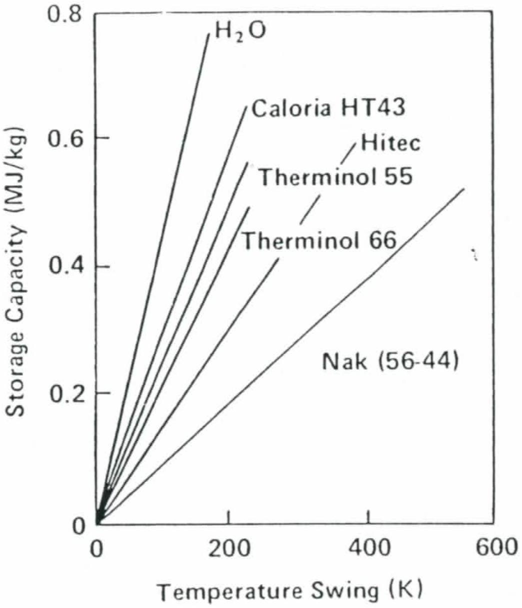

FIGURE 11. The storage capacity temperature swing for selected liquid sensible heat storage media. (From Bramlette, T. T., Green, R. M., Bartel, J. J., Ottesen, D. K., Schafer, C. T., and Brumleve, T. D., Rep. SAND 75-8063, Sandia Laboratories, Albuquerque, New Mexico, March 1976.)

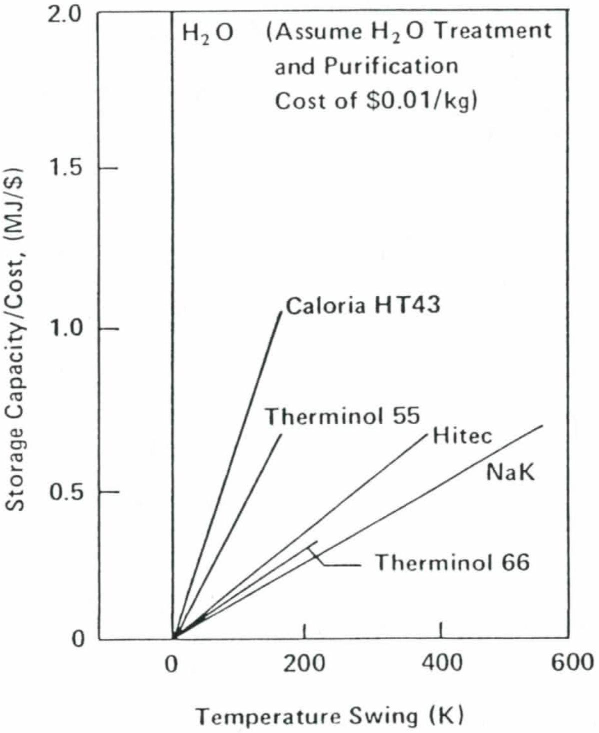

FIGURE 12. The energy stored per unit cost for selected liquid sensible heat storage media. (From Bramlette, T. T., Green, R. M., Bartel, J. J., Ottesen, D. K., Schafer, C. T., and Brumleve, T. D., Rep. SAND 75-8063, Sandia Laboratories, Albuquerque, New Mexico, March 1976.)

TABLE 6

Liquid Sensible Heat Storage Media

Medium	Fluid type	Cost (\$/kg)	Temp. range (°C)	Heat capacity ($Jkg^{-1}K^{-1}$)	Comments
Caloria HT43	Oil	0.30	−9 to 310	2300	Non-oxidizing environment required at high temperatures. Cracking occurs at high temperatures and volatile materials may be formed, lowering the flash point. May polymerize at high temperatures to increase viscosity.
Therminol 55	Oil	0.60	−18 to 316	2500	
Therminol 66	Oil	2.03	−9 to 343	2100	
Hitec	Molten Salt	0.60	150 to 590	1550	Long-term stability unknown above 550°C. Stainless steel or other expensive containers probably required above 450°C. Inert atmosphere required at high temperatures. Heated lines required to prevent freezing.
Draw Salt	Molten Salt	0.44	250 to 590	1560	
Sodium	Liquid Metal	0.90	125 to 760	1300	Stainless steel or suitable alternate containers required. Requires sealed system. Reacts violently with water, oxygen, and other oxidizing materials.
Sodium-Potassium	Liquid Metal	—	49 to 760	1050	

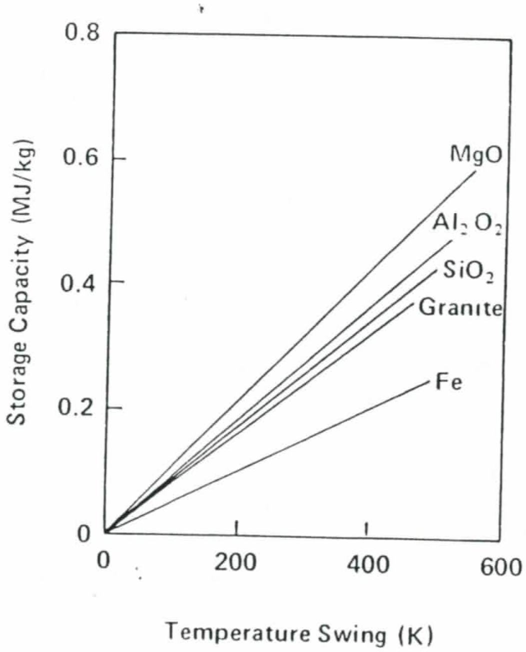

FIGURE 13. The storage capacity vs. temperature swing for selected solid sensible heat storage media. (From Bramlette, T. T., Green, R. M., Bartel, J. J., Ottesen, D. K., Schafer, C. T., and Brumleve, T. D., Rep. SAND 75-8063, Sandia Laboratories, Albuquerque, New Mexico, March 1976.

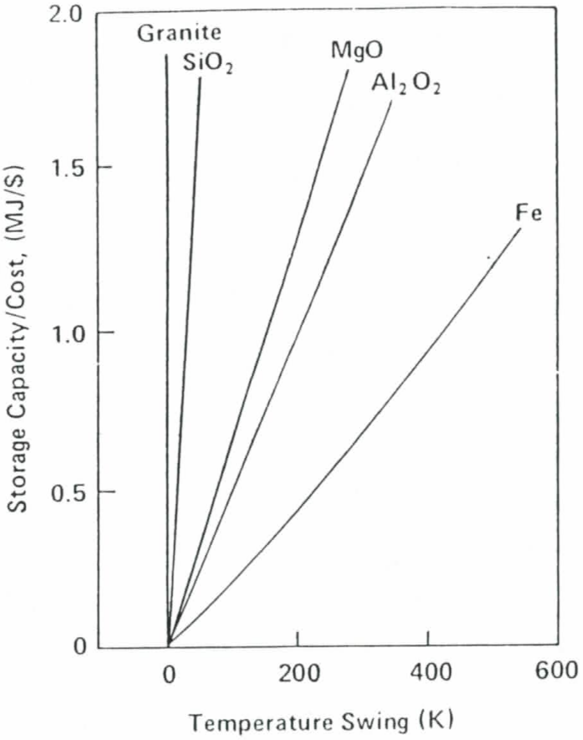

FIGURE 14. The energy stored per unit storage media cost for selected solid sensible heat storage media. (From Bramlette, T. T., Green, R. M., Bartel, J. J., Ottesen, D. K., Schafer, C. T., and Brumleve, T. D., Rep. SAND 75-8063, Sandia Laboratories, Albuquerque, New Mexico, March 1976.

ciated with finding a fluid with low vapor pressure, high heat capacity, and low cost are similar to those for storage in a liquid, but less severe. The properties of many sensible-heat-storage materials have been tabulated.[17]

A steam accumulator schematic for high temperature energy storage is shown in Figure 15. This device is really a pressure vessel to contain liquid water and is currently used in Europe to meet fluctuating steam demands.[19] It can be charged by a base load light-water reactor or solar thermal facility capable of supplying excess steam from the turbine during periods of low demand.[18] This steam is dumped into a vessel containing pressurized water. The vessel pressure may be charged up to as high as 20 atm and discharged down to 2 atm. This gives an energy storage density of about 100 kW,h/m^3.

The net electric power delivered from the steam accumulator depends on two more factors: the thermal turn-around efficiency, η, and the peak power train efficiency, η_g'. The first factor is a measure of the fraction of the energy stored that can be recovered from a storage tank. The second factor is simply a measure of the effectiveness of the thermal storage plant to convert the stored energy into work. Golibersuch et al.[18] show that losses by sensible heat transfer to the accumulator walls are negligible. They also show that for a discharge time of 15 hr and an ambient temperature of 70°F, an insulated tank would have a turn-around efficiency of 97% while an uninsulated tank would have an 83% efficiency. Depending on which cycle is chosen, a power cycle efficiency of the thermal storage plant of between 20 and 25% seems reasonable.

