



Fall 1985

General Characteristics of Thermochemical Heat Storage

Wayne Wentworth

Recommended Citation

Wayne Wentworth, *General Characteristics of Thermochemical Heat Storage*, 25 NAT. RES. J. 1129 (1985).
Available at: <https://digitalrepository.unm.edu/nrj/vol25/iss5/5>

This Article is brought to you for free and open access by the Law Journals at UNM Digital Repository. It has been accepted for inclusion in Natural Resources Journal by an authorized editor of UNM Digital Repository. For more information, please contact disc@unm.edu.

WAYNE WENTWORTH

General Characteristics of Thermochemical Heat Storage

INTRODUCTION

The research and development on thermochemical heat storage have focused on systems which operate at either a low temperature (~ 100 – 150°C or 220 – 300°F) or a high temperature (~ 350 – 500°C or 660 – 930°F). The low temperature systems are intended primarily for heating and cooling buildings and can be operated with high efficiency, double-glazed flat plate solar collectors or slightly concentrating collectors such as parabolic troughs.

The high temperature systems require a highly concentrated solar collector system such as the Power-Tower, where a field of heliostats (basically flat mirrors) focuses the sunlight onto a receiver mounted on a central tower.¹ Alternatively, a smaller reflective surface in the shape of a paraboloid with a diameter of ~ 30 ft. can be used to concentrate the solar energy to attain temperatures in excess of 1000°C or 1830°F . The high temperature storage systems are generally used for electrical power generation but could be used for process heat delivery. In order to generate power efficiently, a high temperature heat source is required. This need is based upon well-known thermodynamic principles, which will be explained later.

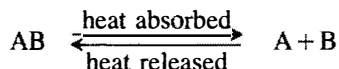
There is very little domestic use of temperatures intermediate of these two regions. Cooking requires temperatures in excess of 100°C , but this is a small fraction of the total energy requirement. On the other hand, there are numerous industrial needs for process heat in these intermediate regions and possibly research interests in the future will focus on energy storage systems for this region.

An energy storage system based on chemical reaction has potentially the greatest storage capacity of the three systems discussed above. Chemical reaction systems store energy by breaking chemical bonds and this requires more energy per mole than the addition of kinetic energy to the molecules (sensible heat storage) or the decreasing of intermolecular

*Professor of Chemistry, College of Natural Sciences and Mathematics, The University of Houston-University Park

1. Hildebrandt & Vant-Hull, *Power with Heliostats*, 198 SCIENCE 1139 (1977); Hildebrandt & Dasgupta, *Survey of Power Tower Technology*, 102 J. SOLAR ENERGY ENG. 91 (1980).

energies (latent heat storage). The chemical reaction can be represented in general by the simple formula



where AB represents the molecule which absorbs the heat and breaks one or more chemical bonds to form the products A and B (forward reaction). The products, A&B, are then stored until heat is required at which time A and B are recombined to give AB and heat is released (reverse reaction). Some chemical reactions require a catalyst to make the reaction proceed. In this case, the products A and B can be stored together, providing they are removed from the catalyst. If the chemical reaction does not require a catalyst, the products must be stored separately.

Generally the reactant, AB, and the products, A&B, are stored at ambient temperatures. This is considered to be a unique advantage of thermochemical heat storage, since storage at ambient temperatures eliminates the cost of insulating the storage containers. Both sensible heat and latent heat-storage require the storage of the material at high temperatures and heat loss to the atmosphere must be kept to a minimum, especially when the storage is for a long period of time.

However, if large amounts of material are stored, the area of the container relative to the volume stored is small and the heat losses are not severe. In this case it may be advantageous to store the products of the reaction at a high temperature and take advantage of the sensible and latent heat associated with heating the reactant AB. This could increase the storage capacity significantly, provided that the sensible and latent heats could be used effectively in the usage of the stored heat. Normally, the heat given off by cooling A&B to ambient temperatures is used to heat AB to the temperature required for the reaction to occur.

The need for storage was discussed previously and it was stated that emphasis would be placed on the use of storage for an intermittent energy source, such as solar energy. In this application the storage must be used on at least a daily basis, as the solar source is not available during the nighttime hours. Of course, as we all know, there can also be daily or weekly cloudy periods when insufficient solar energy is available. In principle, the storage system could also supply these needs; generally one looks to thermochemical storage for long storage periods because the heat losses to the atmosphere can be eliminated with storage at ambient temperatures. However, one must be cautious in these expectations since the storage system must be cost effective, and storage for long periods is very costly. There is a basic cost for the thermochemical system in the chemicals themselves and the cost effectiveness will be reflected in the

savings obtained by using the stored heat. If the storage system is not used frequently, the savings will not be substantial.

