DOE/NASA/0038-79/1
NASA CR 159479
HI #79063

(NASA-CR-159479) ACTIVE HEAT EXCHANGE SYSTEM DEVELOPMENT FOR LATENT HEAT THERMAL ENERGY STORAGE (Honeywell, Inc.) 122 p HC A06/MF A01 CSCL 10A
N79-21554
Unclas
G3/44 19491

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HONEYWELL, INC - ERC

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PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
UNDER CONTRACT DEN3-38

FOR

U.S. DEPARTMENT OF ENERGY
OFFICE OF ENERGY TECHNOLOGY
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NOTICE

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WASHINGTON, D.C. 20545

UNDER INTERAGENCY AGREEMENT EC-77-A-31-1034

ABSTRACT

This topical report describes active heat exchange concepts for use with thermal energy storage systems in the temperature range of 250°C - 350°C, using the heat of fusion of molten salts for storing thermal energy. It identifies over 25 novel techniques for active heat exchange thermal energy storage systems. Salt mixtures that freeze and melt in appropriate ranges are identified and are evaluated for physico-chemical, economic, corrosive and safety characteristics. Eight active heat exchange concepts for heat transfer during solidification are conceived and conceptually designed for use with selected storage media. The concepts are analyzed for their scalability, maintenance, safety, technological development and costs.

A model for estimating and scaling storage system costs is developed and is used for economic evaluation of salt mixtures and heat exchange concepts for a large scale application. The importance of comparing salts and heat exchange concepts on a total system cost basis, rather than the component cost basis alone, is pointed out. Comparison of these costs with current state-of-the-art systems should be avoided due to significant differences in developmental status. The heat exchange concepts were sized and compared for 6.5 MPa/281°C steam condition and a 1000 MW(t) heat rate for six hours. A cost sensitivity analysis for other design conditions is also carried out.

The study resulted in the selection of a shell and coated-tube heat exchanger concept and a direct contact-reflux boiler heat exchange concept. For the storage medium, a dilute eutectic mixture of 99 wt% $NaNO_3$ and 1 wt% NaOH is selected for use in experimenting with the selected heat exchanger concepts in subsequent tasks.

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SECTION 1.0
INTRODUCTION

Historically, the socio-economic pressures of an exponentially-growing demand have been alleviated through technological breakthroughs.[1] The present energy situation appears to have the basic dimensions of an ecocrisis -- exponentially growing demand and diminishing returns. The national response to this problem has occurred along four fronts:

- Energy conservation to slow down the exponential curve.
- Increased utilization of baseload power plants to stabilize the supply.
- Accelerated pursuit of technological breakthroughs in nuclear fusion to fundamentally change the nature of the ecosystem -- from one with finite resources to one with essentially infinite fuel.
- Research and development of alternate energy sources such as solar-thermal, solar electric, wind, ocean and geothermal.

Large-scale conservation of irreplaceable petroleum and natural gas resources would become possible if advanced energy storage devices and systems could power electric vehicles, replace or reduce the utilization of combustion turbines by electric utilities during times of peak demand, allow space heating and cooling with off-peak electric power, and permit a more effective utilization of solar energy.[2]

At present, the only residential and commercial applications of energy storage are based on thermal storage in hot water or ceramic brick storage heaters. The significance of these applications for the energy system as a whole lies in a partial shift of electric energy demand to off-peak hours when it can be met with baseload generation operating on coal or nuclear energy. For electric utilities, the shift tends to result in improved load factors and improved economics of operation. It is generally accepted that, for the solar-thermal generation of electric power, energy storage is necessary as a buffer for plant stability and control and to extend plant operation beyond daylight hours.

Thermal energy can be stored in the form of:

- Sensible heat -- as in water, steam, oil/rock, ceramic bricks, etc. and/or
- Latent heat of phase change or transition -- as in heat of fusion of inorganic salts or other materials.

Stored thermal energy involves degradation of heat. Heat stored at a given temperature will be extracted at a lower temperature due to the heat exchange required. Sensible heat systems typically require a larger temperature differential for the storage and extraction of heat. While the mechanization of sensible heat systems is relatively straightforward, the large system sizes (resulting in high cost of storage vessels and materials) coupled with lower storage efficiencies suggest the need for development of heat of fusion thermal energy storage systems. Successful development of these systems offers the potential of lower acquisition and life cycle costs to the user and a significant achievement toward national energy goals.

The heat of fusion storage concept is simple, but the phase change phenomenon of storage media must be understood to develop viable systems. This phenomenon gives rise to the growth and dissolution of solid particles. A candidate concept must be capable of transferring heat from a source to a solid (or semi-solid) storage medium causing it to melt and resulting in stored thermal energy. It should permit relatively high heat rates while undergoing this phase change.

Likewise, the concept must be capable of extracting the thermal energy stored in the medium and delivering it to a sink at high rates while undergoing a solidification process. The energy is released by crystallization from the melt. However, the solid crystals tend to build up and impede the transfer of heat. Two basic approaches are available to handle this problem. One achieves the heat transfer without mass transport, and the other accomplishes it with mass transport. These are referred to as passive and active systems, respectively.

In a passive system, the medium is allowed to solidify in place, around and between the heat transfer surfaces. The design of such a system typically results in a large number of tubes closely packed throughout the media storage vessel. The capital costs of this system depend very heavily upon thermal capacity (storage tank size) and rate (tube size and spacing).

In an active system, the storage medium is transported to and from the vicinity of the heat exchange surface. Energy removal may be enhanced by actively inhibiting or subsequently removing solid crystal growth on the heat transfer surfaces. The viability of active heat exchange storage systems for future solar power and commercial/industrial applications will depend on the development of heat exchange concepts and heat-of-fusion storage media that perform these functions simply and effectively. It is the purpose of this program to quantify these concepts, identify the critical issues, select the better candidates, experimentally resolve the outstanding issues, and recommend the best concept for continued development and demonstration.

SECTION 2.0
SUMMARY

This topical report documents the results of Task I: Concept Selections as stipulated under Task V-D of Contract DEN 3-38-Active Heat Exchanger System Development for Latent Heat Thermal Energy Storage Systems.

The project is sponsored by the U.S. Department of Energy/Division of Energy Storage Systems and managed by the National Aeronautics and Space Administration/Lewis Research Center. The overall project consists of five tasks to select, design, fabricate, test and evaluate candidate active heat exchanger modules for future applications to solar and conventional utility power plants.

Task I consisted of identifying candidate heat exchanger concepts compatible with a molten salt phase change medium selected for use with steam power cycles in the temperature range of 250°C to 350°C. The selected salt and candidate concepts were compared at a commercial scale of 1000 megawatt thermal with six hours of capacity.

The efforts undertaken during this task have resulted in:

- The selection of a dilute eutectic mixture of 99%(wt) sodium nitrate and 1%(wt) sodium hydroxide as the storage phase change media (PCM) for use in the development of active heat exchanger systems.
- The selection of two active heat exchanger concepts for use with the selected PCM in development of experimental TES modules:
  - Shell and coated tube heat exchanger.
  - Direct contact reflux boiler heat exchanger.

The basic active heat exchanger concepts are shown on Figures 2-1 and 2-2.