Based on the above assumptions and calculations, energy storage is likely to cost between \$7 and \$11 per kW,h based on an accumulator cost of \$700 to \$1060/m^3. If

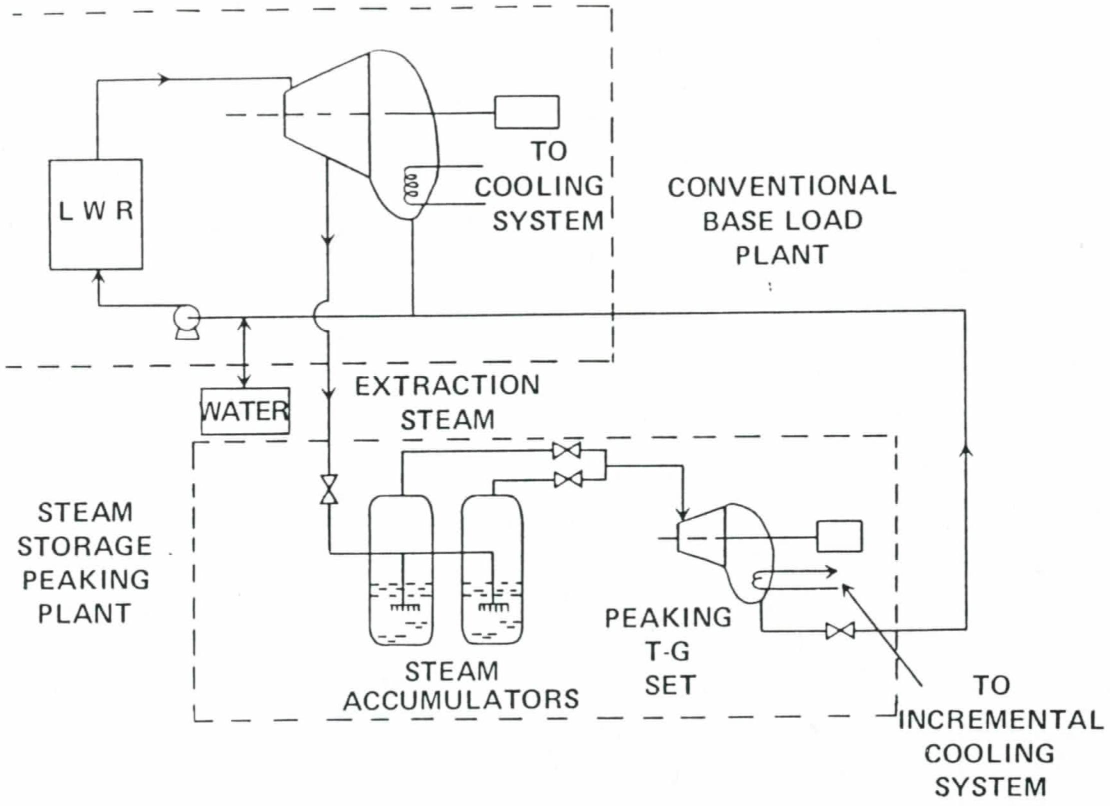

FIGURE 15. Steam storage peaking plant. (From Golibersuch, D. C., Bundy, F. P., Kosky, P. G., and Vakil, H. B., Rep. No. 75 CRD 256, General Electric Technical Information Exchange, Schenectady, New York, December 1975. This figure was originally presented at the Fall 1975 Meeting of The Electrochemical Society, Inc., held in Dallas, Texas.)

nderground caverns at a cost of 17 to $70/m^3 could be utilized, the storage costs ould be reduced substantially to 20 to 70 cents per kW,h storage capacity.

The use of above ground accumulator tanks presents a significant safety hazard. In order to store enough energy to provide 4000 MWh of electrical energy, about $3 \times 10^5 m^3$ of accumulators filled with saturated water at 20 atm is required. If even the minimum volume flashes to steam during a rupture, the released energy is about 8.5×10^6 MJ (2.36 billion Wh).[18]

Another sensible heat storage device for high temperature applications is being developed for commercial scale solar power plants.[15] The storage tank is filled with 25 mm river gravel and 1.5 mm No. 6 silica sand in a 2 to 1 ratio. Then a heat transfer oil, Caloria HT43, is added to the vessel to fill the 25% void fraction. The sand and gravel are added to reduce the quantity of more expensive organic oil used for storage. Moreover, the solids also prevent natural circulation of the oil in the vessel, and temperature stratification is possible. To charge the unit shown in Figure 16, oil is circulated from the bottom of the storage vessel, through a heat exchanger to pick up heat from the source, and back to the top of the tank. A fairly sharp temperature transition or thermocline will occur naturally between the incoming hot fluid and the cold fluid in the bed, and this thermocline will move downward through the bed during charging. During extraction of heat from the bed, the direction of oil flow is reversed, and the thermocline moves upward through the bed as shown in Figure 17a. Essentially a constant outlet temperature is thus provided during both charging and discharging of the system until the unit is almost completely charged or discharged (Figure 17b).[15]

A number of other storage devices have been proposed for sensible heat storage of thermal energy. In general, inexpensive ways of containing the materials are sought,

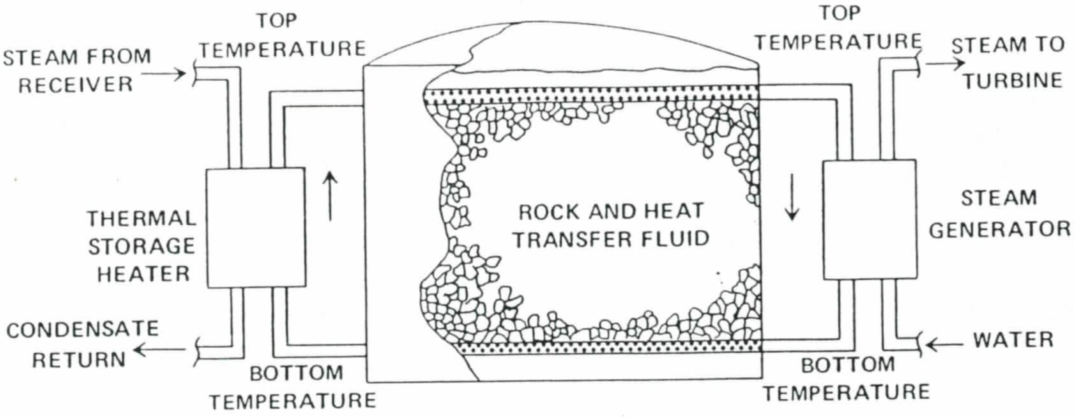

FIGURE 16. Dual medium thermal storage unit. (From Hallet, R. W., Jr. and Gervais, R. L., Rep. SAN/1108-8/5, McDonnell Douglas Astronautics Company, Redondo Beach, Calif., October 1977. With permission.)

since containment often is the major cost barrier. Steam accumulator tanks buried in the ground have significant cost reduction potential. Another proposal would use the soil itself for energy storage at similar costs to the underground steam accumulator. Use of aquifers to store thermal energy in water and sand has very low projected costs for low temperature storage. Table 7 presents a list of these candidates and others with the status and projected costs appropriate for 1975.[12]

B. Latent Heat Storage

A substantial absorption or release of energy generally accompanies a phase change such as from a solid to a liquid or from a liquid to a gas at a particular characteristic temperature. The potentially high energy storage densities over a relatively narrow temperature range make phase change materials attractive for thermal energy storage. Since a high volumetric energy storage density is essential, only solid-liquid or possibly solid-solid transitions are of practical interest. The volumes required to store a fixed amount of energy for heat of fusion materials are usually less than those for sensible heat materials (Figure 18), especially for small storage temperature swings. In Figure 18, sodium hydroxide undergoes a solid-solid phase change within about 25°C of the solid-liquid transformation. Some penalty must usually be assessed against phase change and solid sensible heat storage volumes to allow for passage of a heat transfer fluid.

The literature on selection of low temperature latent heat storage materials is voluminous with summaries available in References 20 and 21. High temperature fused salt storage for residential applications has also been extensively studied.[22] Material requirements include low cost, high heat of transition, high density, appropriate transition temperature, low toxicity, and long-term performance. Paraffin waxes[23] and salt hydrates[20] have been favored for low temperature storage applications although the former is very flammable while the latter is prone to subcooling without crystallization.

For higher temperature uses, some generalizations are possible.[12] Carbonates and possibly carbonate-chloride systems are serious candidates because their good corrosion characteristics make them relatively inexpensive to contain and their cost is reasonable. Nitrates and nitrites are good choices for applications below 500°C since they are relatively noncorrosive and fairly inexpensive. Chloride systems are cheap enough to be attractive but are more corrosive than the previous compounds. Hydroxides as a group tend to be more expensive and corrosive. Fluorides offer relatively high