The decision as to the size of the storage system is quite complicated and depends upon several factors: (1) Frequency at which the energy source, such as solar, is not available for a given period of time; (2) cost of an alternative backup, such as conventional fossil fuels; and (3) cost of the storage system, including the capital costs of additional solar collectors and stored chemicals. From this discussion, it is obvious that it is not economically feasible to be 100 percent solar sufficient because the cost of providing storage for the exceptionally long periods of time is economically prohibitive. During these exceptional periods, the user must be prepared either to be without the energy source, or to use another constantly available source such as fossil fuels. Being deprived of an energy source may seem to be severe; however, in the case of a solar hot water system or solar heating of a building, infrequent periods of insufficient solar energy can be tolerated. This is not unlike the hardships experienced in times of severe weather conditions, storms, or disasters.

CRITERIA FOR DESIGN

In order for a thermochemical energy storage system to be practical it must satisfy several criteria. These have been discussed in detail elsewhere² and are summarized as follows:

Criterion 1

The reversible chemical reaction should be essentially free of irreversible side reactions. These side reactions would result in loss of the chemicals essential to the thermochemical cycle and the cost would be prohibitive when one considers that the reaction will undergo thousands of cycles over the lifetime of several years.

Criterion 2

The temperature at which the reaction releases the stored heat should match the desired temperature for its use. Obviously the temperature of the stored heat cannot fall below the temperature at which it is to be used. On the other hand, it should not be too much in excess since the overall efficiency will be lower than desired.

Criterion 3

The reaction should have a large energy change for the production of a given volume of products. This reaction will give what is called a large

2. Wentworth & Chen, *Simple Thermal Decomposition Reactions for Storage of Solar Thermal Energy*, 18 SOLAR ENERGY 205 (1976).

energy density (energy/unit volume). A storage system with a greater energy density will require less space in which to store the equivalent amount of heat.

Criterion 4

The forward reaction should be fast enough so that the chemical reactor can keep pace with the rate at which the thermal (solar) energy is being supplied. Similarly the reverse reaction rate should be great enough to supply the heat at a rate sufficient for its end use.

Criterion 5

For an uncatalyzed reaction, the products of the decomposition step must be readily separated at the reaction temperature so that they can be cooled to ambient temperature for storage. For catalyzed reactions the products of the reaction must be readily separated from the catalyst at the reaction temperature, and the reverse reaction in the absence of the catalyst must be slow in order to allow storage at room temperature.

Criterion 6

Chemicals should be commercially available in the quantities needed and at a sufficiently low cost that the thermochemical storage cycle is economically feasible.

Criterion 7

Preferably the handling of the chemicals should not require sophisticated technology or expensive equipment.

Criterion 8

The chemicals preferably should not be highly reactive with water or oxygen since both of these are difficult to completely exclude from a closed system.

Criterion 9

It is preferable that the forward reaction give a high yield ($\sim 95\%$) at a temperature within $5\text{--}10^\circ\text{C}$ or $9\text{--}18^\circ\text{F}$ of the thermal source (solar collector).

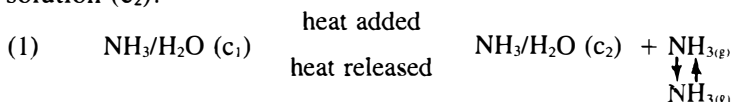
Criterion 10

Similarly, the reverse reaction should go to completion ($\sim 95\%$) at a temperature at only $5\text{--}10^\circ\text{C}$ or $9\text{--}18^\circ\text{F}$ in excess of the temperature required by the use.

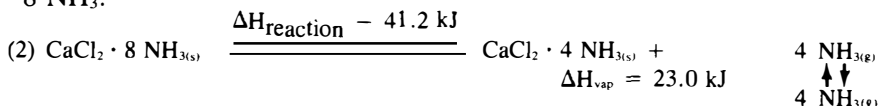
The last two criteria can be evaluated using well-known thermodynamic principles, providing the thermodynamic data are available for the analysis. Obviously no one reaction can satisfy all ten criteria precisely. The criteria are goals that can be used to select the best candidate reactions characteristic of a given thermal source and end use.

CHEMICAL HEAT PUMPS

Research on thermochemical storage reactions in the low temperature range have focused on chemical heat pump reactions. A heat pump cycle involves the addition of heat to vaporize a refrigerant from an absorber solution. For example, an ammonia/water solution (c_1) can be heated to drive off a portion of the ammonia (NH_3) to give a less concentrated solution (c_2).