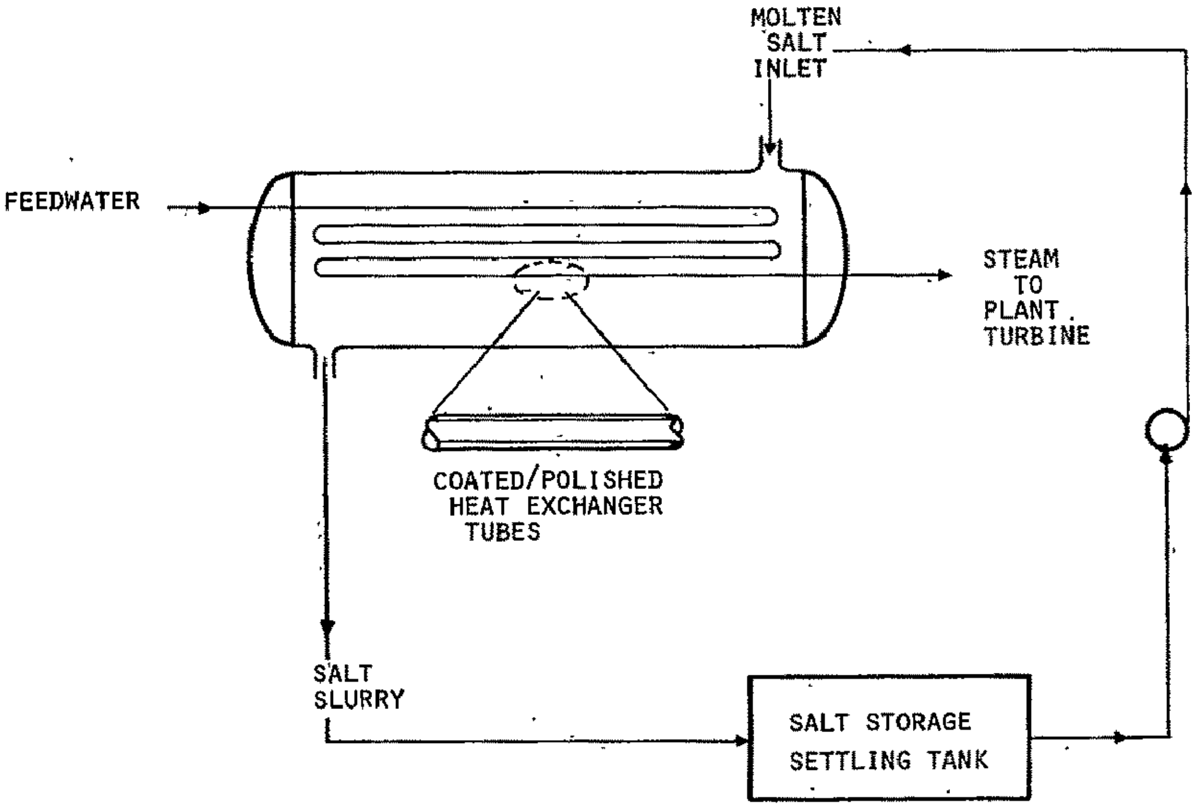


Figure 2-1. Shell and Coated Tube Flow-By Heat Exchange Concept

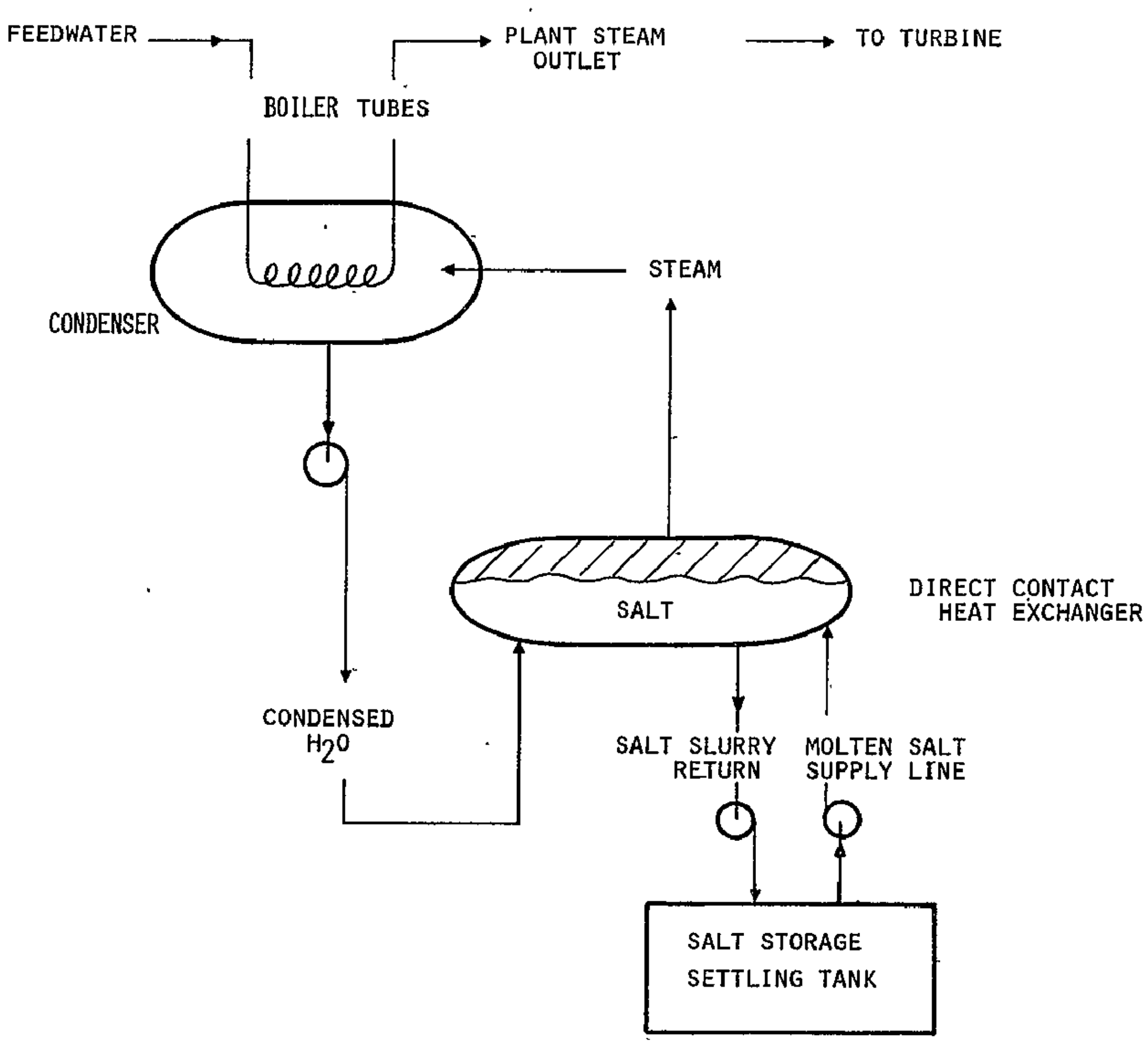


Figure 2-2. Direct Contact Heat Exchange Concept

The shell and coated tube exchanger is based on moderate cost and well developed equipment, but its applicability with a PCM is subject to development of a coating to which salt does not adhere. The reflux boiler concept shown in Figure 2-2 is unique in that the salt freezes away from any heat exchanger surfaces. The experiments to be conducted in the subsequent tasks will demonstrate the feasibility of these two concepts with the selected media.

Approximately twenty-five different techniques were explored to deal with the problem of solids buildup. These included various mechanical, hydraulic and media property characteristics as well as material morphological considerations. A survey of industrial heat and chemical process industries equipment was made to gain insight for the task at hand. A discussion of the various techniques and surveys is presented in Section 3.0.

The PCM was selected after a systematic elimination of phase change inorganic salts and salt mixtures based on various criteria that included stability, availability, energy density, effect of candidate salt on system cost, salt mixture composition, and phase diagram type. This is covered in more detail in Section 4. The selected PCM is a dilute eutectic mixture as opposed to a eutectic or congruent melting composition. Figure 2-3 is a phase diagram of a sample PCM illustrating the eutectic, dilute eutectic and congruent melting compositions. The eutectic and congruent melting compositions freeze (melt) at a constant temperature, more or less like a single salt. The dilute eutectic composition freezes along the solubility curve such that the freezing component (in this case, pure salt) is in equilibrium with the melt of composition given on the solubility curve. The freezing salt of dilute eutectic composition will always have a two-phase region (the freezing component and the equilibrium liquid at the melt temperature) until the eutectic temperature is reached. At that point, the freezing component is the eutectic composition that freezes like a single salt without a two-phase region. Therefore, if the temperature of the coolant or heat transfer surface in contact with the melt is above the eutectic melting

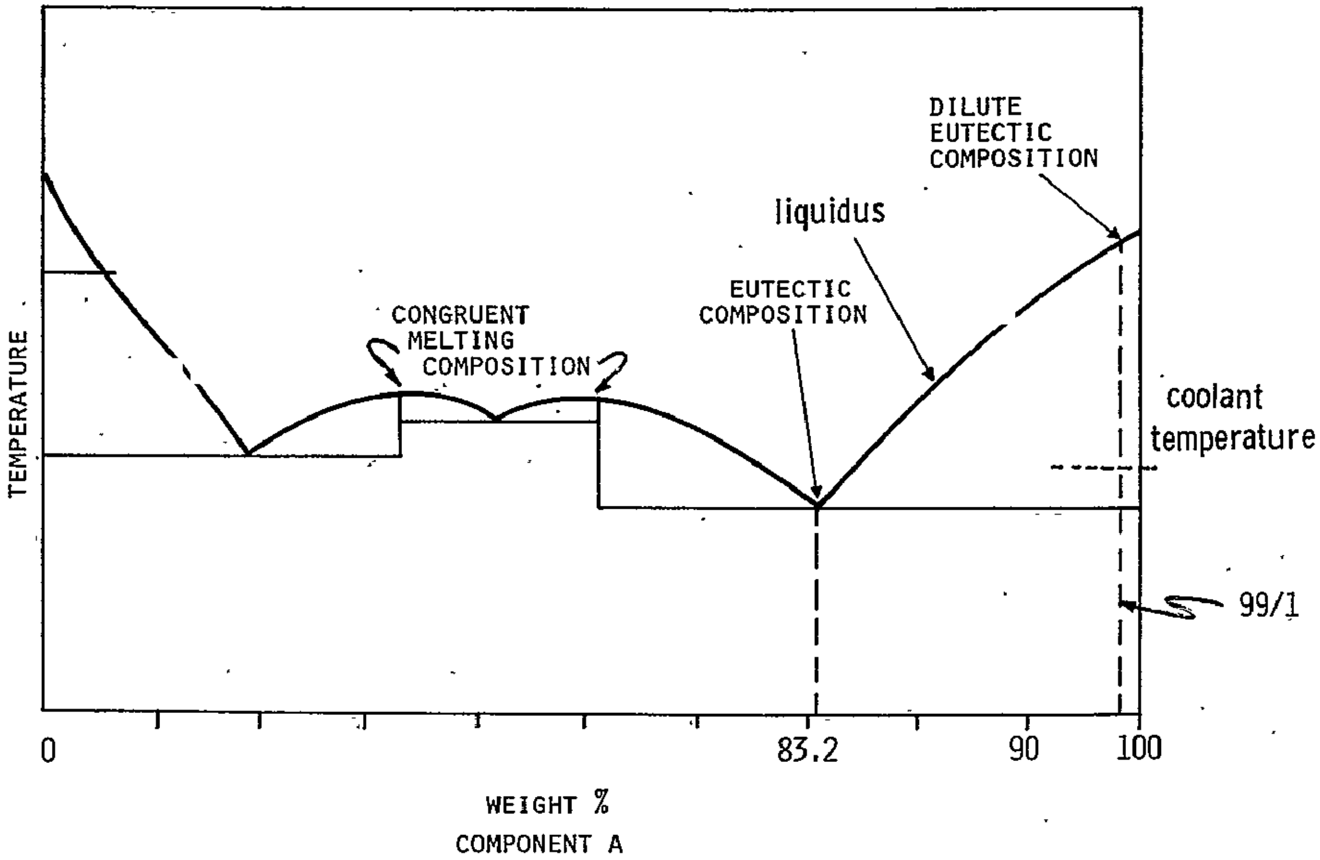


Figure 2-3. Phase Diagram for Sample Phase Change Media

point, there will always be a two-phase region or slush near the surface. The mechanical removal of a slush is easier than that of a pure solid. This concept was developed by Honeywell during the Solar Pilot Plant Engineering model experiments with latent heat PCMs. The experiments involved the mechanical scraping of salts freezing on the outer surface of a tube with a coolant running through it. The difference between the scrapability of a pure salt or eutectic salt and a dilute eutectic salt was observed. With the eutectic salt, the scrapers stalled immediately or needed very high torque to rotate. With the dilute eutectic, the scraping was as smooth as if scraping a slush and required low torque. However, when coolant temperature was dropped below the eutectic temperature, the scrapers stalled immediately with the dilute eutectic.

This suggested the formation of a eutectic composition near the freezing interface in this non-equilibrium freezing. For this and other reasons discussed in Section 4.0, a dilute eutectic composition was selected rather than a eutectic or congruent composition.

Based on the various heat exchange concepts presented in Section 3.0, eight different mechanizations were selected for a more detailed economic and technical evaluation. These are presented in Table 2-1 in summary form. The evaluation criteria included scrapability, maintenance, safety, auxiliary power, technological development, recurring and non-recurring costs. A detailed evaluation based on these criteria is presented in Section 5.0.

The costs, which include cost of heat exchanger manifold, tankage, salt and balance of plant (BOP), are expressed in rate-related and capacity-related costs for a 300 MW_e steam generation application. Column C on Table 2-1 gives normalized system costs (normalized with respect to passive tube-intensive systems) for a six-hour storage, and Column D gives normalized costs without BOP. BOP includes circulation equipment, foundations, auxiliary components, etc. The costs were based on Honeywell build experience and detailed estimates made for a pilot scale latent heat storage system integrated with a solar electric plant. Each concept is compared in terms of an estimated technical development status based on the state of the art of the equipment required. Engineering development is considered near term (2 to 3 years). Advanced and concept developments are intermediate (3 to 5 years) and far term (5 to 10 years), respectively.

The last two columns of Table 2-1 qualitatively identify expected operating and maintenance costs for the selected concepts. This enables total life-cycle costs to be brought into perspective. As a result of this evaluation, the shell and coated tube (3) and reflux boiler (6) emerged as the most attractive heat exchange concepts.

Figures 2-4 and 2-5 show the two selected concepts mechanized for a 300 MW_e six-hour duration steam generating application.

A cost sensitivity analysis revealed that increasing heat rates, capacities and cycle pressures improved the relative cost effectiveness of active over passive systems.

