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THERMAL STORAGE TECHNOLOGIES FOR SOLAR INDUSTRIAL PROCESS HEAT APPLICATIONS

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Presented at the Solar Energy Storage Options Workshop San Antonio, Texas, March 18-21, 1979



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THERMAL STORAGE TECHNOLOGIES for SOLAR INDUSTRIAL PROCESS HEAT APPLICATIONS

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Abstract:

Industrial production uses about 40% of the total energy consumed in the United States of which the major share is derived from fossil fuel. Significant savings of scarce fossil fuel is possible through the use of thermal energy storage and/or solar generated process heat. The state-of-the-art of thermal storage subsystems for the intermediate and high temperature (100°C to 600°C) solar industrial process heat generation is presented. Primary emphasis is focused on buffering and diurnal storage as well as total energy transport. In addition, advanced thermal storage concepts which appear promising for future solar industrial process heat applications are discussed.

Introduction:

The impact of solar industrial process heat generation systems will depend on the successful development and integration of thermal storage/transport subsystems. Initially, storage may only be used for brief (buffering) periods of solar outage by passing clouds or for system integration control. However, as the solar process heat system becomes more cost effective in the mid-term time frame, thermal storage for longer durations (diurnal) will become increasingly important. In the future, large, solar industrial process heat generating stations will be totally reliant on long (seasonal) duration storage/transport subsystems.

The DOE Division of Energy Storage Systems (DOE/STOR) is responsible for formulating and managing research and development in energy storage technologies. As part of DOE's Thermal Energy Storage and Transport Program, the NASA Lewis Research Center (LeRC) was given the primary responsibility for the development of sensible and latent heat storage technologies. As shown in Figure 1, two of the key areas of development in the LeRC project structure relate to the storage of process heat for Industrial and for Solar Thermal Power applications. The following discussion relates to the (sensible, latent and thermochemical) storage technologies which have potential for meeting solar industrial process heat storage requirements.





Figure 1 - Lewis project structure

Currently available storage technologies are limited to relatively few sensible and latent heat concepts capable of delivering hot water, air, low pressure steam, or organic fluids. However, thermochemical storage technologies, as will also be briefly discussed, have unique characteristics which offer several significant advantages not available from the other types of thermal storage. These advantages appear particularly attractive for solar industrial process heat applications requiring thermal transport and/or long-term storage capabilities. Thermochemical storage technologies are being developed for DOE/STOR by Sandia Laboratories at Livermore.

Thermal Storage Technologies

Before discussing specific technologies currently under development in the Industrial and the Solar key project elements, a few general comments must be made from a technical as well as an economic aspect. Technically, the technologies must be "system" oriented and include not only media, but also containment, heat exchange and controls. Classification of these technologies by elements results in figures ? and 3. As is readily apparent, a large matrix can easily result for each storage subsystem. This would be quite evident for solar industrial process heat/transport applications somewhat analogous to an electric utility. In fact, a similar classification of available energy storage subsystems for conventional utility applications resulted in 50+ technologies for consideration (ref. 1).

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SENSIBLE HEAT

LATENT HEAT

SOLID / LIQUID

LIOUIDS

- o HIGH TEMPERATURE WATER
 - o ORGANIC COMPOUNDS
 - (OTLS STL1CONES)
 - o INORGANIC COMPOUNDS
 - ISALTS, SULFUR, METALS)
- o NITRATES o HYDROXIDES
 - o CHLORIDES
 - **D** CARBONATES
 - o FLUOPIDES

- SOLIDS
 - o METALS
 - (IRON / STEEL)

- o MINERALS
 - (SILICONE, GRANITE)
 - o CERAMICS
 - (ALUMINA, MAGNESIA)

Figure 2 - Storage technologies

CONTA INMENT

ABOVE GROUND

- HIGH PRESSURE TANKS (WELDED STEEL, PCIV PCRV)
- LOW PRESSURE TANKS SENSIBLE (THERMOCLINE,
 - PACKED BEDS)
- o LOW PRESSURE TANKS LATENT (PCAI)

UNDERGROUND

- STEEL LINED (AIR / CONCRETE SUPPORT)
- O UNLINED NATURAL (AQUIFERS, SALT DOMES EXCAVATED)

HEAT EXCHANGE

ACTIVE

o SALT REMOVAL FROM SURFACE

PASSIVE

o CONVENTIONAL TUBE / SHELL

Figure 3 - Storage technologies

Economically, the obvious emphasis is on reducing the total cost, (CT), which is a combination of power related (Cp) and capacityrelated (CS,) costs. The power component corresponds to the capability of the storage sybsystems to accept and deliver thermal energy at a given rate and includes items such as manifolds, pumps, piping, and heat exchangers. The capacity component reflects the maximum amount of energy to be contained within storage at any time

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SOLID / SOLID o SULPHATES and includes media and containment expenses. The cost of a storage subsystem capable of containing, h, hours at the rated system load is: $C_t = C_p + h C_s$.