The $\text{NH}_{3(g)}$ is then condensed to liquid and stored. When heat is to be regenerated, the $\text{NH}_{3(l)}$ is vaporized using ambient heat from the atmosphere and subsequently absorbed in the $\text{NH}_3/\text{H}_2\text{O}$ solution at c_2 with the release of heat. A chemical heat pump undergoes a similar cycle with the exception that the refrigerant is driven off in a chemical reaction. An example of a chemical heat pump reaction is the decomposition of $\text{CaCl}_2 \cdot 8 \text{NH}_3$.



In this reaction, four moles of $\text{NH}_3(g)$ are driven off from the calcium chloride octaammoniate ($\text{CaCl}_2 \cdot 8\text{NH}_3$) by the addition of heat equal to the ΔH of reaction. When the chemical heat pump cycle employs a solid reactant, such as $\text{CaCl}_2 \cdot 8\text{NH}_3$, the $\text{NH}_3(g)$ is driven off at a constant reaction temperature. This is in contrast to an absorber solution, such as $\text{NH}_3/\text{H}_2\text{O}$, where the $\text{NH}_3(g)$ is driven off at an increasing temperature as the solution becomes more dilute in NH_3 . Similarly, the heat generated from the back reaction is produced at a constant temperature when using a solid with the chemical heat pump cycle but in a variable temperature when using a solution. This factor can make a difference in the energy density since it is difficult to drive a large portion of the NH_3 from the $\text{NH}_3/\text{H}_2\text{O}$ solution unless excessively high temperatures are used.

One principle advantage of any heat pump cycle is the fact that heating efficiencies in excess of 1 can be obtained.³ This is readily understood

3. Raldow & Wentworth, *Chemical Heat Pumps A Basic Thermodynamic Analysis*, 23 SOLAR ENERGY 75 (1979).

by referring to equation 2. The amount of solar energy required to drive the cycle is given by $\Delta H_{\text{reaction}} = 41.2$ kJ. When the $\text{NH}_{3(\text{g})}$ is condensed to $\text{NH}_{3(\text{l})}$, the $\Delta H_{\text{vap}} = 23.0$ kJ is given off as useful heat for heating a building. When energy is required from storage, the $\text{NH}_{3(\text{l})}$ is vaporized to $\text{NH}_{3(\text{g})}$ using ambient heat from the atmosphere; the $\Delta H_{\text{reaction}} = 41.2$ kJ heat is given off as additional useful heat during the reverse reaction. The efficiency of the heating process is the ratio of the useful heat recovered divided by the heat input and is obviously greater than 1. Letting ϵ represent efficiency,

$$\epsilon = \frac{\text{heat output}}{\text{heat input}} = \frac{\Delta H_{\text{reaction}} + \Delta H_{\text{vap}}}{\Delta H_{\text{reaction}}}$$

$$\epsilon = 1 + \frac{\Delta H_{\text{vap}}}{\Delta H_{\text{reaction}}} \quad \left. \vphantom{\frac{\Delta H_{\text{vap}}}{\Delta H_{\text{reaction}}}} \right\} 5$$

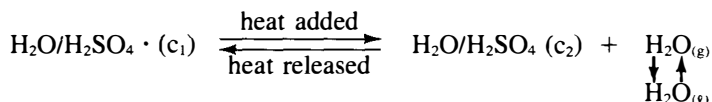
If the heat pump cycle is used for heat storage, the efficiency will not exceed 1 unless the heat released by the condensation of NH_3 is used. Only the $\Delta H_{\text{reaction}}$ is stored energy and the other heat output, ΔH_{vap} , must be used during the portion of the cycle when solar energy is being absorbed. When solar energy is being absorbed, the ambient temperature most likely will be at its highest level, and the building may not need additional heat at that time. In colder climates this is unlikely to occur, but in the warmer, southern climates it may be a very common occurrence.

Another limitation of the heat pump cycle is the use of ambient heat to vaporize the refrigerant, NH_3 in the previous example. If the ambient temperature is too low, the NH_3 pressure will be too low for the back reaction to occur, and the stored energy will not be regenerated. The temperature at which this will occur depends upon the specific absorber or chemical reaction. For the $\text{CaCl}_2 \cdot 8 \text{NH}_{3(\text{g})} / \text{CaCl}_2 \cdot 4 \text{NH}_{3(\text{g})}$ this temperature is about -25°C or -13°F . This reaction will occur during the coldest portion of the winter in northern climates in the United States.

Only two chemical heat pump reactions have been investigated to any degree, and both of these projects were funded primarily by the Department of Energy. At present, there are none which are being marketed commercially. This is not necessarily due to the efficiency of chemical heat pump/storage cycle but rather to the cost of solar energy compared to fossil fuel costs. Furthermore, higher temperatures are required to operate a chemical heat pump storage system compared to direct solar and storage in rocks or water tanks. Consequently, the solar collector must be more efficient, and this standard raises the cost of the collector through multiple glazings, selective absorbers or concentrating collectors.

