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Solar Heat Storage Using Chemical Reactions*

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As an alternative to storage of sensible heat in liquids or solids or as latent heat of fusion, heat storage by means of reversible chemical reactions is under investigation. By this method, a chemical is separated into two components by heating and heat absorption, following which the components are stored in separate vessels and are recombined to generate heat when it is needed. The attractiveness of this concept of heat storage is not only higher energy density, but the capability to store energy as long as desired at ambient temperature, the option of transporting the chemicals to generate heat at another location, and the high temperatures characteristic of some of the reactions which result in high efficiency when the stored heat is used to generate electricity. Many reactions have been proposed and analyzed. Experimental work is in progress on inorganic hydroxide/oxide reactions, the decomposition of ammoniated salts, sulfur trioxide decomposition, ammonium sulfate decomposition, and others. The problems to be solved and potential applications are illustrated by the results of work in progress on $Mg(OH)_2$ and $Ca(OH)_2$ decomposition.

Introduction

In recent years, the subject of energy storage has come under close scrutiny, as a means of better use of a preferred energy source. It is now apparent that there exists a choice of many methods, none of which has a clear advantage over alternative procedures, at this early stage in their development. Economics is usually the most important criterion for the choice. In the case of storage of solar heat, one might think that the provision of sufficient storage for night time and cloudy day needs would be imperative, but the usual result of engineering analyses of particular solar power or heating systems today is that only a rather small storage system is economical, such as enough for 3 to 6 hr operation of the energy load. The alternative, of course, is the use of a backup system powered by fuel or electricity, to take over when the sun is not shining and the store is exhausted. But the subject of solar heat storage is indeed complex. Many factors influence the final choice: the use to which the heat is put, the temperatures delivered by the solar collectors, the cost of alternate heat sources, the character of the solar insolation in the particular geographic locality, and the type of heat storage system.

The most common form of heat storage today is as sensible heat, in which the heat capacity of a fluid or solid is stored and extracted as its temperature fluctuates between two limits. Another method, called phase change or heat of fusion, uses the melting and freezing of a substance to store more heat per unit weight and volume, and this method has also been studied extensively. Finally, heat may be stored by reversible chemical reactions, choosing those which have a substantial heat of reaction. For example, a reactant or reactant mixture is heated, the reaction takes place with absorption of heat, the reaction products are separated, and when heat is desired, the products are mixed to cause the reverse reaction to take place. The reverse

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reaction evolves heat which is extracted and used, and at the same time, the original reactants are regenerated, thus completing the cycle.

The rationale for heat storage using chemical reactions is that energy storage density can be much higher than for other storage methods because reactions can be found for which heats of reaction are much higher than either sensible heat or heat of fusion, and that this leads to smaller containment vessels and potentially lower costs. Furthermore, the reaction products can be cooled to ambient temperature and combined at any later time to generate heat. Another point is that some reactions proceed at temperatures high enough to operate heat engines at high efficiency, as in the generation of electricity, and this high temperature heat is generated at essentially isothermal conditions.

Apparently, the first proposal to use chemical reactions for solar heat storage was a paper by Goldstein (*1*) at the Rome Congress on Solar Energy Utilization in 1955. In his paper, Goldstein made a long list of potential reactions, and pointed out the thermodynamic relations which dictate that the highest heats of reaction will be for those reactions whose equilibria are at high temperatures and have high entropy changes. The pertinent equation is:

$$\Delta F = \Delta H - T\Delta S$$

at equilibrium $\Delta F = 0$ and $\Delta H = T\Delta S$. Of course, the highest ΔS will be for those reactions producing gaseous reaction products. However, storage of a gas would result in a low energy density on a volume basis, and if the gaseous product is condensed to a liquid or solid for storage, some of the energy is released as latent heat of condensation. Nevertheless, it is the reactions involving separation of a vapor product that provide the highest energy storage densities and are the subject of developmental studies. Daniels (*2*) called these "two-vessel" heat storage schemes.