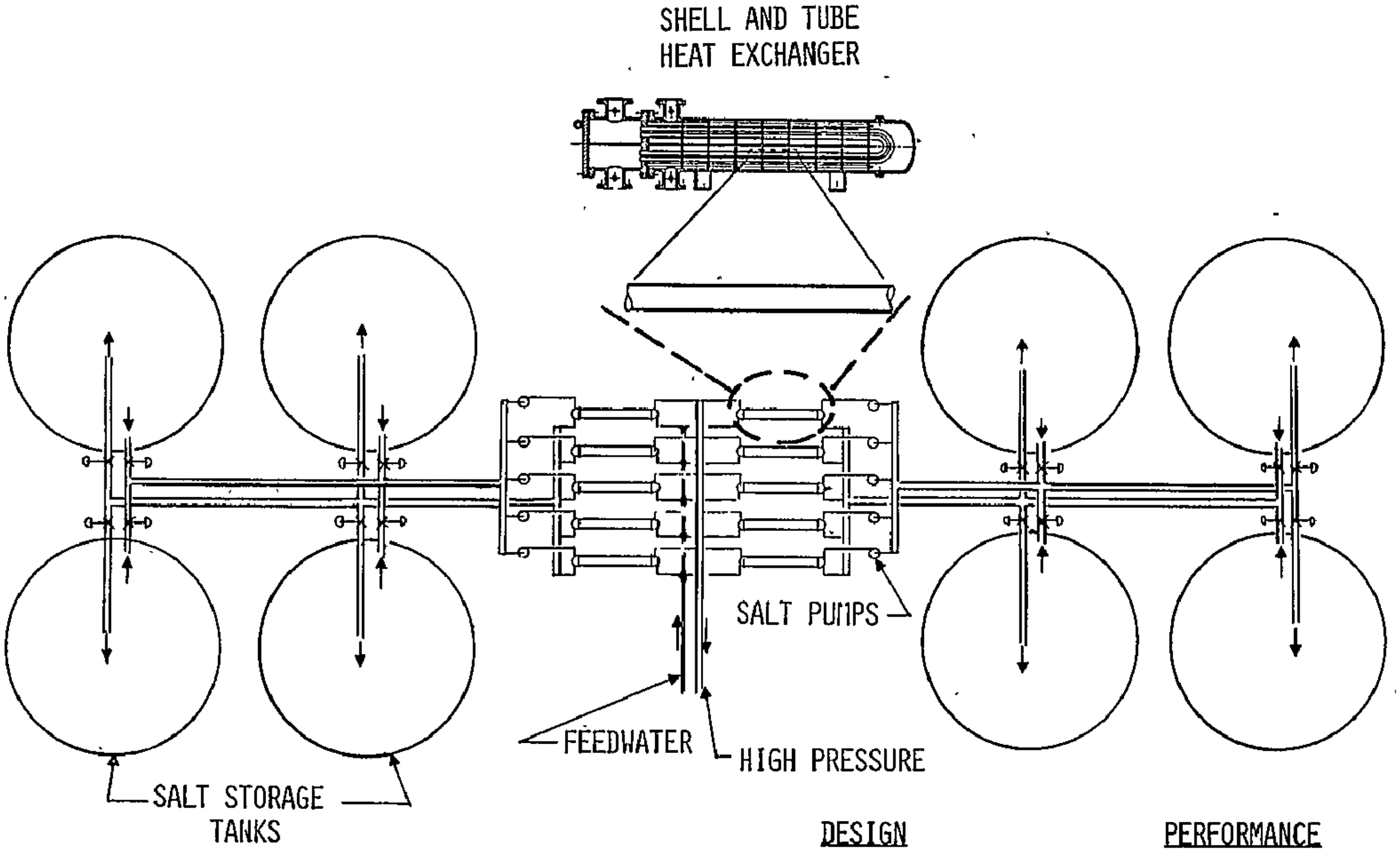
The subsequent sections discuss the candidates, the selection process and evaluations in more detail.

Table 2-1. Economic and Technical Evaluation of Heat Exchange Concepts

	HEAT EXTRACTION CONCEPT / EVALUATION PARAMETER	Ⓐ RATE RELATED COSTS	Ⓑ CAPACITY RELATED COSTS	Ⓒ NORMALIZED TOTAL CAPITAL COSTS	Ⓓ NORMALIZED TOTAL CAPITAL COSTS (W/O BOP)	Ⓔ TECHNICAL STATUS	Ⓕ EXPECTED OPERATING COSTS	Ⓖ EXPECTED MAINTENANCE COSTS
		$/ kWh(t)	$/ kWh(t)	DIMENSIONLESS	DIMENSIONLESS	CD AD ED	HIGH NORM. LOW	HIGH NORM. LOW
1	INTERNAL SURFACE SCRAPER	201	13	1.72	2.2	CD	H	H
2	EXTERNAL SURFACE SCRAPER	55	16	0.90	0.84	AD	H	H
3	SHELL AND COATED TUBE FLOWBY	45	13	0.77	0.62	ED	L	N
4	JET IMPINGEMENT	47	15	0.78	0.63	CD	N	H
5	REFLUX BOILER: SELF PRESSURIZING	50	13	0.80	0.66	CD	L	H
6	REFLUX BOILER: CONTINUOUS SALT FLOW	46	13	0.77	0.62	AD	N	N
7	REFLUX BOILER: OPEN SYSTEM	46	13	0.75	0.59	CD	N	L
8	TUMBLING ABRASIVE	58	13	0.85	0.74	CD	H	H
9	PASSIVE TUBE INTENSIVE (REF)	94	27	1.00	1.00	ED	N	L

CD = CONCEPTUAL DEVELOPMENT (5-10 YEARS)
AD = ADVANCED DEVELOPMENT (3-5 YEARS)
ED = ENGINEERING DEVELOPMENT (2-3 YEARS)
H = HIGH
N = NORMAL
L = LOW

BOP = BALANCE OF PLANT (OTHER THAN TANKAGE, HEAT EXCHANGE, MANIFOLD AND SALT COSTS)



DESIGN

TANKS - 8
H.E. UNITS - 10
CAPACITY - 6000 MWh(t)

PERFORMANCE

RATE - 1000 MW(t)
DURATION - 6 HOURS

Figure 2-4. Overall Concept Mechanization for Shell and Tube Exchanger

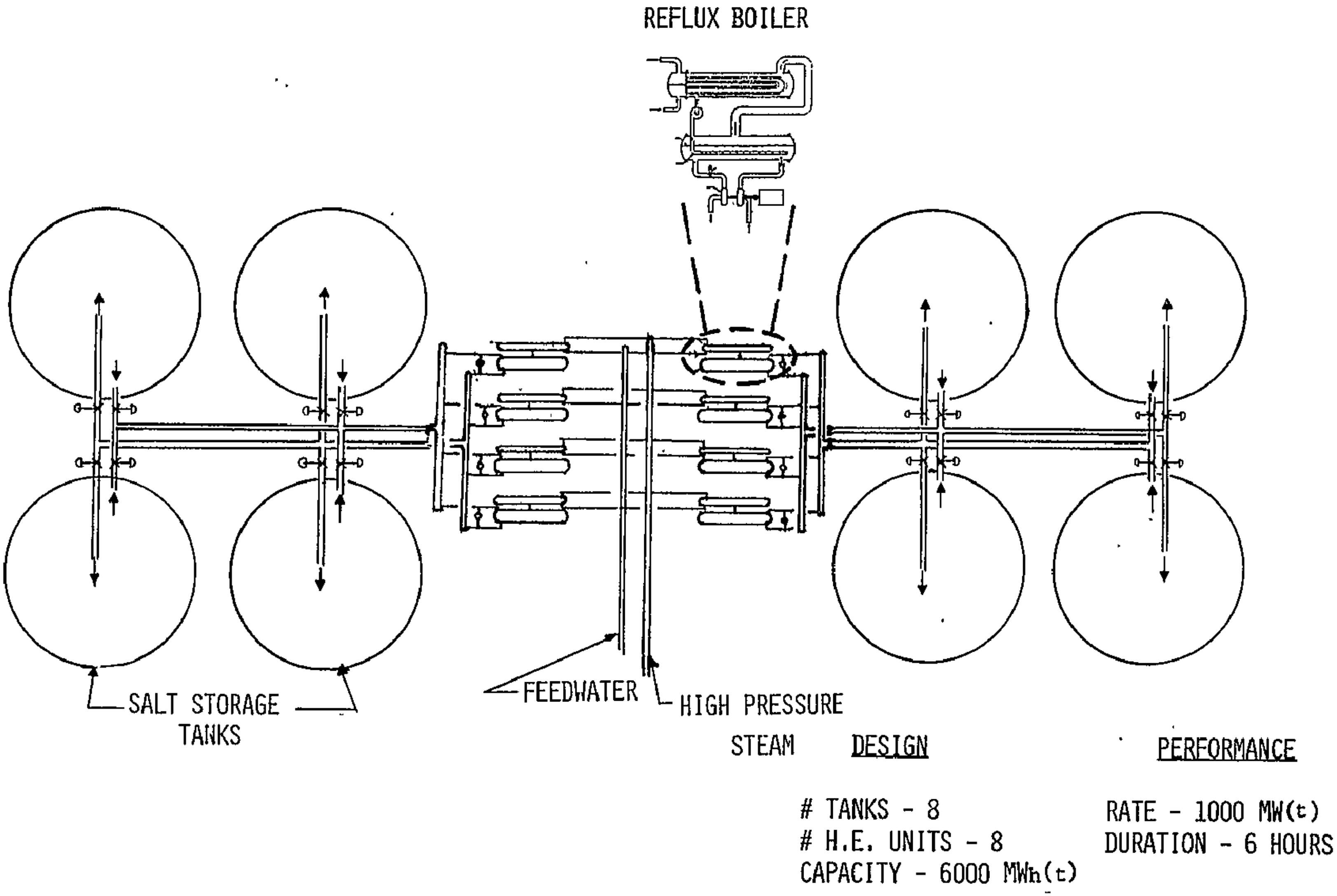


Figure 2-5. Overall Concept Mechanization for Reflux Boiler

SECTION 3.0
CONCEPTS SELECTION

3.1 GENERAL SYSTEM APPLICATIONS AND REQUIREMENTS

Thermal energy storage is important for efficient use of energy resources. Advanced storage technologies can improve the operation and economics of electric power systems by storing excess off-peak energy for later use in meeting peak demands.

In electric utilities, base load is the round-the-clock load that is met with the most fuel efficient equipment. As the daily load increases, the utility incrementally brings the next most efficient equipment on line. For the near term[2], energy storage can effectively increase the utilization of existing baseload equipment. In the longer term, energy storage can increase the percentage of baseload capacity. Thus, there is an economic incentive for utilities to use baseload plants to meet the peaking loads now met by less fuel efficient equipment.

Energy storage is a practical necessity for solar-thermal generation of electric power. It is necessary for plant stability and control issues related to high-frequency solar transients. Two techniques[3] maintain the reliability of the grid with a large solar plant on the line. The solar plant can be backed up with a conventional plant that is pressed into service as needed after available instantaneous solar power has been supplied to the grid. The second method controls the delivery of power to the grid so that the collected energy can be stored when it is available and not needed to meet grid demand. This stored energy becomes available for electric generation when the demand is high and direct insolation is not available.

For these applications, the specific operating conditions and machinery typically used in power plants needs to be considered. The operational regime of conventional turbomachinery is shown in Figure 3-1. In Figure 3-2, operating conditions for current and advanced solar power plants and for utility systems are shown on a steam enthalpy diagram. Here, the turbine pressures are shown with corresponding entry flow temperatures. Notice that most of the steam power plants operate within a band of 4.1 MPa to 16.5 MPa (600 psia to 2400 psia); the saturation temperatures corresponding to these pressures are between 250° and 350°C.

Heat from storage is used to boil water and provide high temperature steam to the plant. To provide steam at 250° to 350°C heat should be stored at a temperature greater than the desired steam temperature. With an assumed temperature drop of 18 C°, the useful temperature range for storage media is from 268° to 368°C. Salts with melting points up to 400°C were thus considered in the media selection.

Media for various steam turbine cycles are shown in Figure 3-3. A temperature difference of at least 18 C° each was allowed for heat transfer from charge steam to salt and from salt to discharge steam. Only standard steam turbine cycles were considered.

3.2 SURVEY OF CONCEPTS

A candidate heat exchange concept applicable to latent heat thermal storage units must be capable of transferring heat from a source into the frozen media causing it to melt. Likewise, the concept must be capable of transferring the thermal energy stored in the media to a sink while the media undergoes a solidification process. In both cases, the concept should permit relatively high heat transfer rates while undergoing the phase changes.