The "chemical" heat pump system which has received the greatest support is the sulfuric acid/water $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ system where water is the

refrigerant and the sulfuric acid solution is the absorber.⁴ In a strict sense this is not a chemical heat pump since it does not involve a chemical reaction. It is analogous to the $\text{NH}_3/\text{H}_2\text{O}$ system in that the refrigerant (H_2O) is simply absorbed in a solution of H_2SO_4 . The system inherently has the characteristic of a variable temperature required to charge the system and a variable temperature at which the stored heat is delivered. The process can be represented by an equation similar to that for $\text{NH}_3/\text{H}_2\text{O}$:



Because water has a low vapor pressure at ambient temperature, this system operates at a low pressure (~ 0.03 atm) compared to one which uses NH_3 as refrigerant (~ 10 atm). This operation appears to be an advantage; however, there are some disadvantages associated with this low pressure. The system must be essentially free of leaks from air so that the air pressure will not build up over long periods of time (~ 10 yrs). Air at atmospheric pressure would interfere significantly with the mass transfer of the H_2O from the $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ solution to the heat exchanger where condensation occurs. Initially, the system must be evacuated which, in itself, is no major task; however, it may be necessary to re-evacuate at periodic intervals as a maintenance requirement of the system if the air leaks are significant. This, of course, would increase the maintenance costs for the system.

This system offers several advantages. First, the cost of H_2SO_4 is very low ($\sim \$0.02/\text{lb}$); it is one of the least expensive chemicals. Second, H_2SO_4 is readily available in essentially unlimited quantities. This chemical has the largest production in the world, its application being primarily in the fertilizer industry. The third advantage of this system is the fact that it is simple and that it works. Absorption of a refrigerant into a liquid solution is fairly simple to carry out. The solution must be stirred or agitated in order to mix the absorbed refrigerant on the surface of the solution with the bulk solution. This activity uses about all the moving parts required for the absorption process to occur. Of course, the total

4. Rocket Research Co., Phase I Final Report, Sulfuric Acid-Water Chemical Energy Storage System, ERDA Contract No. E(04-3)-1185, Rocket Research Report No. RRC-76-R-530 (Aug. 1976); E.C. Clark, Final Report-Phase II-A, Sulfuric Acid-Water Chemical Heat Pump and Storage System, DOE Contract No. EY-76-C-1185, Rocket Research Report No. RRC78-R-595 (Dec. 1978); E.C. Clark, Final Report-Phase II-A, Sulfuric Acid and Water Chemical Heat Pump/Chemical Energy Storage Program, Sandia Contract No. 1804958, Rocket Research Report No. RRC-79-R-627 (Sept. 1979); Hiller & Clark, *Development of the Sulfuric Acid-Water Chemical Heat Pump/Chemical Energy System for Solar Heating and Cooling*, in PROCEEDINGS OF THE 1979 MEETING, INTL. SOLAR ENERGY SOC. (ISES), (Atlanta, Georgia) (May 1979).

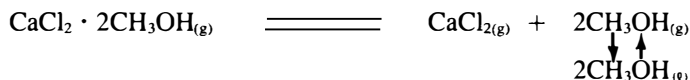
system must have pumps for circulating the fluid coming from the heat source (solar collectors) and the necessary heat exchangers and blowers for heating or cooling the recirculated air in the building.

From the previous discussion it would appear that this system should be commercially feasible at this time. Indeed its simplicity and low chemical costs are significant factors; however, the system also has some drawbacks to be overcome. Previously it was mentioned that the temperature required to drive off the H_2O from the H_2SO_4 solution varies with the concentration of the solution. Initially the concentration of H_2SO_4 is low (c_1) and the water can be vaporized at relatively low temperatures. For example at $c_1 = 68\% \text{H}_2\text{SO}_4$, a temperature of 92.5°C or 200°F is sufficient. As the H_2O is vaporized, the solution becomes more concentrated in H_2SO_4 and the vapor pressure of H_2O is lowered. Higher temperatures are then required in order to increase the vapor pressure of H_2O so that it will condense at $\sim 35^\circ\text{C}$ or 95°F . In order to store a sufficient amount of energy, an upper temperature of 205°C or 400°F is required. This temperature cannot be reached efficiently with a flat plate collector and a concentrating collector is alternatively required. Not only are the concentrating collectors more costly, but they are also in their embryonic stage in terms of commercialization. Small scale concentrating collectors are generally in a fixed position (non-tracking), and this results in a decrease in collection efficiency when the direction of sun is far removed from the optical axis for focus of the collector. Tracking concentrating collectors could be used on larger projects, and this may be the best application for this heat pump system.