Storage cost (C_s) goals for advanced sensible or latent heat subsystems and for thermochemical storage subsystems have been established for solar thermal power applications (ref. 2) as \$1500/10⁶ BTU and \$360/10⁶BTU respectively. Only in a detailed analysis of specific system applications can power related cost be determined.

Industrial Process and Reject Heat Applications

Surveys performed by several organizations (ref. 3, 4) have established the primary energy intensive industries. These are represented in part by those industries, shown in Figure 4, selected for assessment by DOE as a result of a Program Research and Development Announcement (PRDA) of January 1977. Two of these industrial areas, paper and pulp, and food processing were similarly identified by JPL (ref. 4) as specific candidates for solar industrial retrofits in California.

INDUSTRIAL APPLICATIONS

IRON AND STEEL (ROCKET RESEARCH/BETHLEHEM STEEL/SEATTLE LIGHT)

PAPER AND PULP (BOEING/WEYERHAEUSER/SEATTLE LIGHT)

CEMENT (MARTIN MARIETTA/PORTLAND CEMENT ASSOC.)

ALUMINUM (ROCKET RESEARCH/INTALCO/BONNEVILLE POVER)

FOOD PROCESSING (WESTINGHOUSE/HEINZ)

Figure 4 - System studies for thermal energy storage

Paper and Pulp

Boeing Engineering and Construction, with team members Weyerhaeuser Corp. and SRI International investigated for LeRC the application of process heat storage and recovery in a paper and pulp mill. In this study (ref. 5), hog fuels (wood waste produced by various machining operations) and recovered liquors, fuel the boilers for baseload operation, while oil/gas boilers provide for the fluctuating load. The use of thermal energy storage permits substitution of hog fuel for fossil fuels. This could be accomplished by operating the hog fuel boiler at a higher base-load level, storing the excess steam when demand is low, and discharging from storage when demand is high. As shown schematically in Fig 5, typical mill data indicate that a storage time of about 0.5 hr with a steaming rate capacity of 100,000 lb/hr effects a transfer of 60,000 lb/hr in steam load from the fossil fuel boilers to the hog fuel boiler. This corresponds to a reduction of about one half in the fossil fuel consumption for load following. Further, for storage times less than one hour, direct storage of steam using a variable pressure accumulator (Fig. 6) is more attractive economically than indirect sensible heat storage involving rock/oil or rock/glycol media.





Figure 6 - Variable pressure accumulator provides thermal energy storage capability

Crown Zellerbach in the JPL study produces paper from pulp which is mixed with water in an open vat (pulper) and then heated by steam. Most of the water is recovered, stored in temporary storage, and recycled back into the pulpers. A proposed retrofit solar system would supply thermal energy to this recycled water while in temporary storage. The temporary storage is provided by two concrete tanks containing approximately 27,000 gallons of water at 180°F,

For solar industrial process heat, implementation of either thermal energy storage subsystem (steam accumulator or hot water tankage) would require neither technology development nor reduced scale technology validation. In fact, a technology transfer activity is presently being implemented by LeRC in conjunction with ITT Rayonier which has a similar hog fuel/steam storage system "on line" at their Port Angeles, Washington plant.

Food Processing

The H. J. Heinz Company, with Westinghouse as the prime contractor, identified several potential uses of thermal storage in their food processing industry (ref. 7). Planned for demonstration by DOE in CY 81 is the hot water storage subsystem as shown in Figure 7. The factory's main products are baby foods and juices, canned soups, and canned bean products. Thermal energy is applied to the product during the cooking process and is discharged as hot water down the drain system. The main method of heating process water is by the direct injection of steam. Since process water is not recycled to eliminate the possibility of product contamination, condensate losses are high and must be matched by make-up. Therefore, preheating make-up water via solar input and storage would be an excellent application of energy conservation technology.



Figure 7 - Food processing plant energy recovery and storage system

The market potential for solar process heat is considerable. It is estimated that 85% of the fuel utilized by this industry goes to produce process steam and hot water at low temperatures for cooking, sterilization, and equipment/work area cleanup, washing and sanitizing (ref. 6).

Again, it should be noted that these steam and water storage technologies are "off the shelf" for solar industrial process heat applications. Advanced sensible, latent, and thermochemcial storage development efforts will provide increases in performance and cost effectiveness. At the present time, the primary emphasis on the development of advanced storage technologies is in Solar Thermal Power Applications.

Solar Thermal Power Applications

A workshop on Storage for Solar Thermal Power Systems held in February 1978, concluded that the need existed for a comprehensive and agressive thermal energy storage technology development program for solar thermal (electric power/total energy) applications. A plan (ref. 2) was generated for DOE/STOR and CST by LeRC which proposed development efforts in those areas shown in Figure (8).