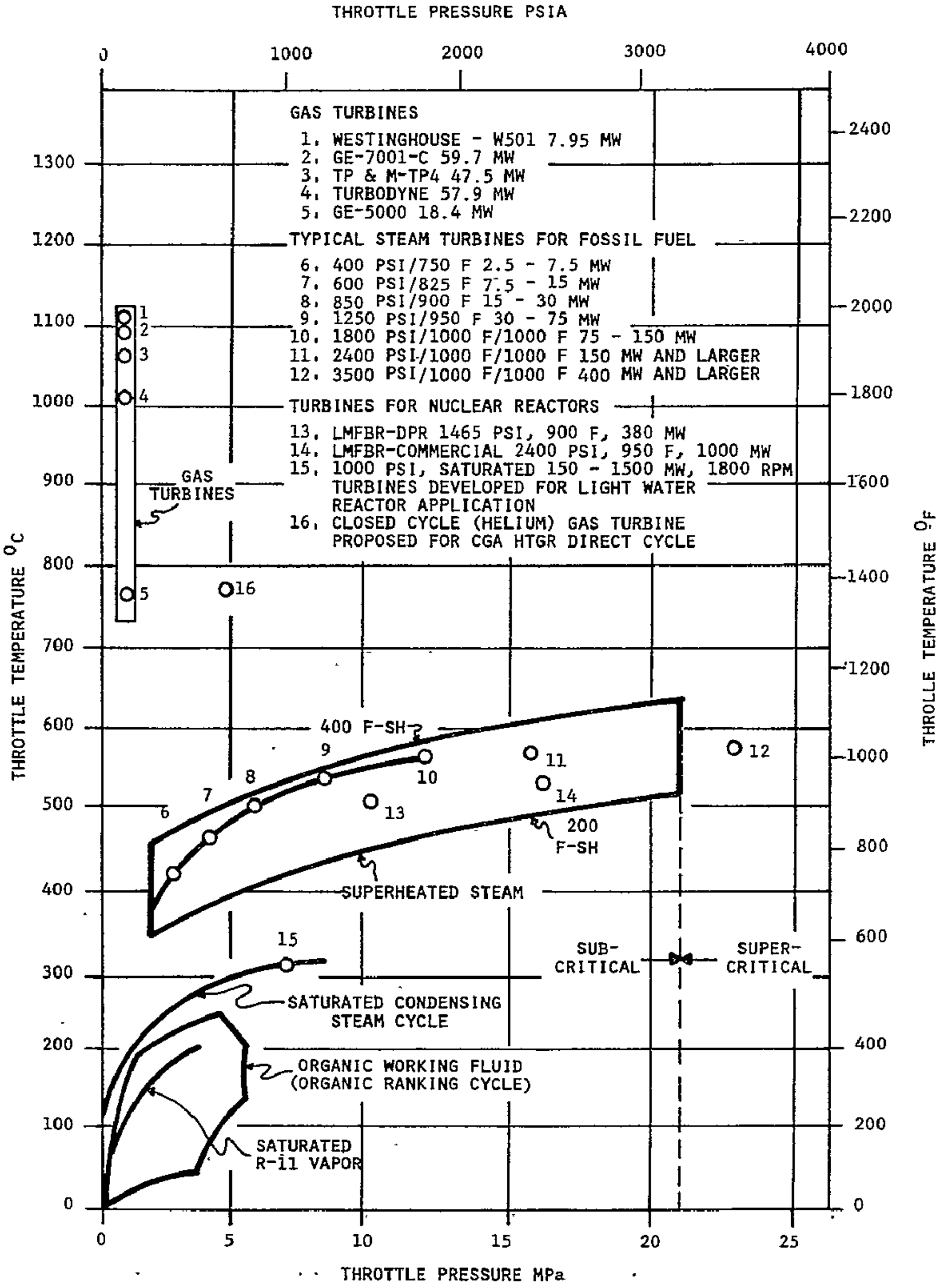


Figure 3-1. Temperature and Pressure Regime of Conventional Turbomachinery

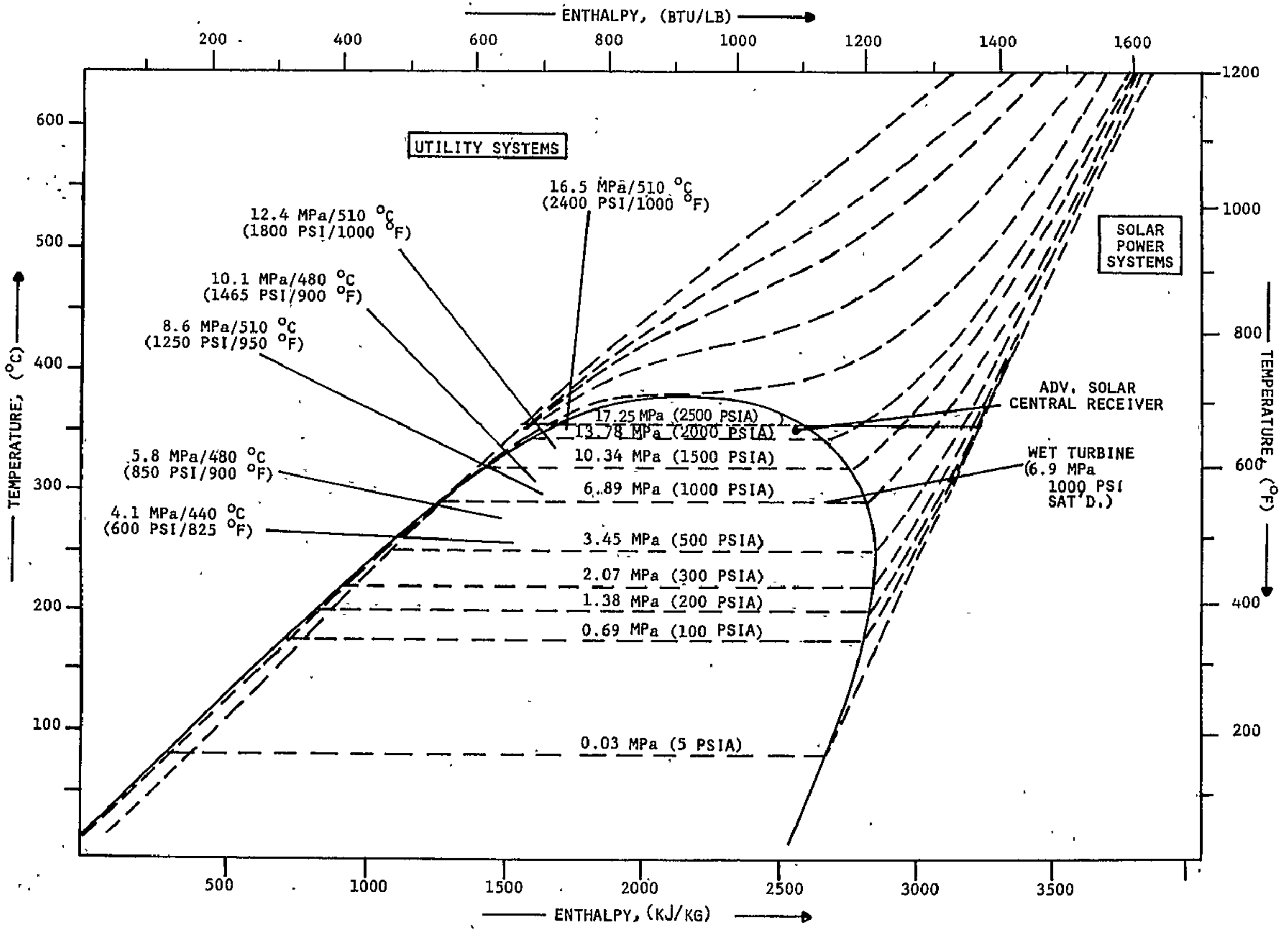


Figure 3-2. Power System Cycles

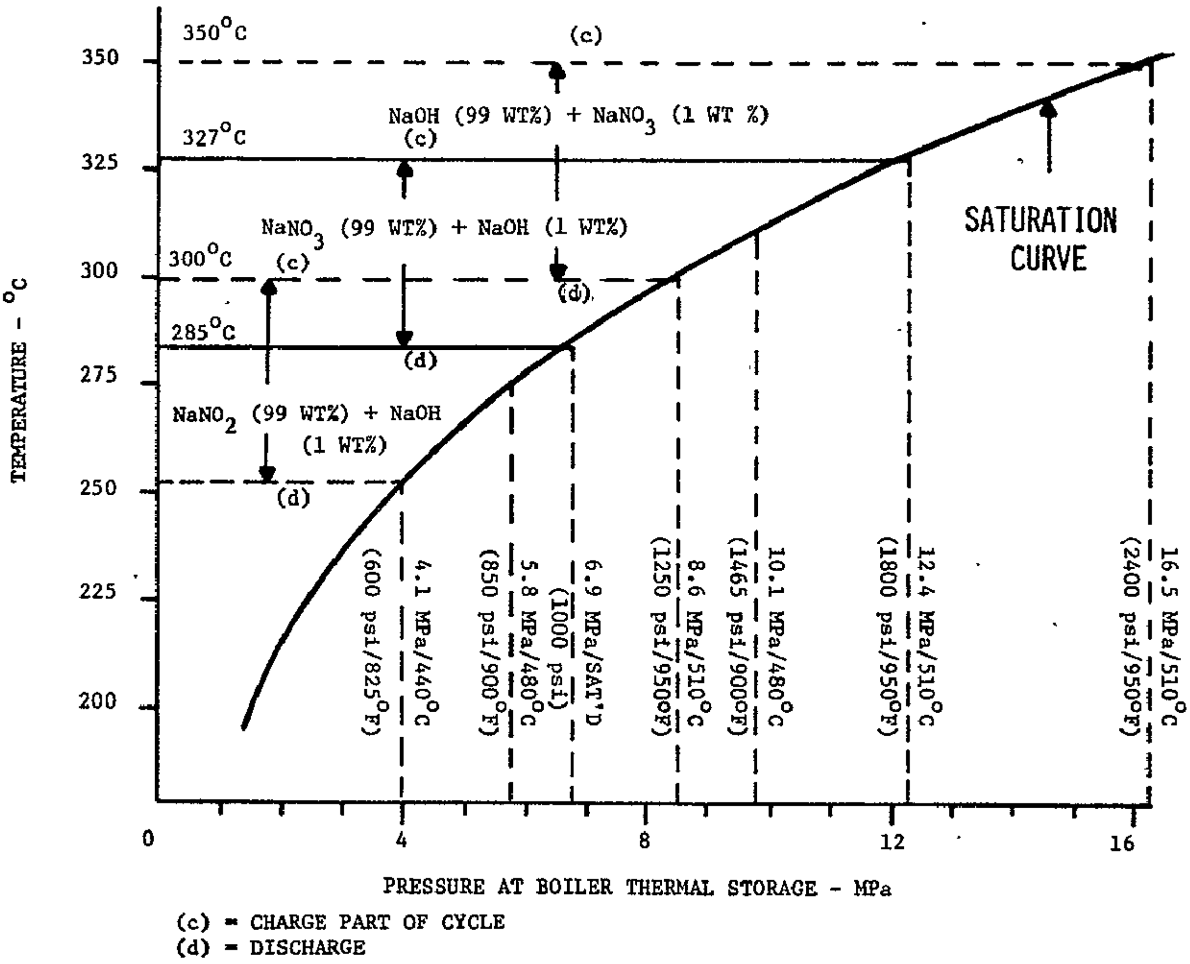


Figure 3-3. Standard Steam Cycles

Because of Honeywell's experience using inorganic salts with active heat exchange devices, a dilute eutectic media was used as a basis in formulating candidate concepts. Experience in working with dilute eutectic media indicates that the charging or melting process is not a critical issue. Solidification from the melt is the major problem that any concept mechanization must address.