There is presently much discussion and planning on energy storage as a means of conserving energy, but in this regard it is worthy of note that an energy storage device is not in itself an energy source but is in fact an energy consumer. Every energy storage system involves an inefficiency such that the energy output is less than the energy input. The conservation value lies in the use of energy which would otherwise be wasted, or in a shift from a scarce or expensive fuel to a plentiful energy source. Solar energy storage is a prime example of a plentiful but intermittent energy source which could be used more extensively if economical storage means were available.

For climate control of buildings, hot water storage can be used and is relatively cheap and convenient. A chemical system can be much smaller but has the disadvantage of the cost of the chemicals and the complexity of the system. As mentioned, solar heat storage appears to be economical only for storage periods of a few hours. This is because the capital-related costs of the heat delivered from the storage system are proportional to the length of time the heat is stored before it is delivered. But now we come to a paradox, that in spite of this factor, storage of heat on a seasonal cycle may become economic. This possibility arises because of additional factors which come into play for the seasonal solar heat storage concept. The most important is that in northerly latitudes, average solar insolation is much higher for summer months than winter months. This makes it possible to provide the heat needed in winter with a relatively small solar collector if the summer sunshine is stored for that purpose. Without solar storage, the collector needed for winter heating would have to be several times as large.

A second factor is that facilities equipped with such large storage systems become independent of other energy sources, which not only saves the cost of an auxiliary system, but avoids problems that otherwise arise with fuel or electricity supply. Finally, there is usually some cost saving per unit of heat stored, because of the larger scale. Even so, long-term storage will make economic sense only if the cost of equipment and materials is very low, because of the high rate of capital charges due to infrequent turnover of the heat store. Heat storage in water is conceivable if the water containment is a natural aquifier or a swimming pool-like tank. If a chemical is to be used, it must be a very cheap chemical and its containment must be a simple storage bin.

During the past year and a half there have been several survey papers (*3–8*) on chemical heat storage, reviewing the principles stated by Goldstein, presenting brief engineering analyses, and usually indicating a favored system or concept. In some of these discussions, the terms "chemical heat pipe" and "chemical heat pump" have been introduced, to describe related functions of chemical heat storage systems. The former refers to the capability of performing the forward reaction, heat absorption, at one location, transporting the chemical products of the reaction through a pipe or otherwise, and performing the reverse reaction, heat release, at a second location where the heat is needed. The latter term, chemical heat pump, refers to the step in some reaction cycles of absorbing heat from the ambient to vaporize condensed or absorbed H_2O, NH_3, or CO_2 to react with the original solid from which it was evolved, to complete the cycle. These terms serve to point up favorable features of the systems, either the ability to transport the stored heat, or to improve the cycle efficiency by absorbing some heat from the surroundings.

Survey of Proposed Processes

A list of chemical cycles proposed as heat storage systems, some of which are under development, is given in Table I. Each proposal will be discussed briefly as to principles, problems, and status. A project on the development of heat storage systems based on the decomposition of alkaline earth hydroxides has been in progress at Atomics International (*9*) for the past 2 years, and this work will be described in a later section.

Decomposition of alkaline earth carbonates provides a cycle similar to hydroxide decomposition but with some important differences. The carbonates decompose at higher temperatures, the heat storage density is significantly higher, and the condensation of the vaporized constituent, CO_2 in the case of carbonates, has both valuable and detrimental aspects. The detrimental aspect is that the CO_2 must be mechanically compressed to liquefy it at room temperature, and in a heat storage cycle, the operation of the compressor is a parasitic loss of energy. The valuable aspect is that the heat of vaporization of CO_2 is not only small but can be absorbed from water or