Figure 8 - Program plan elements for solar thermal power (draft plan)

Many advanced storage subsystems, developed by this effort in the FY 80-85 time frame, will be equally applicable to solar industrial process heat systems in the intermediate to high temperature range. The baseline or current technology available relates to sensible heat storage of the collector fluid in single (thermocline) or multiple (hot/cold) tanks to supply heat for process steam or an organic working fluid. A dual media, rock/oil storage subsystem is shown in Figure (9).





96.3 MWHL 1 TO 30 MWL 3.1 TO 32.1 MWL 3 HR

Figure 9 - Dual media thermal storage systems

This concept is considered to be "state-of-the-art", however, thermal ratcheting and an expensive oil inventory may be sufficient in magnitude to warrant development of other alternative concepts, e.g. trickle oil, taconite or latent heat systems. Consequently, it is the intent of the STOR/CST effort to:

- o Provide <u>Advanced Alternatives</u> offering cost/performance improvements over baseline storage subsystems and,
- Provide <u>Baseline storage subsystems</u> for those applications which presently have no storage subsystems under development.

Some of the advanced subsystem technologies currently being developed that are applicable to intermediate and high temperature process heat are the following:

Media

Thermal energy storage at intermediate to high temperatures can be obtained by utilizing the heat of fusion of molten salts. Many salts are attractive because of their high mass and volumetric heat storage capabilities, their abundance in nature and as a result of industrial processes, and their low cost per unit storage capability. By utilizing the heat of fusion (liquid-solid transition) of various salts, large amounts of thermal energy can be stored and subsequently released at nearly constant temperatures.

In a recent study (ref. 8) conducted by the Institute of Gas Technology (IGT), mixtures of 31 salts were considered for storage subsystem integration with a steam Rankine cycle. These salts were selected because their melting points fell in or near the 4540-538°C (850-1000°F) range and they did not display any particular difficulties in handling, containment, stability or availability. Because of the importance of salt cost in determining the economic viability of the entire storage, cost envelopes of these

salts, (\$/10⁶ BTU), were made as a function of volume, ft³/10⁶ BTU, of the salts. This is presented in figure 10. The highest cost salts are composed of bromides, fluorides, and hydroxides. The lowest cost salts are mixtures of alkali and alkaline earth chloride salts, whereas moderate-to-high cost salts are carbonate salt mixtures and some chloride and fluoride salts. However, several of these low-to-moderate cost salts emit highly toxic fumes when heated, presenting potential safety hazards that could restrict their use and increase cost of containment to prevent leakage.



Figure 10 - Latent heat salts cost comparison

Latent heat storage system concepts which utilize the heat of fusion from a solid-solid phase transition are particularly attractive. The technical problems associated with these systems, such as volume change, are generally less imposing than those associated with the liquid-solid phase change latent heat system concepts. This concept is being evaluated as part of the NASA-LeRC in-house experimental efforts with potential applications existing in solar total energy systems to provide space heating. Calmac Inc. has designed and fabricated a sodium sulfate, solid-solid phase change, thermal energy storage module. The module consists of three interchangeable packed bed configurations to provide the capability of determining the best design to minimize solid particle breakup in a heat transfer fluid. Thermal storage capacity is approximately 58.6 kwh (200,000 BTU).

Containment

For large storage capacity applications consideration is being given to both underground and aboveground storage containment. One potential candidate for underground storage being explored by the University of Houston and Subsurface Inc. (ref. 9) is deep cavern storage of hot oil utilizing solution caverns in massive salt deposits. The essential geologic requirements are known and easily satisfied as evidenced by the many salt domes of the Gulf region of the United States as well as rock salt formations throughout the United States. The cavern construction, as shown in Figure (11) requires an adequate supply of fresh water which is injected into the well and circulated causing dissolution of the salt to form brine.

Several technical and economic issues related to a proposed storage temperature of 342°C (648°F) are being addressed in the current study. Some of the technical issues are high thermal stresses in the well on the cement to casing and formation bonds, cavern constructions designed to minimize heat losses, and a potential problem of plastic flow in the containing salt formation. Economically, the major issue involves the capability to deliver power cycle working fluids at required qualities.



Figure 11 - Schematic of a salt cavern leaching operation

Above ground storage applications can make use of prestressed cast iron vessels (PCIV). The PCIV construction is shown in Figures 12 and 13. Basically, the containment consists of cylindrical cast iron blocks stacked to the desired height. These segments are placed in compression by axial and tangential tendons. A liner and pressurized insulation as well as the necessary fill/drain posts must also be provided as dictated by the respective storage media. A reference PCIV (ref. 10), for application to storage of high pressure, high temperature water of 8000 m³ (282,517 ft³), 275° (527°F) was designed and stress-analyzed. Cost of the reference vessel is estimated to be between $3200-34800/10^6$ BTU.