Other disadvantages are somewhat minor by comparison. H_2SO_4 is a strong acid and must be handled and stored with caution. At the temperatures of concern, H_2SO_4 does not have a significant vapor pressure to present a hazard from its fumes. However, direct contact of the liquid with the skin must be avoided. Since the system must be leak-tight, this precaution will not present a problem unless there is a break in a transfer line, valve, or the reactor itself. The system would be safe if the H_2SO_4 , in the event of a leak, was restricted to an area away from people and appliances. Location in a basement where the unit is placed within a concrete retaining wall would seem to be ideal.

Another disadvantage of this system is the necessity for prevention of corrosion within the unit. Glass is quite inert to H_2SO_4 solutions, even at these temperatures, and it appears that glass-lined vessels and transfer lines would be required. This protection increases the cost, but not prohibitively.

A true chemical heat pump system which has been under development⁵ can be represented by the following equation



In this case the refrigerant is methyl alcohol or methanol (CH_3OH) and the calcium chloride dimetholate complex ($\text{CaCl}_2 \cdot 2\text{CH}_3\text{OH}$) is a solid. CaCl_2 is very inexpensive and available in large supply. The cost of methanol is not trivial but again not prohibitive. The advantage of using methanol as the refrigerant is the convenient magnitude of its vapor pressure. At $\sim 35^\circ\text{C}$ the vapor pressure is ~ 0.2 atm, which is neither very large or small. It is large enough to give good mass transfer but not too large to require high pressure vessels. Since the vapor pressure is much larger than that for water, the system should not be as sensitive to air leaks as the $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ system.

Another advantage of this system is the constant temperature at which the CH_3OH is driven off. A temperature of $\sim 120^\circ\text{C}$ is sufficient to make the CH_3OH condense at $\sim 35^\circ\text{C}$. This temperature is a little high for flat plate collectors when one considers that heat must be transferred from the fluid in the solar collector to the chemical reaction. The temperature in the solar collector would have to be $\sim 10^\circ\text{C}$ higher in order to get sufficient heat transfer. At this temperature, a very highly efficient flat plate collector would be required, which is very expensive. Again, a concentrating collector could be used but the same problems would exist as described earlier.

Probably the most serious problems with the $\text{CH}_3\text{OH}/\text{CaCl}_2$ chemical heat pump are those associated, in general, with the reaction of a solid. Two of the most serious are heat and mass transfer into and from the solid. Generally, inorganic solids such as CaCl_2 are very poor heat conductors, and the addition or removal of heat from a large bed is difficult. Furthermore, the mass transfer of the CH_3OH into and out of the bed must be carried out at a reasonably rapid rate. This is extraordinarily slow

5. P. O'D. Offenhartz, Chemical Methods of Storing Solar Energy 8, 48, paper presented at the Joint Conference of the American and Canadian Sections of ISES at Winnipeg, Manitoba (1976); P. O'D. Offenhartz, J.M. Marston & J.I. Watts, Analysis of Advanced Thermal Storage Subsystems for Solar Heating and Cooling, EIC Corp., Final Report on Contract EG-77-C-02-4483, Argonne National Laboratory, and Offenhartz & Marston, *id.*, in PROCEEDINGS, THIRD ANNUAL SOLAR HEATING & COOLING RESEARCH & DEVELOPMENT BRANCH CONTRACTORS' MEETING 196, U.S. Dept. of Energy (CONF-780983) (Sept. 1978); Offenhartz & Brown, *Methanol Based Heat Pumps for Storage of Solar Energy*, 1 PROCEEDINGS, 14th IECEC 507 (Aug. 1979).

in a packed bed of finely divided solid particles. Finely divided solids are required in order to expose the solids to the reacting CH_3OH gas. One way to satisfy the heat and mass transfer requirements is to support the finely divided solid on aluminum trays within the container for the $\text{CaCl}_2 \cdot 2\text{CH}_3\text{OH}$ solid. The construction must be such that the CH_3OH vapor can readily move throughout the container. The aluminum trays supply the heat transfer to the thin layers of finely divided solid. Although this technique is satisfactory, the volume is considerably larger because of the space between the trays, and the increased cost of construction is not trivial. Unfortunately, most chemical heat pump reactions involve solids and these problems of heat and mass transfer are ever present.

Other gas/solid reactions are potentially useful as chemical heat pump reactions. These can employ different types of refrigerants, but the most common are NH_3 , H_2O , and CH_3OH . Each of these reactions will have a characteristic reaction temperature, and this is of importance to the specific application and to the type of solar collector to be used. Chemical heat pump reactions hold a great deal of promise, but there is much research to be done, and innovative solutions to the previously discussed problems must be sought.