A survey of heat transfer and chemical processing literature was made to determine the equipment used industrially and the chemical and physical processes exploited in extracting the latent heat of fusion from a melt. An investigation of crystallization processes was performed to determine if existing industrial methods might be directly applicable to or provide new ideas for latent heat thermal storage design. The types of crystallization methods used industrially are listed below:

- crystallization through cooling,
- crystallization through evaporation,
- salting out with a common ion or second solvent that reduces the solubility of the crystallizing substance,
- crystallization involving chemical reaction.

In industrial crystallization processes, major concerns are good product quality and low cost. With this in mind, crystallization industries can utilize the most feasible of the above methods for a design base. Since Honeywell's interest lies in the recovery of heat stored in molten salts, consideration is given only to crystallization processes involving cooling. From other process methods, however, it is obvious that certain physical properties of the salt system might be taken advantage of in making the heat exchange processing easier and more efficient.

The literature is limited in coverage of cooling heat-exchanger crystallizers since this approach has often been disregarded in favor of alternatives. The major design and operating problem of a cooling crystallizer is crystal deposits on the heat exchanger tubes. Once this takes place, the accumulation can increase rapidly, and not only does the heat transfer from the melt decrease dramatically, but the solids are not in a mobile form for pumping. The following section presents a summary of methods used in the past and recent innovative ideas put forth by Honeywell engineers to overcome the solid film buildup problem.

3.2.1 Mechanical Solids Removal Techniques

Agitation--The simplest means of attempting to control solid deposition is by agitating the melt solution as it is cooled. The agitation lifts crystals that have been formed so they re-enter the solution to grow in free suspension. The trend toward increased use of mechanically aided heat transfer was followed by the development of more efficient machinery.

Most available data on agitators are for vertical shaft units used for batch operations. These units are subclassified by the impeller type, with the least complex being the simple anchor agitator. More complicated designs include the helical ribbon agitator, with either a single or double helical impeller blade, and the double motion scraper agitator that has agitators rotating in opposite directions to scraper blades. Horizontal shaft units also exist for continuous operations. Two such agitated units are the Swenson-Walker Crystallizer and the Workspoor Disc Crystallizer, shown in Figures 3-4 and 3-5. Both units operate counter-currently and have the same disadvantage, i.e., the temperature difference between cooling fluid and salt must be kept low to keep encrustation to a minimum. For energy storage purposes, these temperature differences should be high to achieve a good heat flux. Another disadvantage is that such devices tend to be expensive due to the many moving mechanical parts and auxiliaries such as rotating seals, complex fittings, etc.

Vibration--Another concept in solids removal is the mechanical vibration of the cooling surface to shake off the encrusted layer.

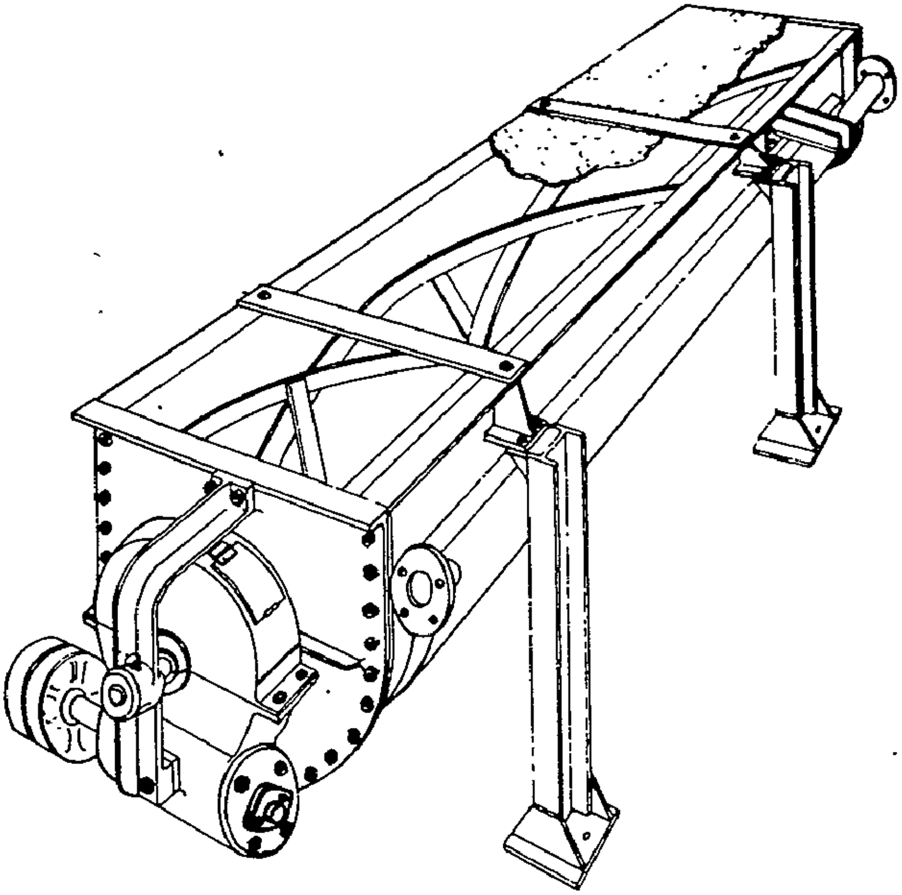


Figure 3-4. Swenson-Walker Crystallizer

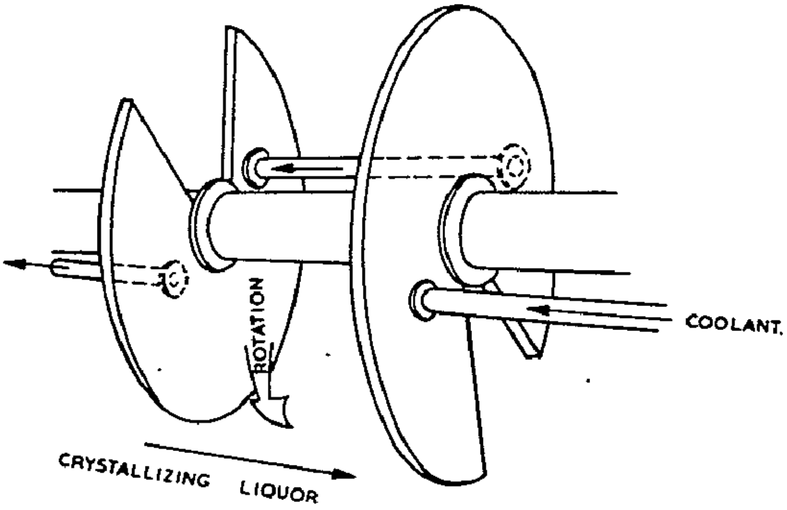
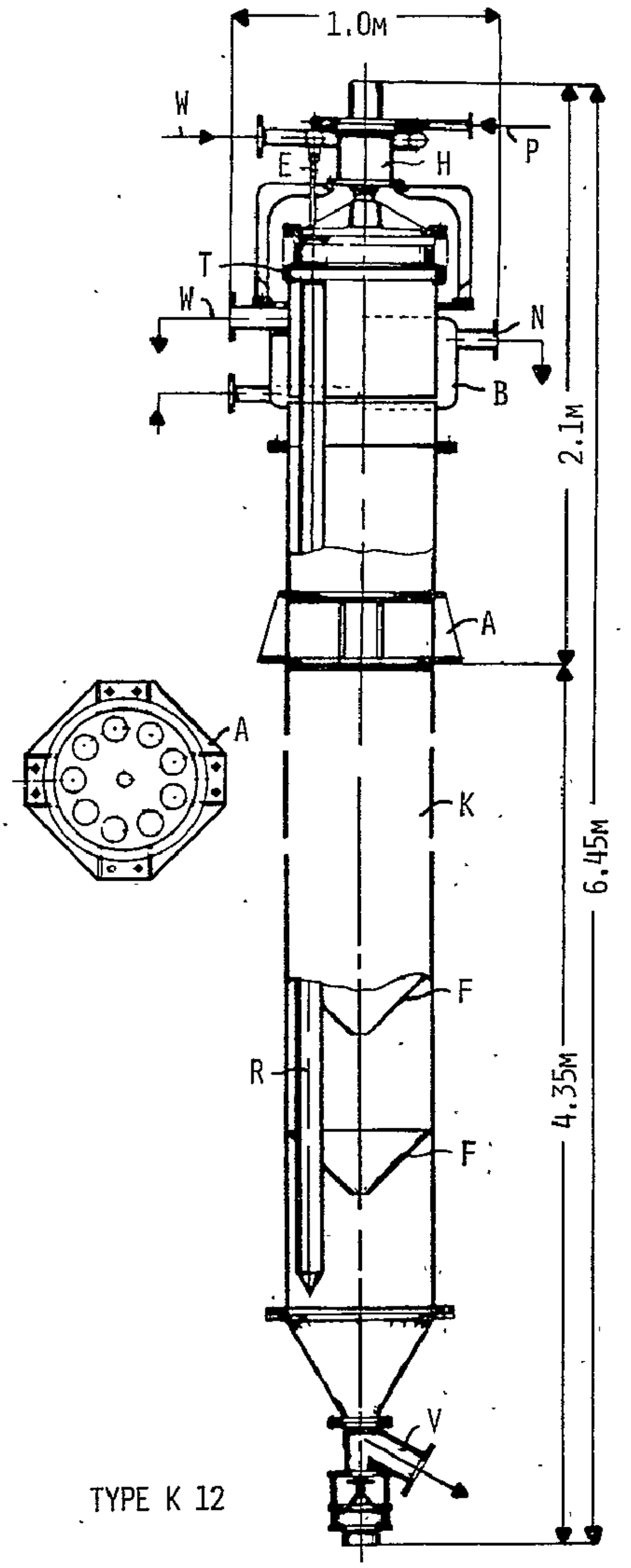


Figure 3-5. Workspoor Disc Crystallizer

The Zdansky-Giovanola Pulsing Crystallizer[4] (Figure 3-6) consists of a cylinder in which a system of cooling tubes is vibrated by means of a pneumatic hammer The oscillations favor nucleation in the melt and supply further nuclei as crystals are sheared off with each stroke of the hammer. This requires that the cooling tubes remain highly polished at all times. This apparatus has been successfully used for the production of dicyandiamide, amino-caprylic acid, fumaric acid, monochloric acetic acid, dinitronaphalate, barium chloride and borax. Units with cooling surfaces of between 1.75 and 240.0 m^2 have been designed for industrial use, with overall heat transfer coefficients of 0.23 to 0.35 kW/m^2 and higher. The combination of highly polished cooling surfaces, vibration, and controlled conditions for crystallization give long continuous operating periods, although a weekly wash-out is recommended by the manufacturer. These concepts of vibration and polishing may have merit in active heat exchange concept mechanizations.

Ultrasonics--Conventional agitators, such as those described above, cannot focus enough intense agitation at the heat transfer surface to completely eliminate crystal deposition. High frequency sonic waves in the salt media may offer an improvement over conventional agitation methods, but only a small proportion of the energy actually reaches the heat transfer surface. Direct coupling the ultrasonic transducers to the heat transfer surface has proved much more effective in discouraging deposition by causing intense agitation of surrounding liquid boundary layer[5]. This technique is still in the developmental stage and may only be applicable in small to medium size crystallizers due to the large driving power requirements. It has been successfully adapted to many systems on the laboratory scale and to one full size industrial application.