TABLE I

RECENT AND CURRENT RESEARCH AND DEVELOPMENT ON CHEMICAL HEAT STORAGE SYSTEMS

Experimental and analytical studies in progress		
$Ca(OH)_2 \rightarrow CaO + H_2O$	525°C	Atomics International
$MgCl_2 \cdot 2NH_3 \rightarrow MgCl_2 \cdot NH_3 + NH_3$ and $CaCl_2 \cdot 4NH_3 + 4NH_3 \rightarrow CaCl_2 \cdot 8NH_3$	275°C	Martin–Marietta
$H_2SO_4 \cdot XH_2O \rightarrow H_2SO_4 + XH_2O$	325°C	Rocket Research
$MgCl_2 \cdot 4H_2O \rightarrow MgCl_2 \cdot 2H_2O + 2H_2O$	107°C	Chemical Energy Specialists
Conceptual and discussion stage		
$BaO_2 \rightarrow BaO + \frac{1}{2}O_2$	700°C	Science Applications
$SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$	900°C	Boeing Corporation
$CH_4 + H_2O \rightarrow CO + 3H_2$	700°C	Naval Research Laboratory
$NH_4HSO_4 \rightarrow NH_3 + H_2O + SO_3$	900°C	University of Houston
H_2O electrolysis → H_2 → metal hydride → H_2 → fuel cell → electricity	—	Brookhaven National Laboratory

TABLE II

PROPERTIES OF ALKALINE EARTH HYDROXIDES AND CARBONATES

	Decomposition temperature (1 atm) (°C)	$-\Delta H$ (298) (kcal/mole)	Energy storage density (theoretical)	
			(Btu/lb)	(kW_t–hr/m^3)
$MgO + H_2O(l) = Mg(OH)_2$	325	9.9	305	465
$CaO + H_2O(l) = Ca(OH)_2$	527	17.6	428	615
$BaO + H_2O(l) = Ba(OH)_2$	988	25.1	264	766
$MgO + CO_2(g) = MgCO_3$	410	28.0	600	1147
$CaO + CO_2(g) = CaCO_3$	890	42.5	765	1340
$BaO + CO_2(g) = BaCO_3$	1297	63.4	579	1657

air at ambient temperature and thus does not reduce the heat storage value of oxide. In the case of hydroxide/oxide cycles, the heat of vaporization of the water must be supplied by the heat of hydration, and is about one-half of the total of hydration in the case of MgO and about one-third in the case of CaO. Decomposition temperatures and heats of reaction for hydroxides and carbonates are compared in Table II.

Apparently, there is no engineering work in progress on a carbonate decomposition heat storage system. However, a study of reaction rates for $CaCO_3$ decomposition and recombination for which the interest was its use as a heat storage material has been published by Barker (*10*) at the Electricity Council Research Centre in England. His experiments showed that the capacity of CaO powder to absorb CO_2 diminished with each cycle, finally leveling off at about one-third of the theoretical capacity. This behavior was not found for $CaCO_3$ with a particle size below 40 μm. However, powders of this fineness have a loose bulk density of only about 10% of theoretical, and Barker concluded that even if compressed to 30% of theoretical density, the storage density per unit volume, of 5 kW thermal per cubic foot, was too low to be of interest for storage of off-peak electricity in homes.

A class of materials that operates in much the same way as the hydroxides and carbonates is the ammoniate salts. Practical heat storage systems based on these chemicals have been proposed by Martin–Marietta Aerospace Corporation of Denver and are the subject of continuing engineering and experimental studies there. The cycles they are studying involve pairs of ammoniate salts, one salt decomposing at elevated temperature with heat absorption and the second salt absorbing ammonia which is later given off at ambient temperature to be absorbed by the first salt with release of the stored heat to complete the cycle.

There are many possible salts and salt pairs but from the point of view of using a cheap chemical, ammoniate salts based on the common chlorides are chosen. The system analyzed used the reaction

$$MgCl_2 \cdot NH_3 \rightleftharpoons MgCl_2 + NH_3,$$

which generates an NH_3 pressure of about 0.2 atm at 300°C. In this way, heat is stored chemically in the resultant $MgCl_2$ and the same quantity of heat is released in the second part of the cycle, when NH_3 reacts with the $MgCl_2$ in accordance with the reverse of the reaction as written.

In the system analyzed by Martin–Marietta, there is a second vessel containing $CaCl_2 \cdot 4NH_3$ which is maintained at ambient temperature and is connected to the high temperature vessel containing $MgCl_2 \cdot NH_3$. The calcium salt is used to absorb the NH_3 evolved from the magnesium salt, which it does at ambient temperature according to the reaction

$$CaCl_2 \cdot 4NH_3 + 4NH_3 \rightleftarrows CaCl_2 \cdot 8NH_3.$$

This procedure is used in preference to condensing the NH_3 to liquid which would involve compression or refrigeration. Heat is evolved during NH_3 absorption but this is not significant in the cycle because the same quantity of heat is absorbed from the surroundings (hence at no cost) when NH_3 is driven off by the reverse reaction, to return to the $MgCl_2$ for reaction and heat release at 300°C. The steps of the cycle are controlled by valving and control of the NH_3 pressure.