Figure 13 - Detail of prestressed cast-iron pressure vessel

Heat Exchange

This area of an energy storage subsystem for solar industrial applications could be the most important factor affecting system performance and cost. A passive type heat exchanger (tube intensive) for phase change media in the 300°C process heat region was examined by Comstock & Wescott for Solar Total Energy Systems (ref. 11, 12). This concept is shown schematically in Figure 14 and specific hardware in Figure 15.



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Figure 15 - Bottom view of heat exchanger

The storage subsystem consists of coiled, mild steel tubing, in a mixture of sodium hydroxide and sodium nitrate. In charging, the solar receiver fluid flows downward through the heat exchanger, and upward when stored heat is being retrieved. A thermal gradient exists within the medium (with the higher temperature in the upper part of the vessel) which moves vertically and changes shape during thermal cycling.

The medium undergoes an increase in volume as it melts, and to accommodate this a clearance space must be allowed at the top of the vessel. This space is open to the atmosphere through a "breather" tube which allows air to enter and leave during cycling, and which insures that the vessel operates unpressurized. The vessel is surrounded by thermal insulation, the outer surface of which is protected by a metallic shroud.

An advanced heat exchange concept currently being developed for DOE by the Naval Research Laboratory (ref. 13) brings many of these technologies together. Ground breaking for a subscale prototype system, shown schematically in Figure (16) occurred on January 4, 1979 at NRL with the first charging cycle scheduled for October 1979. The 2 MWH_{th}Energy Storage Boiler Tank is charged by input heat (possibly from a thermochemcial energy transport system) to a heat pipe fluid which evaporates and produces an increase in the pressure of the heat pipe vapor in the tank. The heat is delivered to an eutectic salt mixture stacked in many individual containers by condensation of the vapor on the container surfaces, thereby melting the salt.



Figure 16 - Energy storage-boiler tank

Energy withdrawal is also accomplished by heat pipe techniques. Near the top of the tank is another pipe network. Heat pipe fluid is sprayed onto the salt cans and evaporated. Water flows through the upper piping, the heat pipe fluid condenses on these pipes and produces steam in direct response to feedwater flow. NRL has projected costs for a storage sybsystem, as described, and utilizing a chloride salt, eutectic mixture with m-terphenyl as the heat pipe fluid at less than \$1500/10⁶BTU, approximately. This cost does not include heat exchangers required for charging and heat withdrawal. This concept could be used for other process heat storage applications at a variety of temperatures based on the selection of heat pipe fluid and storage media. Figure (17) presents some possible combinations of media and heat pipe fluids.

MEDIA		HEAT PIPE FLUID	
Wt. Composition	MP(°C)	Material	BP(°C)
NaCl	801	Potassium	774
19%NaCl 47%KCl 34%CaCl ₂	532	P ₄ S ₇ P ₂ S ₅	523 514
32%NaCl 68%CaCl ₂	506	Mixed phosphorus sulfides	-480
36%NaCl 64%MgCl ₂	450	Tetraphenyl silane Tetraphenyl methane $P_4 S_3$	428 431 408
24.5%NaCl 20.5%KCl 55.0%MgCl ₂	385	m-Terphenyl	365
		Triphenyl amine • Triphenyl phosphoru oxide	365 s>360
37%NaCl 63%FeCl ₂	370	o-Terphenyl	332
CO(NH2)2	133	Toluene	111

Figure 17 - Material sets for energy storage - boiler tank

Concluding Remarks

It is important to recognize that the results of all of the "state-of-the-art" and advanced storage development activities which directly or indirectly support storage for solar industrial process heat applications cannot be presented within the limited scope of this paper. Nevertheless, "visible" subsystem research modules, sufficient in size to validate the developed technology for end-use applications considerations, have or will appear in the near future. Figure (18) projects a scheduled time frame for some of these modules given the planned resources. As solar industrial process heat systems mature to large centralized stations, the long duration storage/thermochemical transport technologies will dominate. 1930 TO 81 - HOT WATER, STEAM ACCUMULATOR, POCK/OIL THERMOCLINE,

AND MULTIPLE (HOT/COLD) TANKS

1981 TO 33 - IMPPOVED SENSIBLE AND LATE'T HEAT STOPAGE SUBSYSTEMS

1983 TO 85 - LONG DURATION (LARGE CAPACITY) SENSIBLE AND LATENT HEAT STORAGE SUBSYSTEMS ORIGINAL PAGE IS

- THERMOCHEMICAL STORAGE / TRANSPORT SUBSYSTEMS

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Figure 18 - Technology validation by subsystem research modules REFERENCES:

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