Internal Scrapers--Mechanical blades may be mounted on a rotating shaft to remove material freezing on the inner walls of a tubular heat exchanger. The mechanically induced turbulence in the equipment makes it possible to handle highly viscous liquids and slurries while maintaining moderately high transfer



A	Vessel Supports
B	Annular space for distribution of the incoming feed liquor
F	Perforated conical baffles
H	Hammer operated by an impulse generator driven by compressed air
K	Crystallizer body
N	Overflow to maintain constant liquor level
P	Compressed air inlet.
R	Cooling tubes
T	Head piece which is vibrated by hammer H
V	Impulse valve operated by compressed air
W	Cooling water inlet

Figure 3-6. Zdansky-Giovanola Pulsing Crystallizer

coefficients. Available data indicate that intense scraper-mixer devices, such as the Helicone and other intermeshing blade batch units, should provide a heat transfer coefficient several times that attainable for simple agitators. The Armstrong unit shown in Figure 3-7 has been used widely in industry, and although there may be some problems associated with the shock cooling and violent agitation producing very fine crystals, it has been considered a worthwhile system to analyze further. Aside from the more typical fixed close-clearance scraper blade design, Armstrong has also designed spring loaded scrapers for the crystallization of high melting point organics and the cooling of viscous fluids. Another scraped tube device that has been used for decades in food, pharmaceutical and chemical processing industries is the Votator. Figure 3-8 shows blade designs of Votator units for various applications. R. Albertins, W.C. Gates and J.E. Powers[6] describe column crystallizers wherein crystals are scraped and conveyed by means of screws, helices, and solid or porous pistons in the freezing section.

External Scrapers--Various design and performance aspects of rotary drum crystallizers are described by J.C. Chaty[7]. Basically, these crystallizers consist of a horizontally mounted hollow cylinder that is partially immersed in the melt with the cooling medium entering and leaving the inside of the cylinder through hollow trunnions. As the cylinder rotates, crystals that have formed on the immersed portion of the cylinder emerge from the melt as a crystalline cake. The cake is mechanically removed by a suitable device, such as a doctor knife. This concept can be traced back to the early 1940's. Graham[8] patented a dual drum crystallizer of this type. The second drum, mounted above the first, served to remove occluded liquid and to provide a refluxing action.

The investigation of external scraping has been performed in experimental work by Honeywell for the 99% $NaNO_3$/1% NaOH system. Similar in function to the internal scrapers described above, the external concept uses elliptical blades on the outside of the circular heat transfer tubes (see Figure 3-9). The

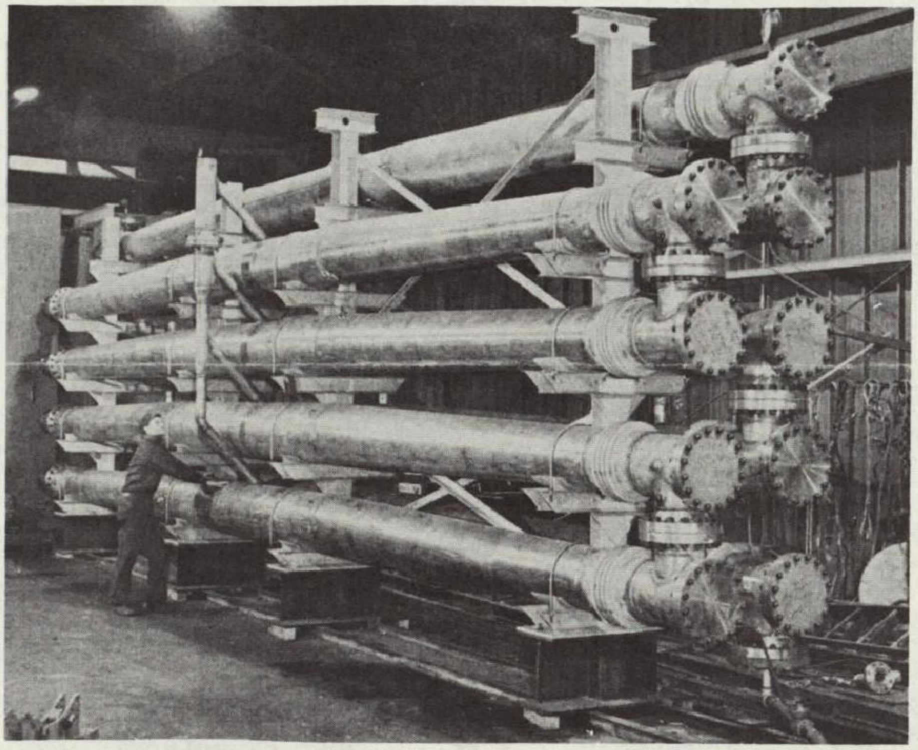


Figure 3-7. Armstrong Dewaxing Exchanger

VOTATOR SCRAPED SURFACE HEAT EXCHANGER BLADE AND TUBE SYSTEMS					
	CONCENTRIC FLOATING BLADES	**CONCENTRIC FIXED BLADES**	**ECCENTRIC FLOATING BLADES**	**OVAL TUBE FLOATING BLADES**	**CONCENTRIC SPRING LOADED BLADES**
General Applications	Heating or cooling heat-sensitive, fouling and/or viscous foods or chemicals. Temperature range—100 to 500°F.	Heating or cooling at high temperatures. Also processing where direct blade contact is prohibited.	Cooling sticky or viscous products.	Cooling unusually viscous products, or extruded products.	Industrial heat transfer applications; 24 hr/day extended service.
Viscosity Range, Centipoises	to 100,000	to 200,000	to 300,000	to 1,000,000	to 100,000
Shaft RPM	100 - 500	100 - 300	50 - 300	20 - 100	10 - 100
Overall Coefficient Range	200 - 600	50 - 200	50 - 400	50 - 200	25 - 200

Figure 3-8. Votator Application Data

Figure 3-9 Close-up View of Bottom of Vaporizer Module Showing Total Scraper

scraper blades are held in place by a series of ribs forming an open cage structure that admits salt to the transfer tubes and permits frozen salt crystals to fall away. This concept has been mechanized by Honeywell in a Storage Subsystem Research Experiment under the Solar Pilot Plant Program[1].

Flexing Surfaces--Similar in concept to the vibration of the heat transfer surface for effective solids removal, a flexible surface would allow crystals to be broken off after solidification occurs. The material and code requirements for such a flexible surface in this application precludes serious considerations.

Tumbling Solids--The effect of tumbling abrasive solids is considered an alternative to processes involving complex mechanical parts. Abrasive inert solids can tumble through a high-velocity or turbulent flow and impinge upon the heat transfer walls with enough force to crack off pieces of solidified material. The relative development risk, cost and heat transfer improvement for a tumbling solids shell and tube exchanger unit needs to be determined and compared with the unaided shell and tube design.

Fluidized Beds--A large heat transfer surface area and a more uniform means of heat transfer to all points in the melt can be accomplished in a fluidized bed heat exchanger. Here, the fluidized bed would be made of inert and thermally conductive solids which, in their collisions with each other and with the heat exchanger surfaces, have an abrasive effect on the solids depositing on the surfaces. In any such installation, adequate provisions must be made for minimizing the bed abrasion of the heat exchange surfaces and the containment vessel walls. Also, the coverage and subsequent growth of deposits on the solids in the bed may be troublesome if they settle and aggregate toward the bottom of the bed.

3.2.2 Hydraulic Techniques

Flow Variations--It may be possible in part to counteract the growth of crystals on heat exchange surfaces by a suitable choice of flow velocities and patterns.

Although this may be helpful in conjunction with some other method, it is not expected that flow variations alone will suffice in maintaining a clean heat transfer surface when operating with a large ΔT. (See Figure 3-10).

Fluid Pulsing--The concept of a pulse pump in the output stream has been found helpful in aiding crystal slurry movement and reflux in several processes. D.L. McKay[9] described the Phillip's fractional solidification process that includes the use of a scraped surface chiller to form a crystal slurry and pulsed hydraulic units to insure continuous movement of the solid crystals through the system.

In another process, Thomas[10] used an end-fed column crystallizer with a pulsating back pressure applied to the contents of the purification section of a column crystallizer by means of a reciprocating piston.

Jet Impingement--By using extremely high velocities in the flow of the melt past the heat exchange surfaces, accumulating solids may be transported away from the surface. In such a case, not only does the melt have a very short residence time at the surface, but the forces of impingement of the liquid salt could be great enough to break off solids that may have been deposited previously. (See Figure 3-11).

Sprayed Surface Exchanger--A method used industrially in making powders is that of a sprayed surface exchanger. It is not expected that this method would be effective unless used with super smooth surfaces that would prevent adhesion and accumulation of solids on the heat transfer surfaces.

Freeze-Thaw--A freeze-thaw operation would use two cooling elements operated alternately. Crystals are allowed to accumulate upon one element until the heat transfer rate falls to a predetermined value. The cooling fluid is then directed to the second element while the first is heated internally with steam. As the temperature of the first element rises, the crystals attached to it drop