One of the requirements of a heat storage system based on ammoniated salts which is common to any process in which a solid, other than a metal, is the storage medium, is that the chemical must be contained in thin layers such that heat transfer paths are short. Put in another way, the power capacity of a device, as distinguished from the energy or heat storage capacity, is directly related to the area of contact with the heat transfer fluid and to the thermal conductivity of the material. A material of low thermal conductivity must be packed in a configuration that provides a high area of contact with the heat transfer fluid, and this means thin layers. The consequent need for an internal structure in the storage container adds to its cost, and in the case of a system using paired ammoniated salts, there are two such heat exchanger salt containers. In spite of these complications, the cost estimate presented (*11*) for a 300 MW plant are at a modest level, a range of $6 to $24 per kW-hr thermal.

Another system rather closely related to the hydroxides and ammoniates just described, and using water again as the preferred vaporizable constituent, is the system described by Greiner (*12*) in which the preferred reaction is:

$$MgCl_2 \cdot 4H_2O \rightleftarrows MgCl_2 \cdot 2H_2O + 2H_2O(g).$$

Its author calls the type of system a chemical heat pump, and the particular system has the distinction of being incorporated in patented devices sold to the public. The articles sold were throwaway portable cooling devices in which, by means of the reverse reaction of the above equation, a container of water in the box to be cooled was evaporated from a wick and absorbed by $MgCl_2 \cdot 2H_2O$ in a connected container outside of the box. By suitable modifications, including regeneration of $MgCl_2 \cdot 2H_2O$ by heating $MgCl_2 \cdot 4H_2O$ (a convenient temperature is 107°C), the cycle could be used for storage of heat or cold.

To complete the list of reversible reactions in which a solid decomposes to a vapor plus another solid, there are two others not now under development, to my knowledge. One on the use of heat of reaction of metal hydride decomposition and recombination was mentioned by Alefeld (*3*) and was also analyzed by Gruen and Sheft (*13*), who described a system using pairs of metal hydrides to avoid having to compress and store hydrogen gas. This necessity lowers the energy density and increases the complexity, but metal hydrides do have the advantage of high thermal conductivity. A disadvantage is high chemical cost.

The other one of these proposals, made by Simmons (*14*) is the decomposition of oxides. His preference was the reaction:

$$BaO_2 \rightleftarrows BaO + \tfrac{1}{2}O_2.$$

The great advantage of a heat storage system based on this reaction is that the vaporized constituent, oxygen, does not need to be condensed or stored, because the reverse reaction will go in air. In fact, this cycle at one time was used for the commercial production of oxygen. The energy density is high and the material cost is moderate, although high enough to be a detrimental factor.

Several reversible reactions have been proposed for heat storage systems which do not involve solids, only liquids and gases, or all gases. Three of these employ sulfur compounds. The decomposition of SO_3 into SO_2 and O_2 was proposed by Chubb (*15*) at the Naval Research Laboratory in a paper presented at the ISES American Section Meeting at Fort Collins, Colorado, in August 1974, not primarily as a heat storage system but as a heat transport means.

Thermal energy would be collected in chemical form from scattered high temperature solar receivers and the heat regenerated at a central chemical reactor (a chemical heat pipe). In later papers (*15, 16*), this chemical transport system has been combined with a heat-of-fusion salt storage tank of special design, and the entire system has been given the name, Solchem.

The SO_3/SO_2 cycle has been analyzed as a chemical heat storage system by Engle and Gintz (*17*) for application to the Boeing Engineering and Construction Company's solar central receiver electric power concept. In their analysis, both the SO_3 decomposition step, which stores heat at about 800°C, and the recombination of SO_2 and O_2, which releases heat, are carried out in catalytic reactors. Further aspects of this analysis are the storage of oxygen at 150 atm and of SO_3 and SO_2 as liquids and the use of a significant level of parasitic pumping power.