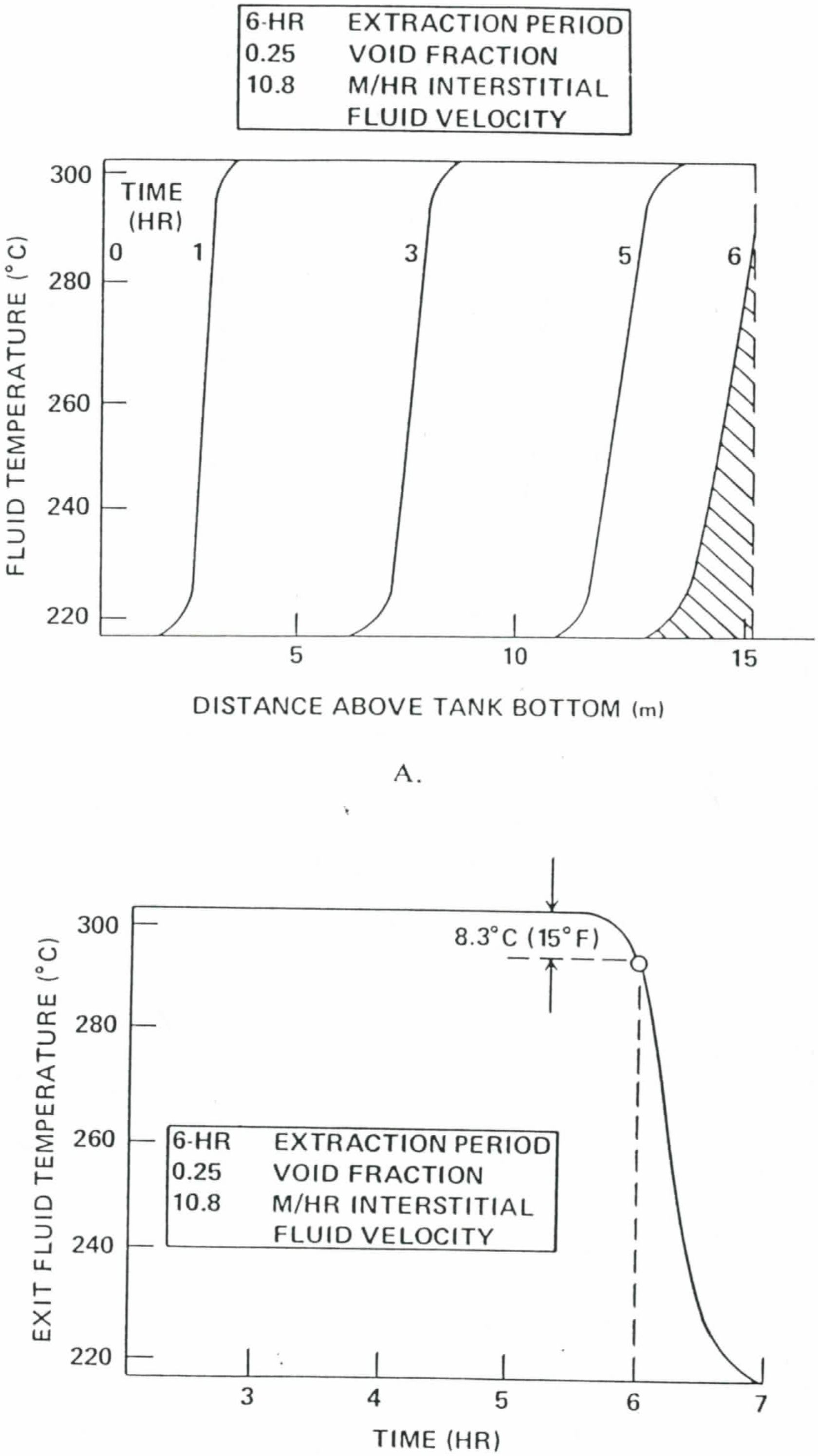

FIGURE 17. (A) Thermoclines during energy extraction from a 10-MW, dual medium thermal storage unit. (B) Fluid temperature at the exit from the dual medium thermal storage unit during six hour extraction. (From Hallet, R. W., Jr. and Gervais, R. L., Rep. SAN/1108-8/5, McDonnell Douglas Astronautics Company, Redondo Beach, Calif., October 1977. With permission.)

TABLE 7

Sensible Heat Storage Systems

Storage configuration	Storage medium	Status	T_{MAX}, °C	T_{MAX}-T_{MIN}, °C	Capacity MW,h	Cost $/kW,h
Aboveground tank	Water	Engineering design	210	87	4.1	8.0
			300	87	4.1	22.0
Aboveground tank	Water	Preliminary testing	232	56	0.41	—
	Therminol		343	56		
Steam accumulator	Water	Engineering design	200		14	3.0
			300		37	6.0
Undergroundtank	Water	Preliminary design	217	141	4370	0.4
Acquifers	Water and sand	Conceptual	170	110	42,000	0.003
Aboveground tanks (other fluids)	Therminol 55	Engineering design	315	55	226	62
	Therminol 66		315	55	226	27
	Caloria HT43		302	83		11
	HITEC		500	300		4
Solid storage materials	Cast iron	Operational	750	480	0.75	∼6.00[a]
			700	430	0.64	∼6.30[a]
Packed beds	Granite	Preliminary design	302	84	195	5.13
	Caloria HT43					
Fluidized bed	Sand	Conceptual	800	400	4000	—
	Fly ash					
Underground	Soil	Preliminary design	100	85	500	0.4—0.8
Rock bed	Rocks	Operational air heating	200	150	—	2.00—3.20

[a] Based on total system cost of $0.20/lb and the temperature swing Tmax-Tmin shown, not in reference cited.

[b] Not in reference cited.

From Bramlette, T. T., Green, R. M., Bartel, J. J., Ottesen, D. K., Schafer, C. T., and Brumleve, T. D., Rep. SAND 75-8063, Sandia Laboratories, Albuquerque, N.M., March 1976.

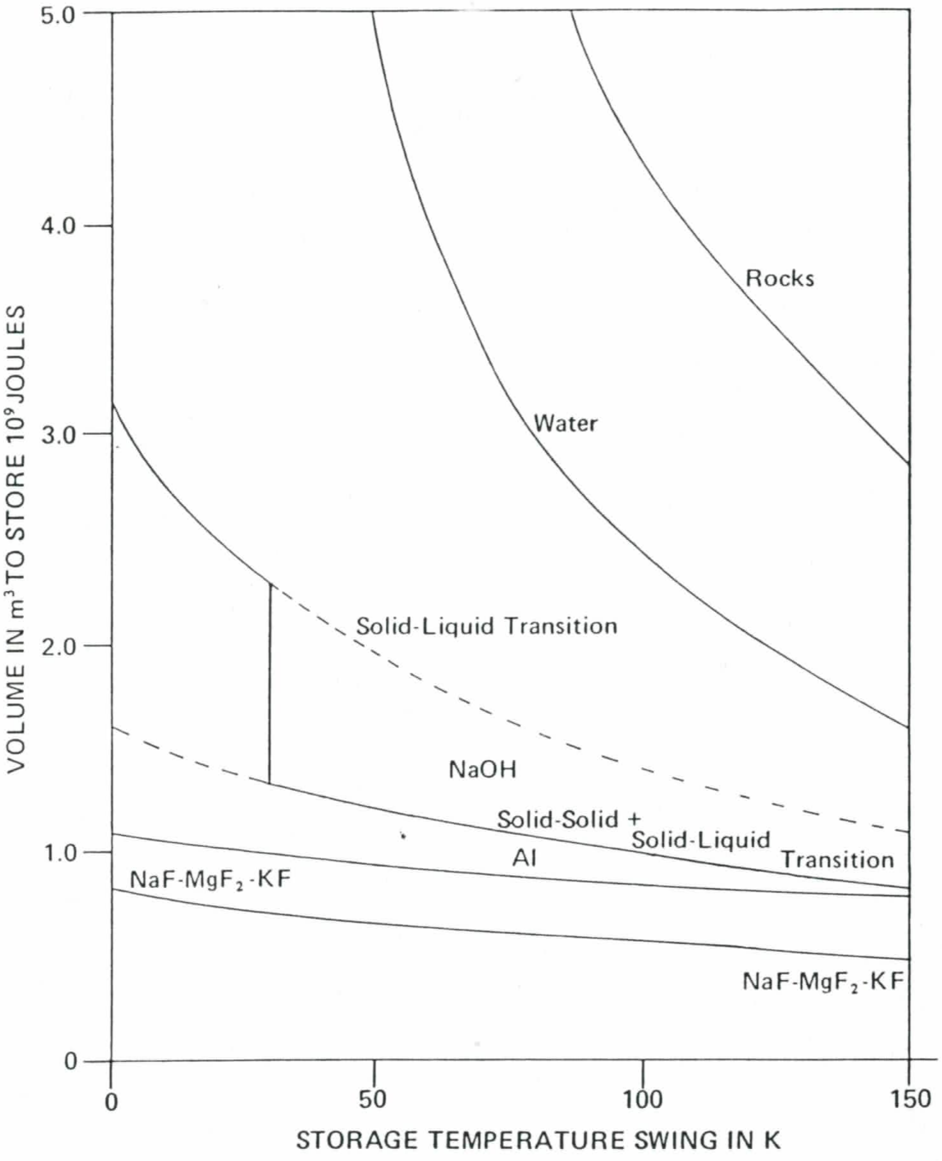

FIGURE 18. Approximate volumes of selected heat of fusion and sensible heat storage materials required to store one gigajoule of energy.

heat storage densities, but their usually high price and corrosive nature make the fluorides more expensive to use than the other salt systems discussed above. Figure 19 clearly shows the storage capacity per dollar of material cost for selected latent heat of fusion storage media. More details on these salts as well as others are in References 12 and 22.

A conceptual study has been carried out on the use of a latent heat storage system in conjunction with a high temperature gas reactor.[18] The system was designed to meet the following specifications: primary coolant: He, 48 atm, 400 to 780°C; storage capacity: 7200 MW$_t$h; charge/discharge capacity: 600 MW$_t$; peak electrical generating capacity: 200 MW$_e$ for 12 hr. The system is presented schematically in Figure 20. About 38 Gg of 70 Gg NaF/30 FeF$_2$ eutectic would be theoretically needed to store 7200 MW$_t$h. In order to keep the mass reasonably fluid as a slurry, the total amount needed would be on the order of 70 Gg requiring a container about 37 m in diameter and 34 m high.