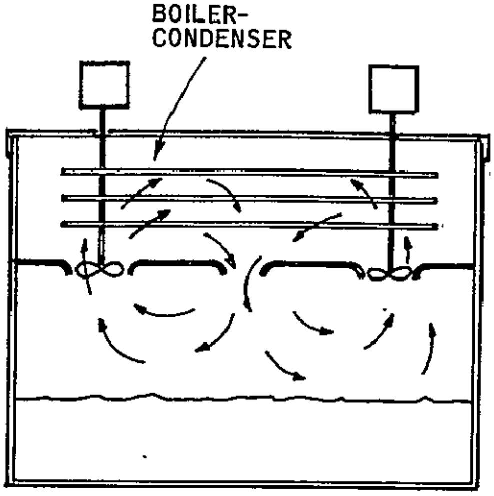


Figure 3-10. Mass Flow Salt Removal

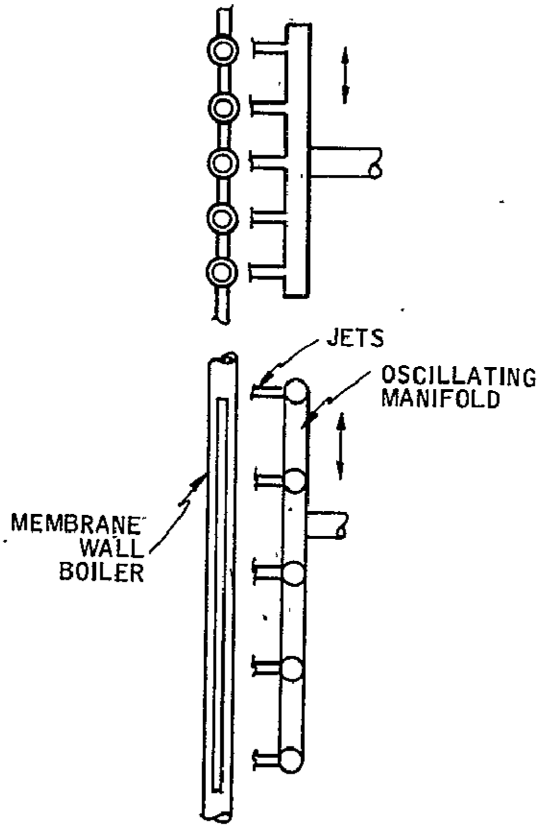


Figure 3-11. Jet Impingement Salt Removal

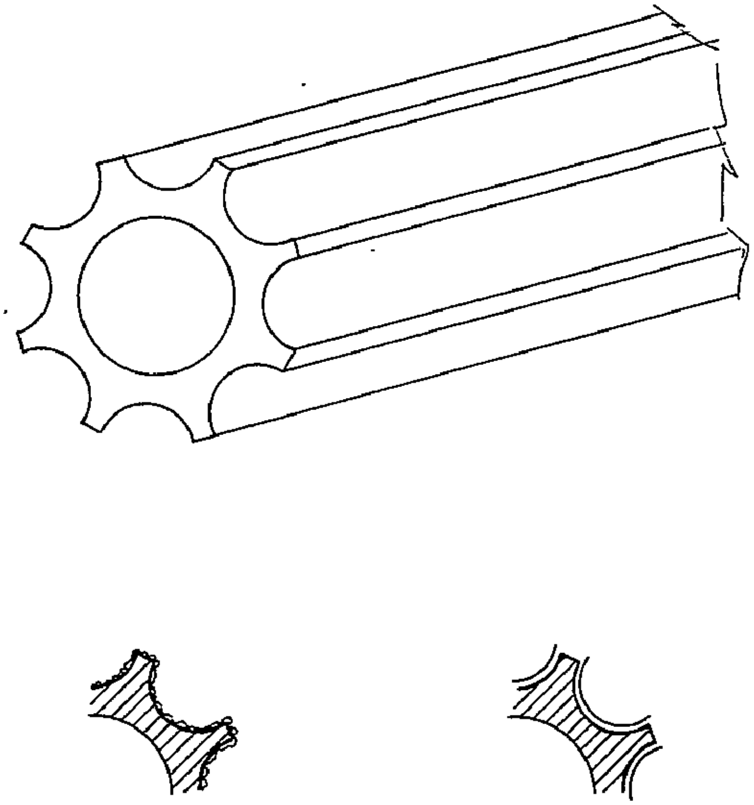
off. By this time, the second element has become encrusted and the cycle is repeated. Although this concept sounds attractive, it may be costly to operate since heat must be added to remelt the crystals.

3.2.3 Techniques Involving Physical Properties of the Salt

Crystal Volume Change--When most salts freeze, they contract in volume. If allowed to freeze on polished concave surfaces with sufficiently small radii, the crystals could possibly be self-removing with a low level of liquid turbulence (see Figure 3-12). Temperature cycling in the heat exchange fluid might be used to assist in salt removal. A critical issue is whether the freezing would occur quickly enough so that the solid can fall away from the surface before the gap between it and the surface is bridged with fresh crystal formation.

Crystal Weakening Additives--Small amounts of materials may be added to molten salts to modify their crystal habits. Such changes may lead to the formation of rather brittle, needle-like or plate-like crystals. By proper additions the bonds between crystals can be made weak and easily breakable. This can be a useful property in terms of the ease with which the solids can be scraped free from the exchanger surface. A similar technique has been used in shipping industrial salt crystals. By spraying these crystals with appropriate agents, they may be kept from aggregating into one large immovable bulk in transport.

Conductivity Enhancing Additives--In a recent report issued by IGT[11], the results of experiments done on salt conductivity promoters are presented. These promoters consist of stainless steel screens and wools and aluminum honeycombs attached to the heat exchanger tubes and extending outward into the bulk of the salt solution. The tests indicated that with 3 volume percent of these conductivity promoters an increase in heat flux of about 20 percent is attained. Similar results were found for finned-tube heat exchanger units. Aluminum wool



A) LIQUID SALT WETS CONTOURED SURFACE.

B) SALT CONTRACTION UPON FREEZING CAUSES A GAP TO FORM BETWEEN SALT AND CONTOUR SURFACE.

Figure 3-12. Contour Effect Salt Removal Concept

was found to be the most cost effective and promising to IGT. The effect of dispersed inert particles on conductivity enhancement in the crystalline phase was not tested by IGT since it was previously shown not to provide significant changes.

Magnetic Susceptibility--A salt having a solid magnetic phase would permit the use of magnetic field to augment separation of solid crystals from the liquid. This would improve concentration of the slurry for higher energy recovery and would increase exchanger surface heat transfer by decreasing the percentage of solids in the immediate vicinity of the heat transfer surface. To date, only one magnetic salt, $FeCl_3$, has been identified in the applicable temperature range. It is not a candidate for further study due to problems with hydrochloric acid formation when exposed to water vapor.

Electrostatic Separation--Electrostatic separation of particles suspended in a fluid requires that a charge be imparted to the particle and that the charge remain on the particle sufficiently long for the particle to be drawn to a neutralizing surface. All molten salts so far identified are electrically conducting; therefore, any electrical charge imparted to the salt crystals will be conducted away through the liquid. Until a molten salt with a high dielectric strength is found, electrostatic separation of solid and liquid phases is not practicable.

Finishing and Coating of Heat Exchanger Surfaces--There are numerous applications in the chemical process industries where finishes and coatings are used to provide anti-stick and release properties for interfacing with the process media. Any coating and/or finish for heat of fusion thermal storage applications should provide a smooth, thin, nonporous, nonreactive surface to discourage firm adherence of the freezing salt to the heat exchanger wall. The heat transfer should not be limited by this film. Surface morphology should minimize nucleation sites for the crystallizing medium. Any coating should be stable at the operating temperatures of the storage medium and should perform for an industrial lifetime. In addition, the coating should show promise of large scale use at reasonable costs.

Materials stick due to mechanical, chemical, electrical and/or magnetic forces between the contacting species. Materials such as teflon and halar are noted for their nonstick and good release qualities. This is primarily due to the chemical inertness of these fluoroplastics. Highly polished metallic surfaces have been used in crystallizers for years to minimize adherence. From the above, it appears that a chemically inert polished surface should be anti-adhesive. A high electrical resistance across the surface may also be helpful. Furthermore, dissimilar crystallography between the coating or tube surface material and the solidifying storage media would be desirable. This would minimize geometric-mechanical bonding. An electroless nickel plating, for example, provides a smooth, amorphous structure on the tube to interface with a crystal solidifying from the storage melt. This concept will be very promising if candidate materials and finishes can be found to survive the storage media environment.

Delayed Nucleation and Supercooling--Freezing requires nucleation sites, and these are usually found in imperfections or rough areas on heat transfer surfaces. Foreign particles in a solution provide such nuclei for crystallization. In many industrial processes, solutions are seeded with other inert ingredients to obtain a uniform product. Such an addition to the melt might help to provide nucleation centers away from the surface; however, it is difficult to say whether these impurities will have any adverse effects. Generating crystals in the melt by the addition of these nucleating agents might be especially effective if the solution could first be supercooled. Supercooling is difficult since any disturbance, such as fluid motion, may remove the system from the unstable supercooled state to one where crystallization is initiated.

3.2.4 Direct Contact Heat Exchange

If the heat transfer fluid (HTF) is allowed to pass through the molten salt in direct contact, the problem of solids adhering to a heat transfer surface is completely avoided. Successful experiments have been carried out with an impinging jet method of direct contact crystallization where jets of cold calcium chloride brine and benzene were arranged so they converged. By adjusting the temperature of the brine and the relative flows of the brine and benzene, at least 95% of the benzene was crystallized while the mobility of the mixture was retained. Other examples of direct contact heat exchange are the shot tower process for making lead shot, and prilling tower crystallization processes for many salts.

Shot Tower Latent Heat of Fusion Concept--An interesting latent heat storage system with immiscible fluids has been suggested by Nichols and Green of Sandia Laboratories, Livermore, California[12]. The elements are a phase change material of the desired melting point, a heat transfer fluid (HTF) that is not miscible with the phase change material (PCM), and techniques for moving the solid material from one storage container to another. Briefly, loose or pelletized PCM is transferred mechanically into a vertically arrayed heat exchanger in which counterflowing heat transfer fluid melts the solid material. The liquid PCM is transferred by gravity into an insulated storage container. When heat is desired, the molten PCM is transferred into a second heat exchanger where it flows through orifices separating the liquid into fine streams. Counterflowing cool HTF absorbs energy from the freezing droplets passing in the opposite direction. The resulting particulate solid is mechanically returned to solid storage.

The system permits both charging and discharging without mechanical heat transfer surfaces. The heat is, of course, transferred from the PCM to another heat transfer fluid where it can be used in heating or cooling applications--generally through a heat exchanger. In this case, a single heat exchanger could be used for both discharging and charging storage. The system is adaptable to low pressures or unpressurized storage tanks since gravity flow is used for liquid transfer. The use of unpressurized storage tanks is very desirable from a cost standpoint.

Prilling Tower Crystallization--This concept has been utilized in many industrial chemical manufacturing processes. One such design, the Cerny Crystallizer, which has been used for the crystallization of calcium nitrate tetrahydrate, is shown in Figure 3-13. In most prilling tower crystallization processes, air is used as the heat transfer medium. The manufacture of sodium nitrate, depicted in Figure 3-14, is an example. In this process sodium hydroxide reacts with nitric acid to produce hot aqueous $NaNO_3$. This solution is injected directly onto the molten salt, where the water is evaporated. Molten salt is then pumped into a prilling tower for crystallization. This concept might be used for generating steam at high pressures if the phase change material could be pumped into pressure vessels and injected with continuously high pressure feed water. The solidified PCM could then be continuously removed as a pumpable slurry.

Liquid Metals/Salt System--Liquid metals have also been considered as direct contact heat exchange fluids due to very high rates of heat transfer. For materials such as liquid Na or K the cost associated with safe handling and containment would be high.

Immiscible Salts--A solution that is immiscible with the storage PCM may also be used to transfer heat. This solution can be allowed to come into contact with the heat exchanger tubes, and the melt acts as an intermediate in the heat exchange. The solution must have a lower melting point than the storage media so that it remains in the liquid phase during all operating procedures. Thus, the media is crystallizing away from the actual exchanger tubes at the interface between the two immiscible salt solutions. Although this avoids the problems of solids depositing on the heat exchanger tubes, it has been found that the salt-to-intermediate-fluid interface becomes blocked by crystal accumulation resulting in loss of heat transfer efficiency. (See Figure 3-15.)