Another proposed cycle using sulfur compounds is the decomposition of ammonium bisulfate, which has been analyzed by Wentworth and Chen (*18*) for application to the University of Houston's solar tower power concept. The equation is:

$$NH_4HSO_4(l) \rightleftharpoons NH_3(g) + SO_3(g) + H_2O(g)$$

and the temperature for one atmosphere total pressure is 467°C. This system has a high energy density and has the advantage that the heat-absorbing chemical is a liquid and can be pumped. Separation of the vaporized constituents needs development, and will be costly either in terms of complex equipment or the need for additional chemicals which will also increase the volume and decrease the overall heat storage density. Experimental work on a part of the cycle is in progress.

The third proposal on the use of sulfur compounds relies on the well-known heat of dilution of sulfuric acid. A heat storage system based on the H_2SO_4/H_2O cycle has been analyzed in detail by Huxtable and Poole of Rocket Research Corporation (*19*). In their design, a 70% H_2SO_4–H_2O solution is heated at 325°C to boil off H_2O and leave a residue of 98% H_2SO_4, and the steam is condensed and stored as liquid water. The system has the disadvantage that two-thirds of the total heat absorbed to boil down the 70% acid is in the form of the latent heat of water which is evolved during condensation of the steam. This heat of condensation must be used at the time (during sunlight hours) or it will be wasted. This need to use rather than store such a large fraction of the total heat absorbed greatly reduces the flexibility of the system and restricts the type of application for which it will store heat efficiently. Nevertheless, this chemical system has the advantage of using large, inexpensive tanks for storage and much smaller components for distillation of the dilute acid and for mixing concentrated acid and water.

The system analyzed by Huxtable and Poole was a building heating and cooling system using concentrating solar collectors and with the storage system scaled to take care of the building needs completely, that is, a seasonal storage system. The total heat requirements for the year for both heating and cooling of a 20,000 ft^2 building in an eastern United States location were taken to be 1500 × 10^6 Btu per year. A storage capability of a maximum of 430 × 10^6 Btu was provided, and the analysis showed that the available energy in the store started to increase in the spring and all during the summer and fall, reaching the maximum about the end of November, following which the store would be used up during the winter months to supply the heating load of the building. The analysis included a cost comparison between a sulfuric acid system and a hot water system which showed that the sulfuric acid system would be about 20% cheaper. The catch is that this cost is very high, about \$40/10^6 Btu delivered, based on 15% annual capital charges. This illustrates how expensive it is to provide a storage system with a capacity equal to almost one-third of the total quantity of heat used during the year, whose cost is twice that of the solar collector system alone.

Two other systems for storing solar energy chemically need to be mentioned for completeness. One is the gas reforming–methanation cycle:

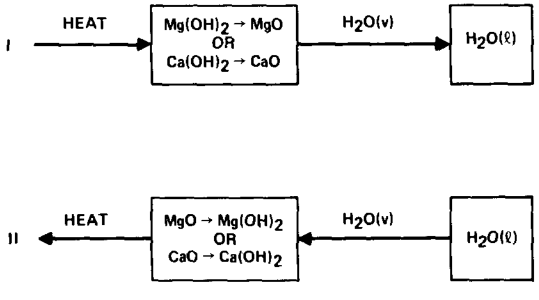
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2.$$

Reactants and products are all gases. The forward reaction proceeds to near completion at about 700°C in the presence of a catalyst. This cycle is a candidate for chemical heat pipe application but is conceivable also for heat storage either in pipelines or in natural underground caverns.

The other is a means of producing fuel by solar heat: the generation of electricity by solar thermal means followed by electrolysis of water to produce hydrogen. The hydrogen thus produced has many alternate uses, can be pumped long distances through pipelines, and can be stored under pressure or as a metal hydride (*20*). The versatility and nonpolluting features of hydrogen as a fuel and means of energy transport have generated a lot of discussion and enthusiasm in recent years. As an energy storage medium, hydrogen incurs a large efficiency penalty if it is produced with today's technology, i.e., produced by electrolysis, and used by burning as a fuel. The possibility of a breakthrough on the production step is that an efficient and economical thermal decomposition sequence will be developed. At the other end of the cycle, there is hope that the development of a hydrogen fuel cell will reach the commercial stage. Until one of these new developments can be put to use, hydrogen does not appear to be an attractive medium for solar energy storage.