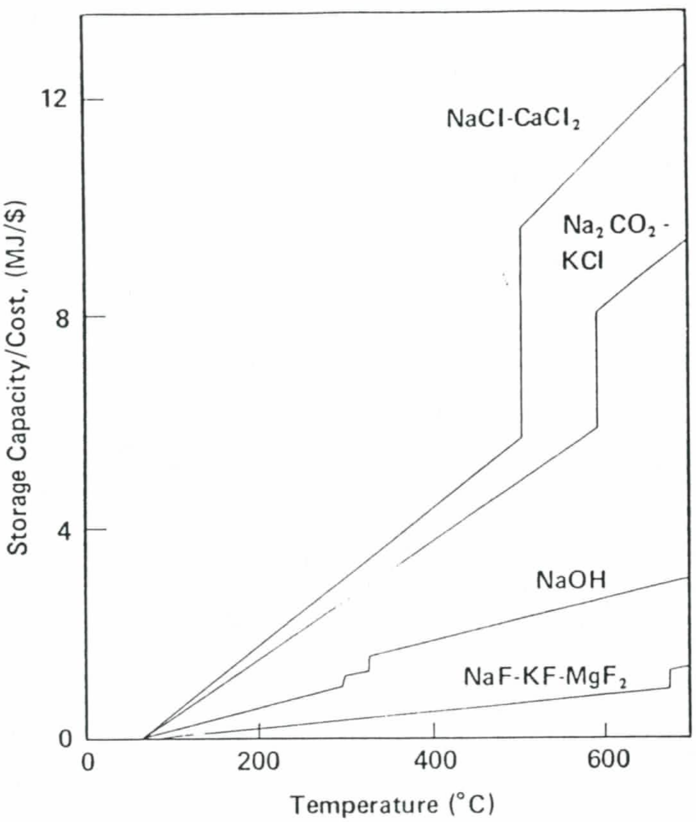

FIGURE 19. The energy stored per unit cost for selected latent heat of fusion storage media. (From Bramlette, T. T., Green, R. M., Bartel, J. J., Ottesen, D. K., Schafer, C. T., and Brumleve, T. D., Rep. SAND 75-8063, Sandia Laboratories, Albuquerque, New Mexico, March 1976.)

example. Such direct contact heat transfer also circumvents the high cost of containment and heat exchange usually associated with phase change materials. During discharge, the lead would be "rained" in the top of the slurry at about 370°C and would be heated to near 680°C as the globules of lead sink to the bottom. Similar direct contact systems which rely on an oil that rises through the storage reservoir are being developed for low temperature uses,[24] and a diagram of this system is shown in Figure 21.

Bundy et al.[17] concluded that all medium to high temperature storage systems using latent heat of fusion materials in conventional metal heat exchanger-containers tend to be quite expensive, and in many cases, there are serious chemical and mechanical problems associated with containment of the storage material. There are basic problems in achieving adequate and efficient heat transfer at reasonable cost.[12,17,25] In addition, at higher temperatures, small-sized units appear to suffer from excessive thermal leakage. The realistic general conclusion is that thermal energy storage as the latent heat of fusion is currently difficult to apply commercially in a competitive, efficient manner. Direct contact heat exchange devices such as the example promise one solution to the high price of containment and heat exchange, and plastic containment may be effective for lower temperature heating and cooling uses. Table 8 summarizes the 1975 projected costs of some latent heat storage systems.

C. Reversible Chemical Reaction Storage

Thermal energy may also be stored as the bond energy of a chemical compound by

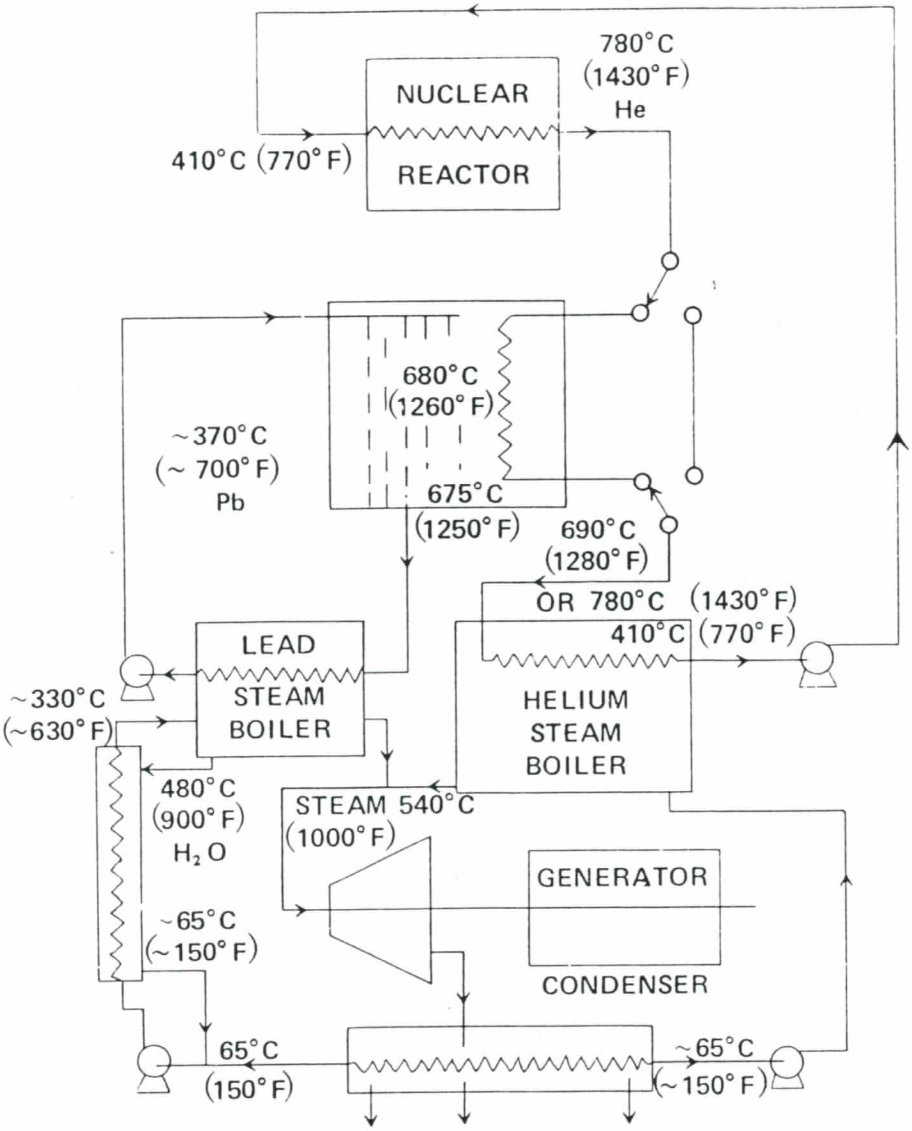

FIGURE 20. Latent heat steam storage system. (From Golibersuch, D. C., Bundy, F. P., Kosky, P. G., and Vakil, H. B., Rep. No. 75 CRD 256, General Electric Technical Information Series, Schenectady, New York, December 1975. This figure was originally presented at the Fall 1975 Meeting of The Electrochemical Society, Inc., held in Dallas, Texas.)

means of reversible chemical reactions. An endothermic forward reaction absorbs energy from the source under conditions which favor significant conversion to a high enthalpy chemical species. The reaction can only proceed until the equilibrium concentrations are reached. Then, to release the stored energy, the conditions are altered to favor high conversion by the exothermic reverse reaction to the low enthalpy species. The equilibrium concentrations of the species may be altered by: (1) changing the concentration (or pressure) of the chemical species and/or (2) changing the temperature of these species.

The energy storage density by reversible chemical reactions is generally higher than for phase change storage. Chemical storage also has significant cost potential since some of the materials are available for pennies a pound. Chemical storage has the added advantage in that significant energy storage densities are possible even at ambient conditions.[26] However, careful heat exchange between products and reactants is required to minimize sensible heat losses and provide efficient storage of energy.

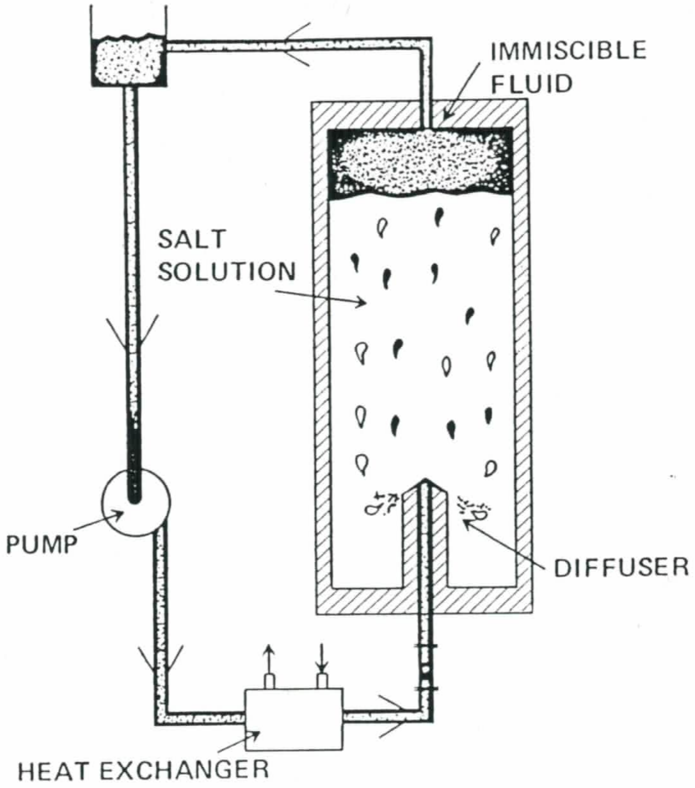

FIGURE 21. Heat of fusion storage system using an immiscible fluid for heat transfer. (From Edie, D. D., Melsheimer, S. S., and Mullins, J. C., Proc. Second Annual Thermal Energy Storage Contractors' Information Exchange Meeting, Gatlinburg, Tennessee, September 1977.)

TABLE 8

Heat of Fusion Storage Systems

Storage configuration	Storage medium	Status	T_{MAX}, °C	Capacity kW,h	Cost $/kW,h
Annulus	LiH	Lab scale experiment	688	1.87	—
Cylinder	LiH	Lab scale experiment	680	0.281	—
Cylinder	Lif/LiOH Eutectic	Lab scale experiment	427	3.51	—
Cylinder	NaOH	Lab scale experiment	510	40	
Cylinder	NaOH	Operational units	482	193	4.60
Rectangular models	NaOH	Operational units	482	117	5.10
Cylinder	NaF/FeF_2 Eutectic	Conceptual	680	9.6×10^6	21

From Bramlette, T. T., Green, R. M., Bartel, J. J., Ottesen, D. K., Schafer, C. T., and Brumleve, T. D., Rep. SAND 75-8063, Sandia Laboratories, Albuquerque, N.M., March 1976.