One possible solution to the problems associated with gas/solid reactions involves suspending the solid in an inert but polar solvent. The polarity of the solvent is required to provide a weak interaction between the inert liquid and the solid so that they can be suspended as small particles. The liquid provides the heat transfer medium from the solar collector directly to the finely divided solid particles. Furthermore, the refrigerant should be sufficiently soluble in the inert solvent so that the mass transfer can be carried out through the solvent. This approach has been applied to the $\text{CaCl}_2 \cdot 8\text{NH}_3$ reaction, and it was shown that the gas/solid equilibrium is obtained even in the presence of the polar, inert liquid.⁶ This could be a viable solution to the problem of gas/solid reactions but much more research must be carried out.

HIGH TEMPERATURE THERMOCHEMICAL HEAT STORAGE

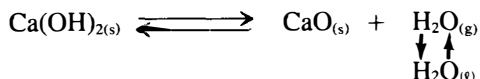
Chemical reactions that can be used for storing solar energy for subsequent use at high temperatures have additional problems compared to the low temperature chemical heat pump reactions. Most of these problems stem from the higher temperatures where corrosion with the reactors and unwanted side reactions are more prone to occur.

If temperatures on the order of 400–500°C or 750–930°F are desired, the molecular species must be very simple in nature in order for the

6. Wentworth, Johnston & Raldow, *Chemical Heat Pumps Using a Dispersion of a Metal Salt Ammoniate in an Inert Solvent*, 26 SOLAR ENERGY 141 (1981).

reaction to give specific products. Larger and more complicated organic molecules would be prone to react along different pathways to give a variety of products. This type of reaction would be difficult to reverse back to the starting materials. Thus, the restriction to simple molecules seriously limits the number of reactions that can be considered for this purpose. Additional restrictions of low cost and availability in large amounts further restrict the choice of viable candidates.

Some possible decomposition reactions that could be used for this purpose have been presented along with a simple way of estimating the reaction temperature. Most of the reactions provide for the decomposition of inorganic salts giving off a single product gas which can be condensed to a liquid for storage. In this sense they would qualify as chemical heat pump reactions although they are seldom referred to in this way since they are not used in the conventional heat pump application. The reaction which has received the greatest research and development is the decomposition of calcium hydroxide (Ca(OH)_2).

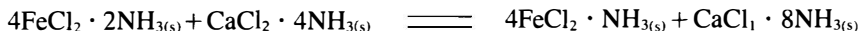


This reaction has been studied extensively by a group at Rockwell International, and their results can be found in several progress reports.⁷

Calcium hydroxide is inexpensive and readily available in large quantities. The energy change associated with the reaction is relatively low (~ 108 kJ/mole Ca(OH)_2) and this lowers the energy density. This energy change is not nearly as serious a problem, however, as the difficulty of carrying out the gas/solid reaction. This is the same problem discussed earlier with respect to the chemical heat pump reactions. In addition, when H_2O is reacted with CaO , a coating of Ca(OH)_2 covers the particles and prevents the reaction from continuing. It can even cause caking which further prevents the H_2O from reacting with CaO particles in the bulk of the sample. This problem can be overcome by the addition of a small amount of silica (SiO_2) to the solids, which tends to keep the particles dispersed. Heat transfer is an additional problem, especially at these high temperatures. A rotating drum was used to spread the solid over a metal surface for heat transfer, but this solution met with limited success. Research on this storage cycle has ceased and apparently some innovative features are needed in order to overcome some of these problems.

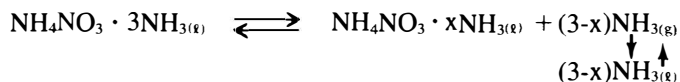
7. G.L. Bauerle, Preliminary Specification for Magnesium Oxide-Hydroxide and Calcium Oxide-Hydroxide Heat Storage Materials, AI Internal Doc. No. N162T1120001 (Oct. 18, 1976); G. Ervin, Jr., D.K. Chung & T.H. Springer, A Study of the Use of Inorganic Oxides for Solar Energy Storage for Heating and Cooling of Buildings, Final Report June 1, 1974 to July 31, 1975, NSF/RANN/SE/GI-44126/FR/75/2, A175-63 (Oct. 1975); Ervin, Jr., *Solar Heat Storage Using Chemical Reactions*, 22-1 J. SOLID STATE CHEM. 51-61 (1977).