Status of $Mg(OH)_2/MgO$ and $Ca(OH)_2/CaO$ Cycle Development

The chemical steps of heat storage and heat recovery are hydroxide decomposition and subsequent formation from the oxide as shown in Fig. 1. This heat storage cycle will be more competitive on an economic basis if it is applied to a solar-powered system that makes good use of two special features of the cycle. One is the high temperature needed for decomposition of the hydroxides, and the corresponding high temperature of heat recovery by hydration. The application should be one which benefits from high temperature, which could be an industrial process, or heat engine generation of electricity. But there is a second requirement to avoid an inefficient heat storage cycle. The heat of condensation of the steam that is driven off by decomposition of the hydroxide is a large fraction of the total, half in the case of MgO, and one-third in the case of CaO, and that heat must be used at the same time that the remainder of the heat is being stored, unless it is to be wasted. This means a system that has a daytime need for heat at about 100°C. These two system requirements must be met at least in some



HEAT IS STORED
BY CONVERTING
HYDROXIDE TO
OXIDE

HEAT IS RELEASED
BY CONVERTING
OXIDE TO HYDROXIDE,
TO COMPLETE THE
STORAGE/RELEASE
CYCLE

FIG. 1. Hydroxide/oxide heat storage concept.

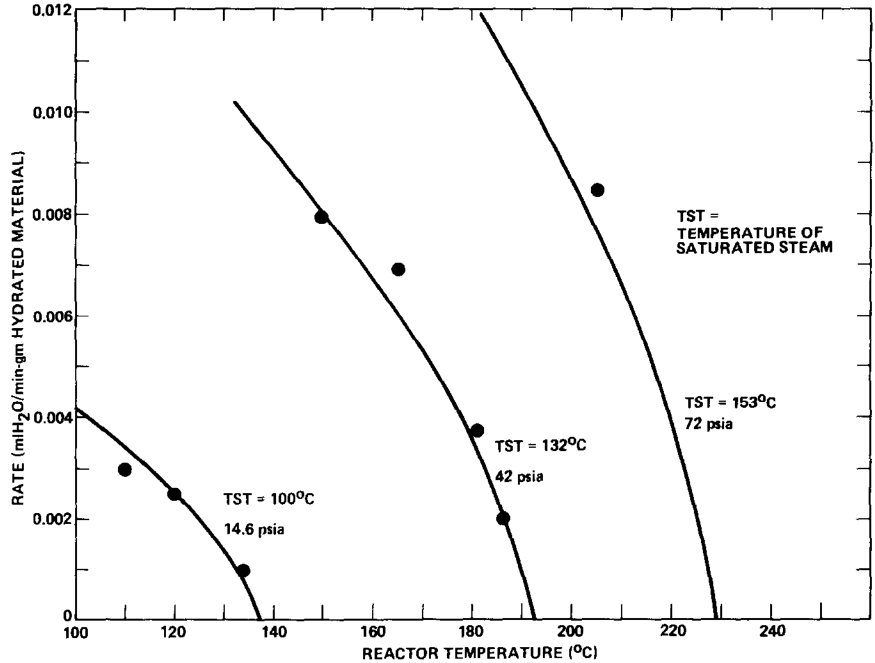


FIG. 2. Hydration of MgO in saturated steam showing cut-off temperature increasing with steam pressure.

degree if these storage cycles are to show an economic advantage.