Despite all the promise offered by chemical reaction storage, the technology is at such an early stage of development that systems can not be generally used for commercial applications. Indeed, relatively little experience has even been compiled in the laboratory to date; and significant scale demonstration units have not been run. Research and development are therefore needed to show:

- Reversibility of reactions with minor degradation of the chemical species and catalysts, when required
- Satisfactory kinetics, specificity, and conversions of the reactions
- Acceptable heat transfer rates in cost-effective containers and/or heat exchangers
- Easy storage and transportation (when required) of the chemical species
- No excessive corrosion
- Sufficient energy storage densities
- Acceptable storage efficiencies

Due to the generally immature information on the engineering design of reversible chemical reaction storage, this discussion will focus only on the operating concepts presently considered for storage of thermal energy. Reasonable cost projections will have to await further research to clarify the design of storage systems.

Table 9 presents some possible reactions for thermochemical storage of thermal energy.[27,28,29] Since a high energy storage density is essential at low ion cost in most applications, only reversible reactions with reactants and products which can be stored as liquids or solids are of practical interest. For example, solid calcium hydroxide (slaked lime) will endothermically decompose to solid calcium oxide (quicklime) and water vapor if it is heated to 520°C at one atmospheric pressure. The water vapor is condensed for storage. When heat is to be supplied from storage, water and the calcium oxide are mixed and the exothermic reverse reaction of the two species produces energy.[30-32]

The "turning temperature" T^* in Table 9 is defined as the temperature for which the equilibrium constant is one and is approximated by the ratio of the standard enthalpy change to the standard entropy change for the reaction:[27]

$$T^* = \frac{\Delta H^\circ}{\Delta S^\circ} \tag{3}$$

When $T > T^*$, the endothermic storage reaction is favored; while for $T < T^*$, the exothermic reaction dominates.

Figure 22 illustrates the chemical heat pump mode of operation in which a dilute sulfuric acid solution is concentrated by using solar energy (or any other energy source) to evaporate water. The water vapor is condensed for storage, and the heat of condensation is given off to the load if it can be used at the condensation temperature or to the environment if it cannot. When heat is demanded from storage, energy from the atmosphere evaporates the liquid water and, provided the temperatures of the water and acid solution are properly regulated, the water vapor will condense in the solution. Consequently, the heat of condensation as well as the heat of mixing is released for the load, pumping energy from the environment. If all the energy is useful, more energy can be supplied in principle to the load than was captured by the sun. By interchanging the load and environment positions in Figure 22, the chemical heat pump may be used for air conditioning as well. Table 10 presents a number of reactions suitable for chemical heat pumping.[29,32,33] The temperatures shown are those typically

TABLE 9

Thermochemical Storage Reactions

Reaction	Heat of reaction, $\Delta H°$, kJ	Turning temperature, T^*, K
$NH_4F(s) \rightleftharpoons NH_3(g) + HF(g)$	149.3	499
$Mg(OH)_2(s) \rightleftharpoons MgO(s) + H_2O(g)$	81.04	531
$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$	100.6	670
$NH_4HSO_4(l) \rightleftharpoons NH_3(g) + H_2O(g) + SO_3(g)$	337	740
$Ca(OH)_2(s) \rightleftharpoons CaO(s) + H_2O(g)$	109.2	752
$LiOH(l) \rightleftharpoons \frac{1}{2} LI_2O(s) + \frac{1}{2} H_2O(g)$	56.7	1000
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	178.4	1110

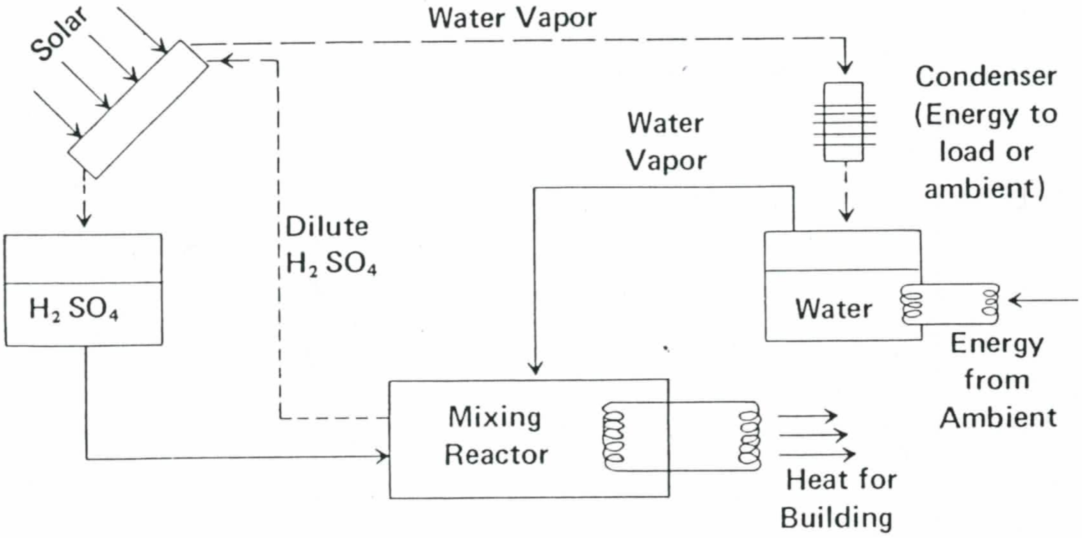

FIGURE 22. Chemical heat pump storage for sulfuric acid concentration/dilution with the charging cycle shown as dashed (- -) lines and discharging cycle by solid (—) lines.

considered. For ammonia systems, a second salt or liquid which reacts with ammonia at low temperatures such as $CaCl_2$ is often used to store the vapor.

IV. HYDROGEN

Batteries can be considered to be a special case of chemical energy storage where the functions of the initial conversion of electric to chemical energy, storage of this energy, and its reconversion to electric energy are combined in a single device. Thermal energy storage in reversible chemical reactions transforms thermal energy to chemical bond energy for storage and converts it back to heat at a later time by reversing the original reaction. One potentially important example of chemical energy storage with a separate process to release the stored energy is the use of hydrogen as a storage medium. Hydrogen may be produced either electrochemically or thermally.

Hydrogen is not a primary fuel. As such, its available energy is less than the energy from the source used to produce it due to inefficiencies. Its value lies in its ability to store and transport energy and in its potential to supplant oil and natural gas for those types of services for which they are most noted. Hydrogen has received a good deal

TABLE 10

Chemical Heat Pump Reactions

Reaction	Temp., K
Ammoniated salt pairs	
$CaCl_2 \cdot 8NH_3(s) \rightleftharpoons CaCl_2 \cdot 4NH_3(s) + 4NH_3(g)$	305
$NH_4Cl \cdot 3NH_3(l) \rightleftharpoons NH_4Cl(s) + 3NH_3(g)$	320
$MnCl_2 \cdot 6NH_3(s) \rightleftharpoons MnCl_2 \cdot 2NH_3(s) + 4NH_3(g)$	364
$MgCl_2 \cdot 6NH_3(s) \rightleftharpoons MgCl_2 \cdot 2NH_3(s) + 4NH_3(g)$	408
$MnCl_2 \cdot 2NH_3(s) \rightleftharpoons MnCl_2 \cdot NH_3(s) + NH_3(g)$	521
$MgCl_2 \cdot 2NH_3(s) \rightleftharpoons MgCl_2 \cdot NH_3(s) + NH_3(g)$	550
Hydrated salts	
$MgCl_2 \cdot 4H_2O(s) \rightleftharpoons MgCl_2 \cdot 2H_2O(s) + 2H_2O(g)$	380
Concentration-dilution	
$H_2SO_4 \cdot nH_2O(l) \rightleftharpoons H_2SO_4 \cdot (n - m)H_2O(l) + mH_2O(g)$	<600

of attention in the context of the "hydrogen economy" in which, for example, electricity generated by base-load nuclear power plants could be used to electrolyze water to hydrogen and oxygen. Then the hydrogen could be stored or transported to appropriate sites via pipelines; and at the load site the hydrogen could be used directly as fuel, or could be converted back to electricity via fuel cells or high temperature turbines. However, it is possible to conceive of a less grand scheme that would permit hydrogen to act as a storage medium both for utility load leveling applications and as a fuel for vehicles.

Production of hydrogen for use in central-station or transportation applications might be done by electrolyzing water into its constituents: hydrogen and oxygen. Another possibility is the thermochemical splitting of water using sources of high temperature process heat. At present, water electrolysis is a well established technology but is handicapped by a modest efficiency and high capital costs. Some observers[5] believe that with the development of advanced technology, the conversion efficiency might approach 100% with capital costs of $40 to $70/kW.

Unlike electrolysis systems which are available essentially as off-the-shelf items, the development of thermal processes for water splitting is still in the conceptual stage. Overall efficiencies and economics of thermal splitting might be superior to those offered by electrolysis, particularly if sources of high temperature heat — such as high temperature, gas cooled reactors — were available. It should be recognized that the establishment of technically and economically feasible processes for thermal splitting of water will undoubtedly require very extensive development efforts.

Hydrogen can be stored in metals. When pressurized hydrogen gas comes in contact with the metal surface, it readily diffuses into the metal and forms a metal hydride compound. A number of metals, usually alloys, have been and are being investigated. The hydride formation is exothermic, and the heat generated during the reaction must be removed. Later, heat must be applied to the metal hydride to evolve the hydrogen. These processes both occur at close to the ambient temperature. Storage of hydrogen in liquefied or compressed forms also has been proposed.