A series of reactions involving the transfer of NH_3 between inorganic complexes was considered at length for this program. The reaction temperature, however, was considerably lower ($\sim 275^\circ\text{C}$). This work was carried out by Martin-Marietta and the results can be found in several technical reports.⁸ A representative reaction is:



This reaction necessitates two solid reaction beds, amplifying the problem of handling gas/solid reactions. The project using solids has been disbanded.

A more recent study by this same group has proposed the use of an ammonium complex which is liquid.⁹



Investigators propose that the reaction not be carried out to completion so that the NH_4NO_3 can be dispersed in the liquid $\text{NH}_4\text{NO}_3 \cdot 3\text{NH}_3$. They noted the much greater rate of reaction due to better heat and mass transfer. The explosiveness of NH_4NO_3 is apparently not a problem at the conditions for this reaction. The reaction temperature is somewhat lower than that desired for efficient power generation and is more applicable to heating and cooling.

The maximum efficiency for power generation is given by the well-known expression:

$$\epsilon = \frac{T_2 - T_1}{T_2}$$

which is derived from thermodynamic principles applied to the Carnot cycle. ϵ is frequently referred to as the Carnot efficiency and is approximately correct even if alternate cycles are used. Temperature T_2 is the absolute temperature of heat input and T_1 is the absolute temperature of the waste heat from the cycle. Note that ϵ becomes larger as T_2 becomes larger, obviously suggesting the input heat be at a higher temperature. The effects of the high temperatures on the mechanical equipment must also be taken into account.

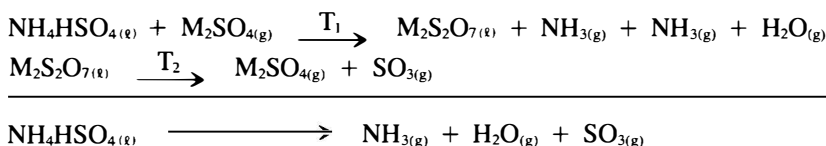
Another system which involves a liquid reactant and liquid products is the decomposition of ammonium hydrogen sulfate (NH_4HSO_4), com-

8. F.A. Jaeger et al., Final Report—Development of Ammoniated Salts Thermochemical Energy Storage Systems—Phase Ib (May 1978).

9. Jaeger & Hall, *Ammoniated Salt Heat Pump/Thermal Storage System*, in THERMOCHEMICAL ENERGY STORAGE 399-412 (Gunnar Wettermark ed. 1980) (Doc. D25:1980, Swedish Council for Building Research, Stockholm, Sweden).

monly abbreviated as AHS.¹⁰ This reaction is capable of generating heat in excess of 410°C and will be more efficient at power generation than the $\text{NH}_4\text{NO}_3 \cdot 3\text{NH}_3(\text{g})$ cycle. At higher pressures and proper reaction conditions, temperatures on the order of 500°C can be obtained. The reaction for storing the energy must be carried out in two steps so that the products can be separated prior to storage. The products of the reaction must be separated in order to prevent the back reaction from occurring.

Two different separation schemes have been investigated. The first uses K_2SO_4 or Rb_2SO_4 to form an intermediate pyrosulfate which is decomposed at a higher temperature. The following reactions describe the process:



The first reaction occurs around 400°C and the second reaction at 850–900°C. The second reaction also produces some $\text{SO}_2(\text{g})$ and $1/2 \text{O}_2(\text{g})$ rather than $\text{SO}_3(\text{g})$ and these can be recombined to give $\text{SO}_3(\text{g})$ by lowering the temperature in the presence of a catalyst. The reaction process design has been carried out by Prengle *et al.*¹¹

An alternate scheme uses zinc oxide (ZnO) to form an intermediate ZnSO_4 intermediate, again forming the products NH_3 and H_2O in the first step. The ZnSO_4 is then decomposed to give SO_3 or $\text{SO}_2 + 1/2 \text{O}_2$ and the ZnO. In both schemes, the $\text{SO}_3(\text{g})$ is separated from the $\text{NH}_3(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. All products can be condensed and stored as liquids. The ZnO separation scheme employs solids and is not as convenient as the metal sulfate/metal pyrosulfate liquid system. A satisfactory liquid medium is being sought for the ZnO separation scheme.