Preliminary laboratory studies of reaction kinetics indicated that a layer of $Mg(OH)_2$ or $Ca(OH)_2$ about $\frac{1}{2}$ in. thick would dehydrate to 80–90% completion in 2–4 hr and would hydrate in wet steam in an hour or less. Later experiments indicated that these times were shortened to about 20 and 10 min, respectively, for a layer only $\frac{1}{8}$ in. thick. These results and related ones suggest that in the usual case the reactions are heat transfer limited, because of the poor thermal conductivity of MgO or $Mg(OH)_2$ especially in powder form or highly porous layers. This need for containing the materials in thin layers in order to have reasonably fast reaction adds greatly to the cost of the storage vessel, because an internal structure must be provided.

One way to avoid the internal structure is to granulate the material and transfer heat into and out of it in a fixed bed, by flowing gas, such as air or steam. A system of this kind was tested successfully, using equipment holding about 20 lb of material. It was shown both experimentally and analytically that pure steam is necessary for rapid hydration, and pure steam (superheated) was also used for dehydration.

It was found that MgO was inert to hydration in highly superheated steam, the extent of superheat for which reaction occurred being 35–75 °C in the temperature range below 230°C. Reaction rates decreased with increasing temperature as shown in Fig. 2. This finding confirms earlier published studies of MgO hydration (*21*). The phenomenon is not observed for CaO, which was found to hydrate rapidly at temperatures very close to the $Ca(OH)_2/CaO$ equilibrium temperature for the particular steam pressure existing. The practical effect of this upper temperature limitation on MgO hydration is to reduce the efficiency of heat engine operation that could be performed with the $Mg(OH)_2/MgO$ cycle. For this reason alone, the $Ca(OH)_2/CaO$ cycle is more attractive. Other reasons for a preference for the calcium system are that it has a higher storage density than the mag-

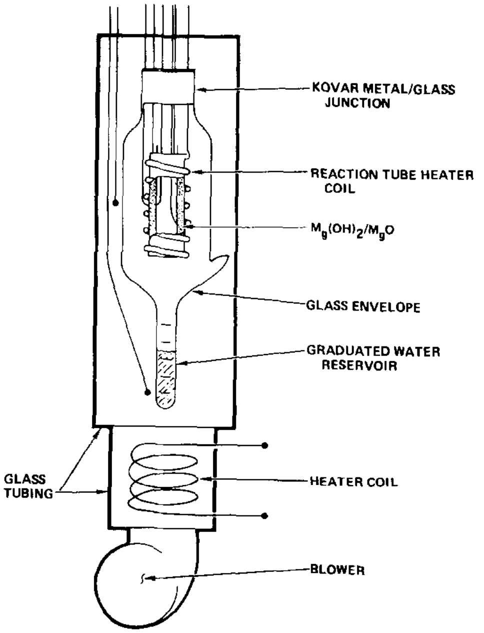


FIG. 3. Sketch of hydration/dehydration cycling apparatus.

nesium system and the chemical is much cheaper. Also, the cycling test results for $Ca(OH)_2$ have thus far been much better.

Repeated cycling tests were performed using the apparatus shown in Fig. 3. The hydroxide/oxide powder was held in a $\frac{1}{8}$ in. thick annular space inside a $\frac{1}{2}$ in. diameter furnace. The thermal mass was kept relatively small to allow for very rapid heating and cooling and thus permit frequent cycling. The time for a complete dehydration and hydration was as short as 45 min. Five hundred cycles were completed on $Mg(OH)_2$ and 211 cycles on $Ca(OH)_2$. The capacity of the $Mg(OH)_2$ to lose and absorb water started out at about 95% but dropped within 40 cycles to 60–70% and stabilized there for the balance of the 500 cycles. There was no noticeable change in the rates of hydration or dehydration. The capacity of the $Ca(OH)_2$ started out at about 95% and remained there throughout the 211 cycles but there was a gradual decrease in rate which stabilized at about 190 cycles. The change was from 30 min for 95% complete dehydration at 550°C and 15 min for hydration, to 1 hr for dehydration and a $\frac{1}{2}$ hr for hydration. Dehydration/hydration cycles were performed at constant temperature at 450°C or 500°C by simply increasing the steam pressure from 0.03 atm for dehydration to 2 atm for hydration.