Hydride storage of hydrogen could be used for storing electric power if off-peak power were used to electrolyze water into hydrogen and oxygen. At times of peak demand, the hydrogen could be recovered and used to power fuel cells. One difficulty with hydrogen for storing electrical energy is that the overall efficiency of systems based on available fuel cells is only about 40%. Fuel cells at present are expensive. However, improvements in fuel cells operating on pure hydrogen are projected to permit system efficiencies of 65%. The alternative of converting hydrogen to electrical power via high temperature turbines is also awaiting advances in technology.

V. MECHANICAL STORAGE OF ENERGY

A. Pumped-Storage Hydroelectric Plants

The potential energy stored in water by virtue of its elevation can be converted into electricity with a high efficiency. In recent years a technique has been developed that allows the construction of hydroelectric plants that have some of the characteristics of storage batteries. They are called pumped-storage plants. At present they are the only practical way for large-scale storage of electrical energy.

Pumped-storage plants generally operate by transferring large amounts of water from a river or lake up to a reservoir at higher elevation. Power from base-load plants is used to drive the pumps during off-peak hours when these plants normally have excess capacity. During hours of peak demand, the water in the reservoir is allowed to fall back through the pump to the river or lake below. However, the pump now serves as a water driven turbine. The power from that turbine turns the electric pump motor backwards, and the motor is designed to act as an electrical generator when reversed. Thus excess electrical capacity available during off-peak hours can be stored until needed at peak demand.

The power used during off-peak hours is relatively cheap. All efficiencies considered, it requires about three cheap kilowatt-hours of off-peak electricity to produce two kilowatt-hours at peak demand. Thus, the system has an overall efficiency of about 67%. If peak pricing were employed, this type of storage would be even more attractive since the two kilowatt-hours sold during a time of high demand would command premium prices.

Pumped-storage units also have the ability to respond to rapid changes in load. A spinning turbine can be fully loaded in minutes, and the newer installations can be converted from pumping to generating in 5 to 10 min. Pumped-storage units can be combined with conventional hydroelectric plants or can be pure pumped-storage plants. The need for this kind of system is clear from the growth now projected; in 1970 there was 3,600 MW of pumped storage, by 1980 there will be 27,000 MW, and by 1990, 70,000 MW.

B. Compressed Gas Energy Storage

There are relatively few geographical locations that have a topography suitable for pumped-storage plants. However, by storing energy in air instead of water, the topographical problem can be overcome. An air-storage power plant employs a conventional gas turbine modified so that the compressor and turbine sections may be uncoupled and operated separately as shown in Figure 23. During off-peak, low-load periods, the turbine clutch is disengaged and the compressor is driven by a motor with power from base-load power plants in the system. The compressed air is stored for use during peak-load periods, at which time it is mixed with fuel for combustion, burned, and then expanded through the turbine. During these periods, the compressor clutch is disengaged, and the entire output of the turbine is used to drive the motor to generate electricity.

Storing air for this purpose in fabricated containers would probably be too expensive for the large storage volumes needed. The least expensive storage volumes would include dissolved-out salt caverns, porous-ground reservoirs, depleted gas and oil fields,

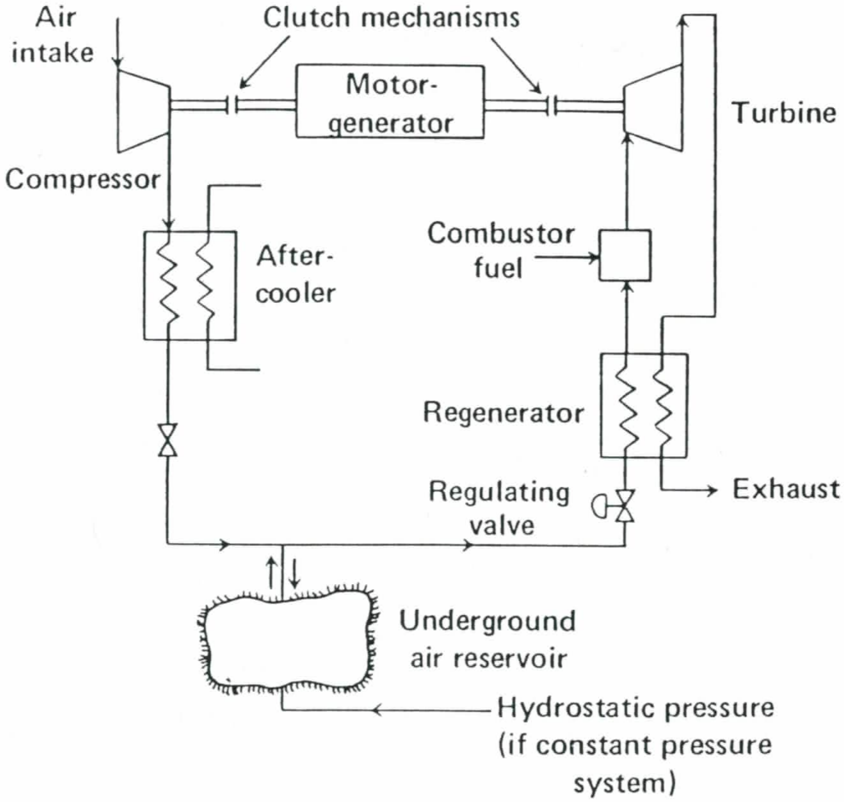

FIGURE 23. A compressed-air energy storage system. During charging, the motor drives a compressor which stores air under relatively high pressure in an underground reservoir. During discharge, the air is used to burn a fossil fuel which drives a gas turbine connected by means of a clutch to a generator.

and abandoned mines. Olsson[34] suggests that the air in abandoned mine storage regions could be kept under more or less constant pressure by hydrostatic pressure of water from a nearby lake or reservoir. Wide variations in stored gas pressure, however, can be tolerated with some penalty in performance.

The cavern volume required for a certain mass flow of compressed air is inversely proportional to the air pressure and proportional to the required number of hours of peak-load operation per day. Technical data for a 220 MW air storage plant is given in Table 11. Olsson asserts that such a plant could be built for $50/kW (1970 prices) excluding the cost of land, roads, and taxes.[34] Though no such plant is presently in operation, the technology for constructing such a plant is available.

C. Energy Storage In Flywheels

Flywheels have been used as energy storage devices for centuries. Today they are used widely in the internal combustion engines of automobiles, trucks, and diesel locomotives to carry the rotation of the engine between pulses of energy delivered by the pistons. Until recently, it was thought that employing flywheels to store energy in a wider range of applications was out of the question because of cost and because not enough energy could be stored for a given flywheel weight to satisfy the foreseeable needs. However, this picture has now been changed by recent advances in materials technology. These advances have come largely as a result of research and development in the aerospace industry.

Energy storage in a flywheel is governed by the mass of the rim and by how fast the wheel is spinning; the stored energy varies as the square of the rotation speed. The

TABLE 11

Technical Data for a 220-MW Air-Storage Power Plant

Station rating	220 MW
Air flow to storage at 5°C (41°F)	351 kg/sec (775 lb/sec)
Maximum storage pressure	43.5 atm (640 psia)
Air temperature in cavern	15°C (59°F)
Cavern depth	435 m (1425 ft)
Compressor power at 5°C (41°F)	161 MW
Turbine inlet temperature	800°C (1470°F)
Continuous power at 5°C (41°F)	73 MW
Efficiency/heat rate	
(1) at peak load	71.5%/4770 Btu/kWh
(2) continuous	27%/12,650 Btu/kWh
Power ratio: off peak kWh/peak kWh	0.76
Cavern volume per hour/day peak load operation	27,400 m³ (970,000 ft³)

After Olsson, E. K. A., *Mech. Eng.*, November 1970. With permission.

limit to the amount of energy stored is ultimately set by the tensile strength of the material from which the rim is made. The tensile strength must be great enough to withstand the so-called "hoop stress" resulting from centrifugal forces or else the wheel would fly apart. As with the energy stored, these forces are proportional to the mass of the rim and increase as the square of the rotation speed. Thus two properties of the material determine the amount of energy that can be stored in a flywheel: mass density which provides kinetic energy and tensile strength which resists centrifugal forces.

Quantitatively the above description can be expressed as:

$$E = \frac{1}{2} I \omega^2 \qquad (4)$$

or

$$E\,(\mathrm{kJ}) = 5.0 \times 10^{-4}\, I\,[\mathrm{kg{-}m^2}]\ \omega^2\ [\mathrm{rad/sec}]^2 \qquad (5)$$

where I is the moment of inertia and ω is the angular velocity of rotation. An equivalent way of picturing the energy stored in a flywheel is as the energy in the "spring" formed by the tension created in the rim of the flywheel by the centrifugal force, which slightly expands the diameter of the flywheel.

The theoretical maximum specific energy that can be stored in a flywheel is fixed by the strength-to-density ratio of the material from which it is made.[35]

$$\frac{E}{W}\left(\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 1.31 \times 10^{-3} K_W\, \sigma(\mathrm{MPa})/\delta(\mathrm{Mg/m^3}) \qquad (6)$$

where σ and δ are the stress-level and density of the structural material and the numerical factor derives from the choice of units. K_w expresses the efficiency with which the particular design utilizes the material's strength and is a maximum if the stress is distributed uniformly throughout. In an optimum design for isotropic materials, both radial and tangential stresses would be equal and uniform, and K_w can approach a value of one. In designs optimized for materials such as fiber-reinforced composites, only one stress direction can be utilized; and the maximum value of K_w is 0.5. With either class of materials, the absolute maximum value of K_w is reached only in very slender or "flimsy" configurations with vanishing energy per unit volume of enclosure.