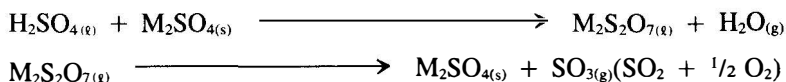
The decomposition of AHS appears to be a viable candidate for high temperature energy storage. However, there is additional work to be carried out and there is the ever present problem of corrosion. Molten salt mixtures predominantly contain ions, and these not only promote reactions but they also, unfortunately, promote corrosion. Ceramic materials are usually the most resistant to corrosion and these may be required

10. Wentworth, Batten, Schuler, Ibanez, Lopez, Cook, Chen & Ray, *The Storage and Regeneration of High Temperature Thermal Energy by Means of Reversible Chemical Reactions—The Ammonium Hydrogen Sulfate System*, in PROCEEDINGS OF THE 1978 MEETING, ISES (Denver, Colorado) (1978); W.E. Wentworth, C.F. Batten, J. Merrill, T. Schuler, J.G. Ibanez & C.J. Cook, *The Storage and Regeneration of High Temperature Thermal Energy by Means of Reversible Chemical Reactions—The Ammonium Hydrogen Sulfate System*, paper prepared for American Society of Mechanical Engineers Meeting (Mar. 12-15, 1979).

11. Prengle, Jr., Hunt, Mauk, & Sun, *Solar Energy with Chemical Storage for Cogeneration of Electric Power and Heat*, 24 SOLAR ENERGY 373 (1980).

for the process. Another potential problem is the completeness of the first reaction; otherwise, the NH_3 carried over will decompose at the higher temperature of the second reactor.

A reaction similar to the AHS reaction is the decomposition of sulfuric acid. If separation into H_2O and SO_3 is desired, a separation scheme similar to that for AHS could be employed:



Again, the fraction of products from the second step into $\text{SO}_2 + \frac{1}{2} \text{O}_2$ can be recombined to give SO_3 . The energy density would be considerably lower for this storage reaction than for AHS. On the other hand, the possible decomposition of NH_3 is alleviated. Since the same separation scheme is used for both H_2SO_4 and AHS, any combination of these chemicals could be used. An advantage of a combination is the lowering of the melting point of the mixture compared to AHS. This may assist in transporting the AHS.

The decomposition of H_2SO_4 can also be carried out in a single step if the decomposition is carried to SO_2 . The reaction must be catalyzed to facilitate the decomposition into SO_2 and O_2 . A convenient catalyst for this decomposition is vanadium pentoxide (V_2O_5).

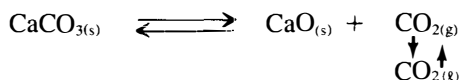


The $\text{O}_{2(g)}$ could be vented to the atmosphere after the SO_2 is condensed to liquid. SO_2 has a boiling point of -10°C and can be condensed to a liquid at ambient temperature (30°C) at a pressure ~ 5 atm. The H_2O could be condensed from the $\text{SO}_{2(g)}$ and probably would condense any SO_3 that is also formed in the process.

Aside from the corrosiveness of H_2SO_4 , especially at high temperatures, the only other problem to overcome is the need to be certain that the O_2 vented to the atmosphere contains less than the allowable SO_2 . As is well known, SO_2 in the atmosphere eventually causes acid rain. The removal of SO_2 in this case should be much easier than from the combustion products from high sulfur coals since the gas should be clean, containing only SO_2 , O_2 , and trace H_2O .

If heat storage at higher temperatures is desired, more stable metal salts such as carbonates or sulfates can be used. The decomposition of CaCO_3 has been considered for some time:¹²

12. Barker, *The Reversibility of the Reaction $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$* , 23 J. APPL. CHEM. BIOTECHNOL. 733-42 (1973); Barker, *The Reactivity of Calcium Oxide Toward Carbon Dioxide and Its Use for Energy Storage*, 24 J. APPL. CHEM. BIOTECHNOL. 221-27 (1974).



Carbon dioxide can be condensed to liquid if the storage temperature is less than the critical temperature of 31°C (88°F). Relatively high pressures of ~70 atm are required for the condensation. This decomposition occurs at ~860°C and could be used efficiently for power generation using a Brayton cycle. Again the problems associated with gas/solid reactions must be addressed.

For still higher temperatures, metal sulfate decomposition should be considered. At present we are not aware of any research done in this area. These would be temperatures in excess of 1000°C and the technology for using heat at these temperatures lies in the future.

In conclusion, we see that no thermochemical heat storage system has been developed to the point that it can be put on the commercial market. For the lower temperature region for heating and cooling buildings, the H₂O/H₂SO₄ cycle could become viable if stationary concentrating collectors become commercially competitive. The inorganic salt complexes of methanol also could be acceptable if modifications of the medium to enhance heat and mass transfer were developed. In regard to the higher temperature region for electrical power generation, the decomposition of sulfuric acid would seem to be simplest for commercialization. Corrosion problems and the SO₂ removal must be solved. The AHS system is more complicated but should not be far behind in development and in being put into practice. Again, the reactions involving solids also could be acceptable if the heat and mass transfer problems were solved. It appears that all the problems have not been solved at the present, but the solutions do not seem to be too far out of reach.