A fixed bed heat exchanger type design has been the basis for engineering and cost calculations, but designs in which the powdered or granulated solids are conveyed from a bin to a reactor are under consideration for possible cost savings. Such a design would be particularly worthwhile for a seasonal storage system, for which the quantity of material stored is many times the quantity reacted in any one day. Solids handling is conventional but reactor design for such a system may require an advance in the state of the art.

Summary

Table III shows energy densities and capital cost estimates for proposed chemical heat storage systems along with the temperature of operation and special problems or other special features. The hydrogen electrolysis–metal hydride storage–fuel cell cycle is included for comparison, although this is not a reversible chemical reaction cycle in the same sense as the others. Also included for comparison are two nonchemical systems, one of which is sensible heat only, the other a combination of sensible heat and heat of fusion.

One impressive feature of this tabulation is that all of the chemicals and reactions are commonplace and well known, with the possible exception of the ammoniate salts which are a somewhat exotic combination of commonplace chemicals. The energy storage density which is attainable in practice is always much less than theoretical, especially for the solids because of their low bulk density. The figures in the column on total costs are the ones of most interest, and in the first place there are many gaps. Secondly, the ones listed are very speculative and the degree of optimism no doubt has varied from one to the other, making comparisons of cost of doubtful

TABLE III

SUMMARY OF CHEMICAL HEAT STORAGE SYSTEMS[a]

Chemical cycle	Developer	Ref.	Temp. (°C)	Energy density (Theor.) kW_t–hr/m^3	Energy density (Practical) kW_t–hr/m^3	Capital cost estimates Chemicals \$/kW_t–hr	Capital cost estimates Total \$/kW_t–hr
$Ca(OH)_2 \rightleftarrows CaO + H_2O$	Atomics International	*(9)*	525	615	246	0.15	8
$CaCO_3 \rightleftarrows CaO + CO_2$	—	*(10)*	860	1339	566	0.07	—
$FeCl_2 \cdot 2NH_3 \rightleftarrows FeCl_2 \cdot NH_3 + NH_3$	Martin–Marietta	*(11)*	273	310	53	2.82	24
$MgCl_2 \cdot 4H_2O \rightleftarrows MgCl_2 \cdot 2H_2O + 2H_2O$	Chemical Energy Specialists	*(12)*	107	162	65	1.70	—
$BaO_2 \rightleftarrows BaO + \frac{1}{2}O_2$	Science Applications	*(14)*	825	655	262	4.97	—
$SO_3 \rightleftarrows SO_2 + \frac{1}{2}O_2$	Boeing Engr'g & Construction	*(17)*	650	142	70	0.44	24
$NH_4HSO_4 \rightleftarrows NH_3 + H_2O + SO_3$	University of Houston	*(18)*	900	858	137	0.22	—
$H_2SO_4 \cdot XH_2O \rightleftarrows H_2SO_4 + H_2O$	Rocket Research	*(19)*	324	125	100	0.54	2
$CH_4 + H_2O \rightleftarrows CO + 3H_2$	—	*(15)*	700	0.8	—	0.01	—
Electrolysis → H_2 → FeTiH → H_2 → fuel cell	Brookhaven National Laboratory	*(20)*	—	—	75	2	22
Sensible heat (rocks and oil)	Rocketdyne	*(22)*	316	75	60	3	9
Sensible and heat-of-fusion combination (NaOH)	Comstock & Wescott	*(23)*	482	516	434	1.58	5

[a] (1) Practical density of systems using solid chemicals is 40% of theoretical, except for the ammoniate salt system which is based on figures given in the Martin–Marietta reference.

(2) Practical density of NH_4HSO_4 system is estimated from information given in the University of Houston reference based on the use of Na_2SO_4 solution to absorb SO_3.

(3) For the other systems, the practical energy density is calculated from information given by authors of the referenced reports.

(4) The chemical costs are either those given by the author or are from prices given in a recent issue of Chemical Marketing Reporter.

(5) Total capital cost estimates are calculated from cost estimate information given by the authors.

value. All are rather high for long-term storage, especially for seasonal storage. Corrosion and toxicity limit the desirability of many of the systems, in addition to the other problems. There is still a great need for long-term storage to help make widespread use of solar energy feasible. It is a very difficult problem, but reversible chemical reactions remain a reasonable possibility.

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