In order to compare various types of flywheel configurations it is convenient to define a volumetric specific energy as the maximum energy stored per unit volume of the cylinder enclosing the flywheel's maximum axial height and its maximum radial dimension.[35]

$$\frac{E}{V}\left(\frac{kJ}{m^3}\right) = 1.0 \times 10^4 K_\nu \sigma \text{ (MPa)} \qquad (7)$$

Again the numerical factor derives from the choice of units. K_v expresses the efficiency with which the particular design fills the cylindrical volume as well as utilizing the material's strength; for a uniform density material, it equals K_w times the fraction of the cylindrical volume occupied by the flywheel.

Figure 24 illustrates how the weight efficiency factor K_w and the volumetric efficiency factor K_v are related for several classes of high-performance flywheel designs. Table 12 summarizes the estimated realizable properties of some candidate materials for flywheel construction.[35] The normalized parameters provide an indication of the relative energy storage performance (strength/density) and cost effectiveness [strength/(density-cost)] expected for rotors made from different materials using equivalent designs.

It is unlikely that flywheel energy storage can displace existing battery technology on the basis of weight, volume, or cost savings for a given amount of energy stored. On the other hand, power levels, and probably service life, may far exceed the capabilities of common battery systems.

VI. EVALUATING STORAGE METHODS

A. Governing Relationships

In this section a first order economic analysis of energy storage systems is presented. This analysis, though based on a conventional utility's needs, can clearly be generalized to a nonutility system. This work follows that which has been outlined by Golibersuch et al.[18]

In this analysis it is assumed that electrical energy being produced during nonpeak demand hours by a thermal central-station plant is being stored for use during peak hours. The costs of heat and electricity during peak and off-peak periods are summarized as follows:

$$w_o = q_o / \eta_g \qquad (8)$$

$$w_e = f_e / t + w_o / \eta_e \qquad (9)$$

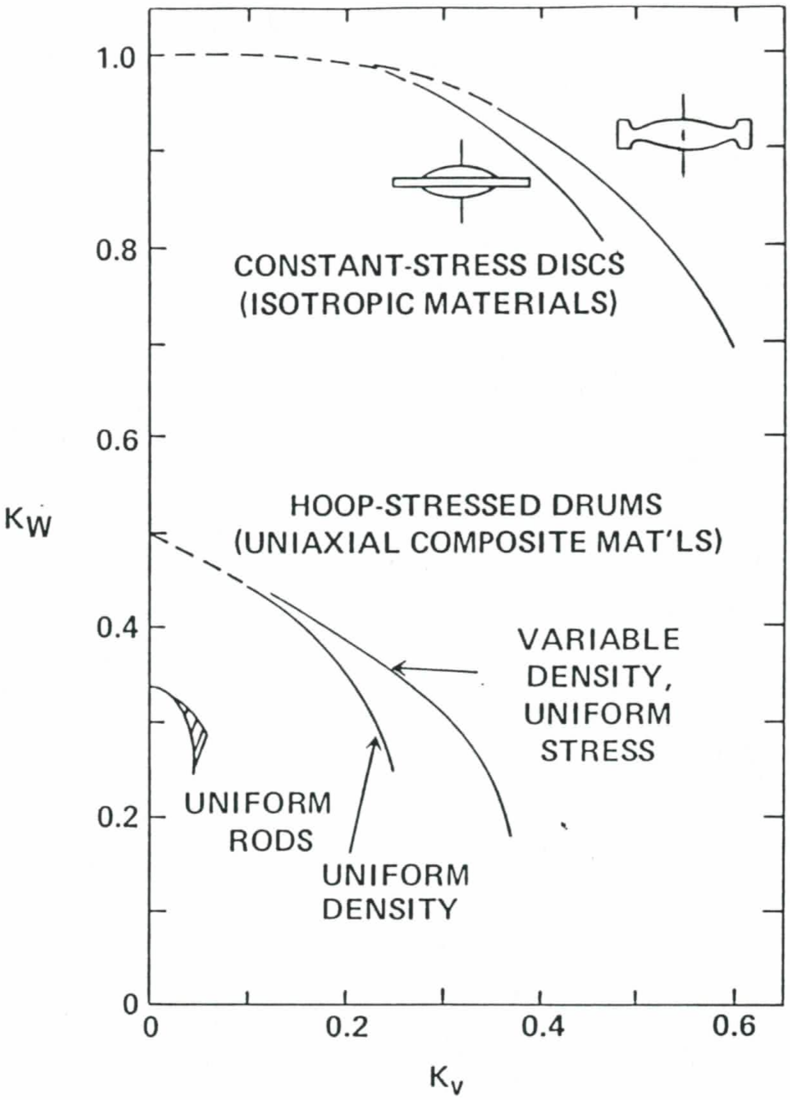

FIGURE 24. Relationship of weight-efficiency factor K_w and volumetric-efficiency factor K_v for high-performance flywheel designs. (From Fullman, R. L., Rep. No. 75 CRD 051, General Electric Technical Information Series, Schenectady, New York, April 1975; Proc. Tenth Intersociety Energy Conversion Engineering Conference. Permission granted by the Institute of Electrical and Electronic Engineers, Inc., New York.)

$$q_{th} = f_{th}/t + q_o/\eta_{th} \tag{10}$$

$$w_{th} = f_{g'}/t + q_{th}/\eta_{g'} \tag{11}$$

where f_e = annual fixed cost, nonthermal storage (mills/kW_e-year); f_g' = annual fixed cost, thermal storage power plant (mills/kW_e-year); f_{th} = annual fixed cost, thermal storage (mills/kW_e-year) t = hours of peak operation per year; q_o = cost of off-peak heat (mills/kW_{th}-hr); q_{th} = cost of on-peak heat (mills/kW_{th}-hr); w_e = cost of peak electricity, nonthermal storage (mills/kW_e-hr); w_o = cost of off-peak electricity (mills/

TABLE 12

Properties of Candidate Flywheel Materials

	Density (mg/m^3)	Cost (\$/kg)	Cycles	Working stress (MPa)	Stress density (km)	Stress Density × Cost (kg · kg/\$)
Maraging Steel (18 Ni-#250)	8.000	6.60	10^4	696	8.9	1.3
			10^5	340	4.3	0.65
4340 Steel	7.83	1.30	10^4	430	5.6	4.3
			10^5	280	3.6	2.8
Ti-6-4	4.43	6.60	10^4	630	14	2.1
			10^5	280	6.4	0.97
Al 2024-T3	2.77	1.10	10^4	230	8.5	7.7
			10^5	120	4.4	4.0
60 v/o S-glass/ epoxy	1.96	1.80[a]	10^4	1000	52	29
			10^5	760	39	22
60 v/o E-glass/ epoxy	1.99	1.10	10^4	830	42	38
			10^5	620	32	29
62 v/o Graphite/ epoxy	1.69	33[a]	$\leqslant 10^6$	830	50	1.5
63 v/o Kevlar®[b] 49 epoxy	1.36	7.70[a]	$\leqslant 10^6$	1000	75	9.7

[a] Based on anticipated fiber price reductions.

[b] ®DuPont trademark.

From Fullman, R. L., Rep. No. 75 CRD 051, General Electric Co., Schenectady, N.Y., April 1975; Proc. Tenth Intersociety Energy Conversion Engineering Conference. Permission granted by the Institute of Electrical and Electronics Engineers, Inc., New York.

kW$_e$-hr); w_{th} = cost of peak electricity from thermal storage plant (mills/kW$_e$-hr); η_e = nonthermal storage efficiency; η_g = overall power cycle efficiency base-load plant; η_g' = overall power cycle efficiency thermal storage plant; η_{th} = thermal turn-around efficiency.

For purposes of comparing electrical generation and thermal storage systems, it is convenient to relate the cost of peak electricity to off-peak electricity for both cases. Combining Equations (8), (10), and (11) one obtains:

$$w_{th} = (f_{g'} + f_{th}/\eta_g')/t + \frac{\eta_g}{\eta_g'}\,\frac{w_o}{\eta_{th}} \qquad (12)$$

The fraction η_g/η_g' takes into account the generally lower grade of thermal energy available from storage than from primary sources and the correspondingly different efficiencies of the two types of power plants (conventional power plant and thermal storage plant).

The annual fixed cost is determined by multiplying the installed cost by the capital recovery factor. The fixed cost for the storage plant, f_{th}, includes two terms: one determined by the cost per unit of installed power capacity and a second determined by the cost per unit of installed energy storage capacity times the number of hours of storage required for the particular duty cycle (Equation 1). Operating and maintenance costs have been neglected as they are generally small and difficult to estimate.

Figure 25 summarizes the cost range estimates for a number of particular peak power thermal energy storage plants based on the equations in this section[18]. Also shown is

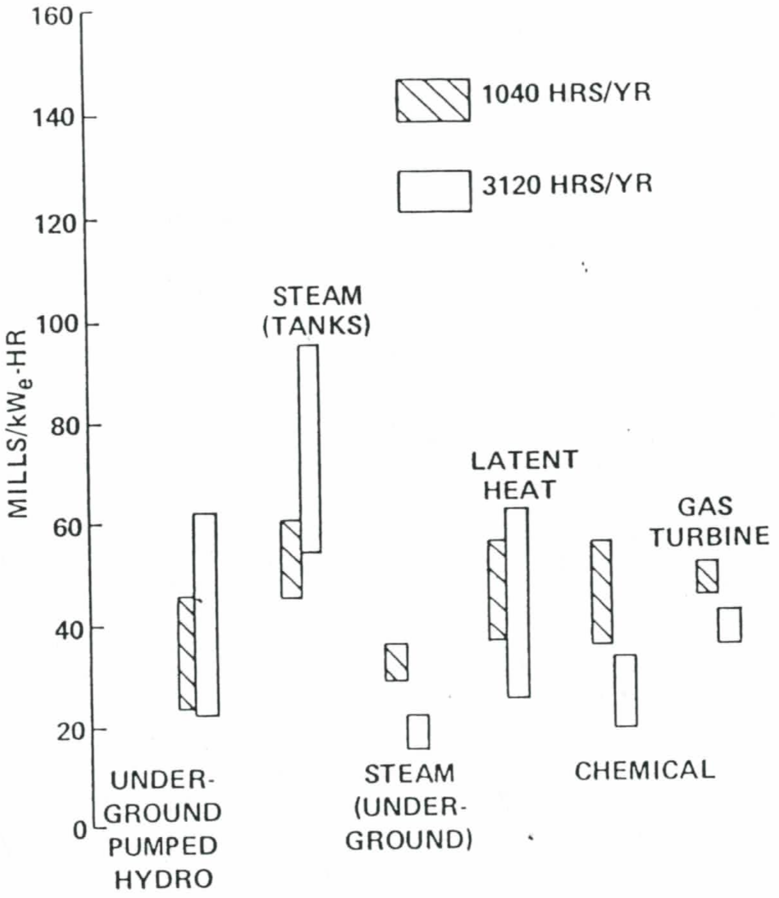

FIGURE 25. Peak power costs using various storage and direct production options. (From Golibersuch, D. C., Bundy, F. P., Kosky, P. G., and Vakil, H. B., Rep. No. 75 CRD 256, General Electric Technical Information Series, Schenectady, New York, December 1975; This figure was originally presented at the Fall 1975 meeting of The Electrochemical Society, Inc., held in Dallas, Texas.)

the cost of peak energy based on simple cycle turbine generation with an installed cost of \$100/kW$_e$, thermal efficiency of 28%, and a fuel cost of about \$3/GJ (\$3 per million Btu). The cost of off-peak electricity, w_o, is taken to be 5 mills/kW$_e$-hr. This is equivalent to a nuclear fuel cost of about 50¢/GJ (50 cents per million Btu). The assumed cost of off-peak electricity has little impact on the relative economic comparisons of various storage options.

B. The Cost of Stored Energy

To conceptualize the impact of energy storage on delivered energy costs, the energy in a storage device is arbitrarily broken down into fictitious elements according to usage. A solar installation is considered for which the demand is regular and somewhat independent of the season. The final conclusions should apply to any system, however.

Initial blocks of storage added to the system are used nights and during periods of cloud cover, and substantial amounts of energy pass through these elements of storage. Eventually, a point is reached where additional blocks of storage are only useful nights. Once enough storage is available to last the shortest night, additional storage elements are only discharged during longer nights in the year and cloudy periods which follow sunny days. Storage blocks beyond those required to last the longest night have lower utilization since cloudy and sunny days rarely alternate in a regular pattern. This di-

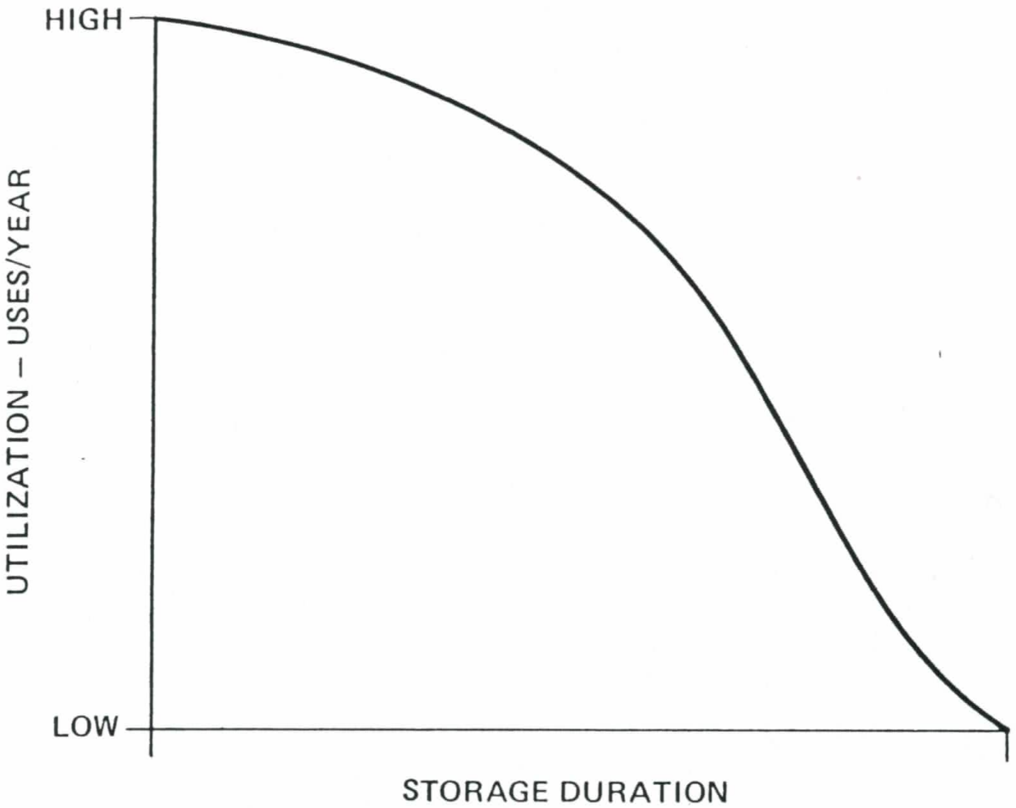

FIGURE 26. Utilization of last element of storage added to system vs. the storage duration to that point.

minishing utilization of additional storage elements continues until enough storage is added to provide a 100% solar powered system. Any storage beyond that amount is not used at all. Figure 26 presents an idea of how the storage element utilization might change as elements are added.

The degree of utilization of storage discussed above has important consequences on the price of the energy delivered from the storage subsystem. For example, from Table 7, a price of \$6.00 per kW_t-hr of capacity would be a reasonable projected cost for a sensible heat storage system. If that unit were amortized at 10% interest over 20 years, the yearly cost of the unit would be about \$0.70/kW_t-hr. If the device were used 300 times per year to meet evening loads and periods of cloud cover, the cost of the energy from the storage unit would be about:

$$\frac{\$0.70/\text{kW}_t\text{-hr-year}}{300\ \text{uses/year}} = \$0.0023/\text{kW}_t\text{-hr delivered}$$

This cost neglects the price of collectors, hardware, etc., required to charge the unit. The cost is low enough that storage is not a major cost barrier for such high utilization.

If the storage block added to meet extended cloudy periods is examined, its utilization is far less. Perhaps this fictitious block of storage would be used only four times per year. With the same capital recovery factor as above, the cost of energy delivered from this element is approximately:

$$\frac{\$0.70/\text{kW}_t\text{-hr}}{4\ \text{uses/year}} = \$0.175/\text{kW}_t\text{-hr delivered}$$

Now, when the costs of collectors, hardware, etc., are added, the delivered energy cost is certainly not promising. Furthermore, for a utility, the costs must be divided by the efficiency of thermal to electric generation to obtain the cost for electricity. Thus for applications where the utilization of storage is low, it is critical to develop very low cost storage subsystems such as the aquifers in Table 7. In all cases, a complete analysis of the system with storage and an appropriate capital recovery factor is required to determine the cost of delivered energy.

C. Summary

The energy storage systems considered here are at varying levels of development. Accordingly, some of the economic evaluations projected for these systems represent hardly more than speculation. However, it is not unreasonable to state that even these preliminary economic and technical projections indicate that several energy storage methods have reasonable potential for achieving application. Table 13 presents some options for the storing of electric energy for utilities. It is clear that pumped storage is the one application that is available now at a reasonable cost. (Lead-acid storage batteries, though available now, appear to have too high a cost per kilowatt-hour stored to make them useable on a commercial basis.) Because each of these storage methods has specific advantages and limitations, the choice of a storage device will be quite dependent on the application.

TABLE 13

Storage Options for Electric Utilities

	Round trip efficiency (%)	Capital ($/kW)	costs ($/kWh)	Energy density (kWh/m^3)	Development stage	Potential application
Mechanical						
Pumped hydro	67—75	100—140		1.4	Existing application: engineering studies for underground	Central energy storage for peak shaving and load leveling
Compressed air-gas turbine system	65—75	120—150	3—10	3.5—17.5	First commercial demonstration 1977	Central energy storage for peak shaving and load leveling reserve generating capacity
Flywheels	70—85	80—120	50—100	17—70	Initial development	Distribute energy storage: power factor correction emergency generating capacity
Thermal						
Steam (pressure vessel)	70—80	150—250	15—25	up to 35	Historical installations, engineering studies of modern systems	Central energy storage integrated with baseload steam generation
Hot oil	65—80	150—250	10—50			
Batteries						
Lead-acid	60—75	60—100	25—50	35—70	State-of-the-art	Distributed energy storage for daily peak shaving: stand-by and emergency generating capacity; vehicle propulsion; energy storage in solar energy systems
Advanced aqueous	60—75	60—100	15—50	35—100	Small prototypes	
High-temperature	70—80	60—100	15—35	70—170	Laboratory cells	
Redox	60—70	100—200	5—15	17—70	Conceptual and laboratory studies	

From Kalhammer, F. R., *Energy Storage: Applications, Benefits and Candidate Technologies*, Proc. Symp. Energy Storage, Berkowitz, J. B. and Silverman, H. P., Eds., The Electrochemical Society, Princeton, N.J., 1976. With permission.

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