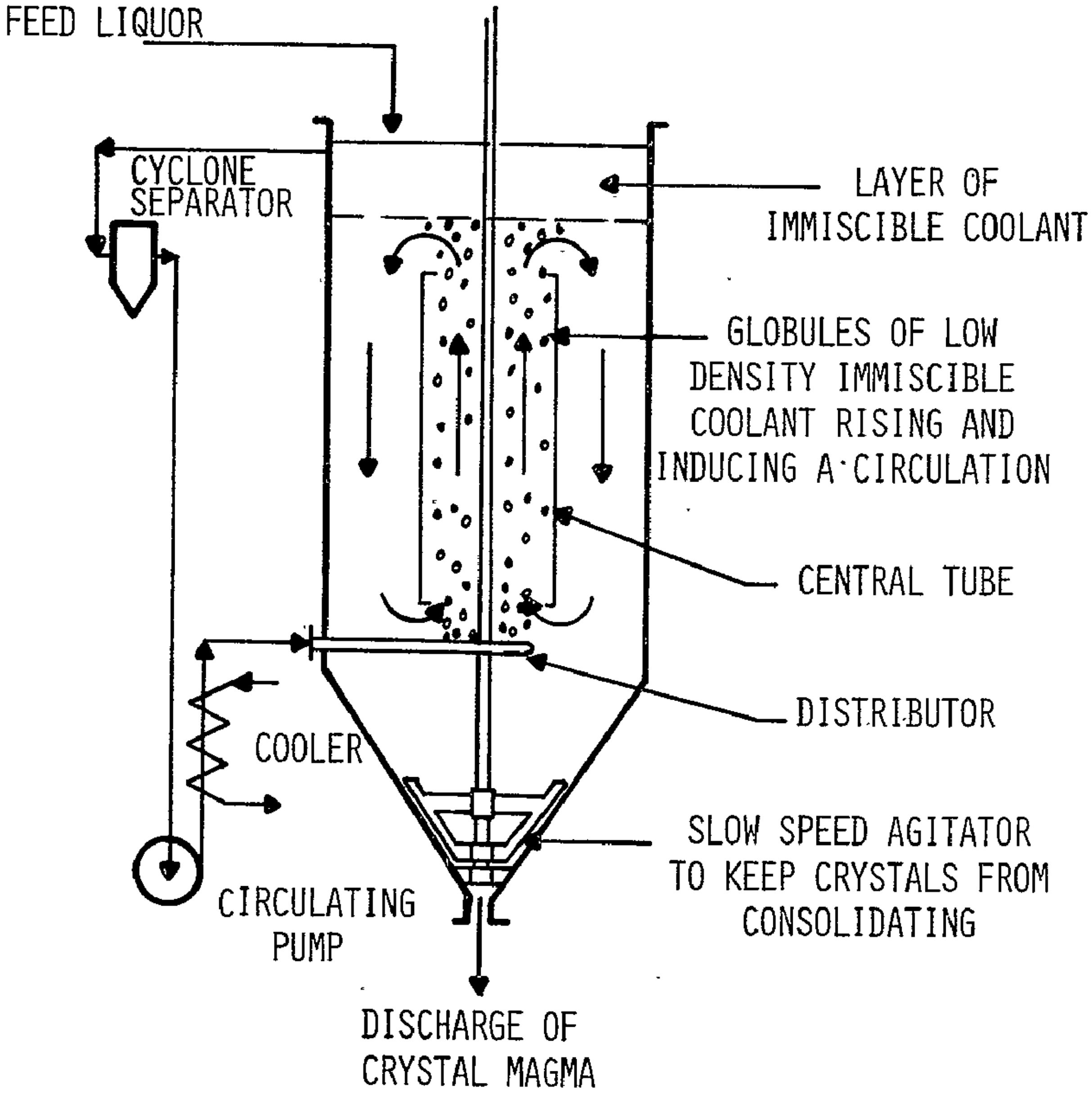


Figure 3-13. The Cerny Crystallizer

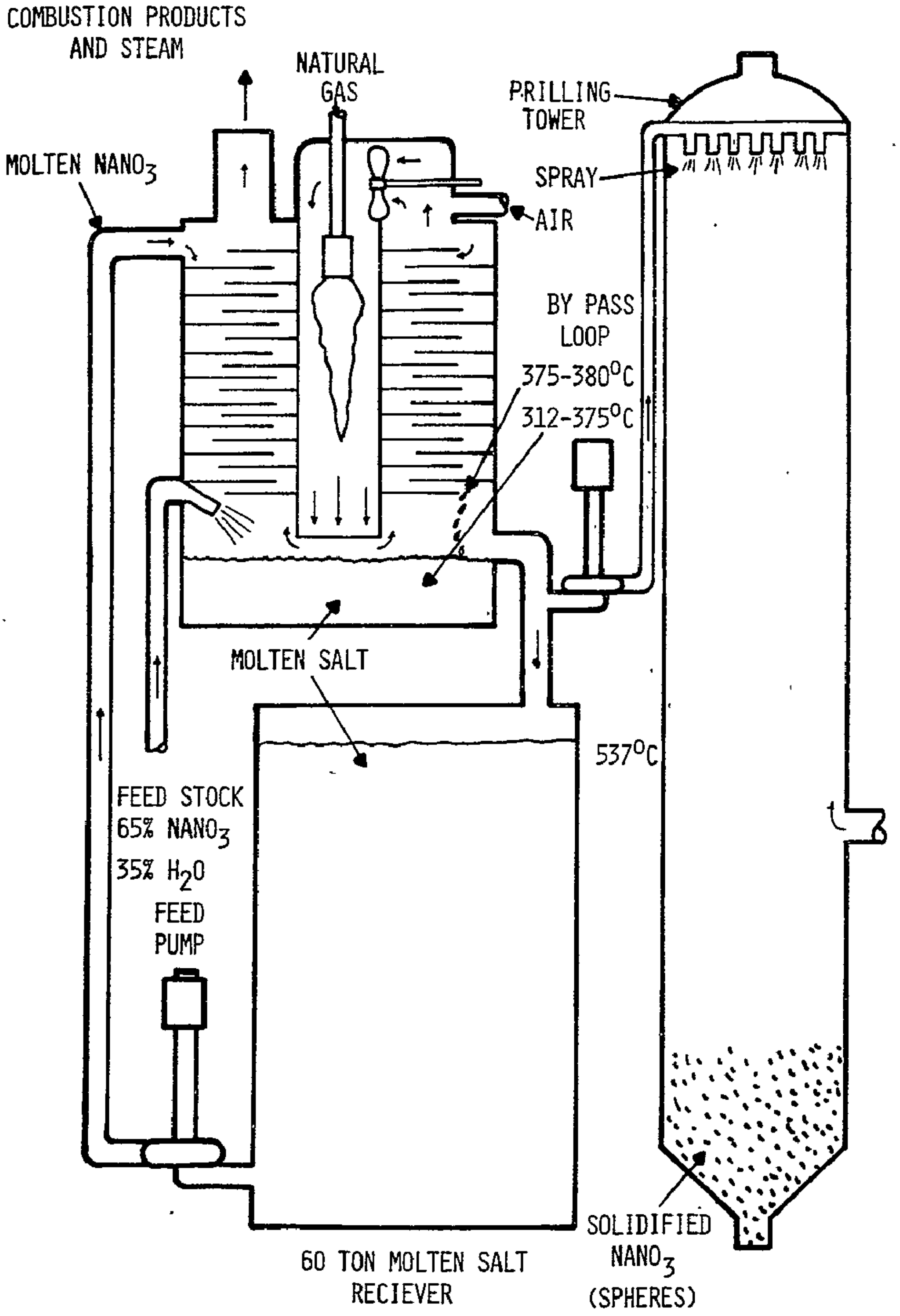
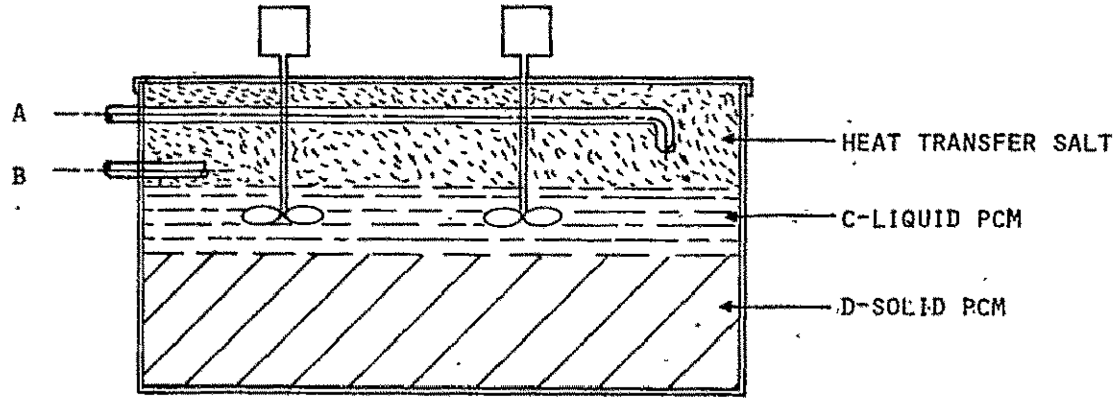


Figure 3-14. Sodium Nitrate Manufacturing Process



HEAT TRANSFER AFFECTED BY EITHER:

1) Pumping hot fluid through 'A' and heating salt layer 'C' above eutectic point. Impellers force hot 'C' down to melt 'D'.
2) Pumping cool fluid through 'A' heat is extracted from 'C' and impellers keep heat transfer rates high - solids fall to the bottom.

Figure 3-15. Immiscible Salt Heat Storage System

3.2.5 Other Concepts

Encapsulization--Molten salt contained inside heat exchanger tubes is allowed to crystallize via heat exchange with steam. Aside from the large heat transfer surface required, this design requires two pressure resistent surfaces (tube surface, containment vessel surface) since the steam is on the outside of the tubes. An alternative design would use an intermediate heat transfer fluid to transfer heat from the capsules to a shell and tube exchanger. This would require an extra heat exchange process and would have the additional temperature drop associated with it.

Distributed Tube Exchanger--This design is similar to that described above as it is a tube-intensive system that gives a large heat transfer surface. The difference here is that the steam is contained inside the exchanger tubes allowing for a lower cost design. The total heat transfer area must be large enough so the desired fraction of melt solidifies before the heat transfer coefficient drops too low to maintain the desired heat rate.

3.2.6 Concepts Chosen for Evaluation

From the survey and discussion of concepts given above, Honeywell selected the concepts listed below as candidates for further evaluation.

	1. Internal surface scraper
	2. External surface scraper
	3. Shell and tube flowby
	4. Jet Impingement
Direct Contact Heat Transfer	5. Reflux Boiler/self-pressurizing 6. Reflux Boiler/continuous salt flow 7. Reflux boiler/continuous salt flow with hydraulic head recovery
	8. Tumbling abrasive

These concepts embody the most conventional and promising heat transfer processes. The passive-tube intensive system was chosen as a reference system against which cost comparisons could be made.

SECTION 4.0
STORAGE MEDIA SELECTION

4.1 THERMAL ENERGY STORAGE SYSTEM COST EVALUATION FOR SALT SCREENING

Thermal energy storage (TES) system purchased cost will be the parameter in determining the usefulness of storage to utility and solar plants. A 1976 study on molten salt indicates that heat storage systems for utility applications should cost less than \$7-10/kWh(t)[11]. A recent study of molten salt heat exchange[13] indicates a nominal \$16/kWh(t) for a 900 MWh(t) capacity thermal storage for 6 hours of peaking capability. A 'should cost' versus capacity range could be determined if a study were done on the integration of TES into electric utility systems. A study on the value of solar generation to electric utilities has been carried out by J.W. Ballance[14].

Honeywell has developed a model to compare the capital costs of candidate TES systems. The model was based on build and detailed cost estimates for latent heat systems for the Solar Pilot Plant program. Figure 4-1 shows a logarithemic plot of storage installed cost as a function of storage capacity based on small-scale, SRE and pilot plant experience. The figure indicates that active heat exchange TES system costs on the order of \$20-\$30/kWh(t) are realizable by capacities of 500 MWh(t) and \$10-12/kWh(t) for capacities of 900 MWh(t) using Honeywell's current active heat exchange technology. The advanced concepts selected in this program 'should cost' less. The figure also shows that TES costs follow an exponential relationship. The cost exponent of the slope of the curve in Figure 4-1 was determined to be -0.34 and was used for scaling storage system costs for salt systems. The model is described in Appendix A.

TES system costs include the costs of storage media, containment, heat exchangers, circulation equipment for working fluid and storage medium, instrumentation and control, storage medium handling and support equipment, foundation and site preparation. For latent heat systems, the energy density of the salt, which includes its heat of fusion will determine system size. Storage in high energy

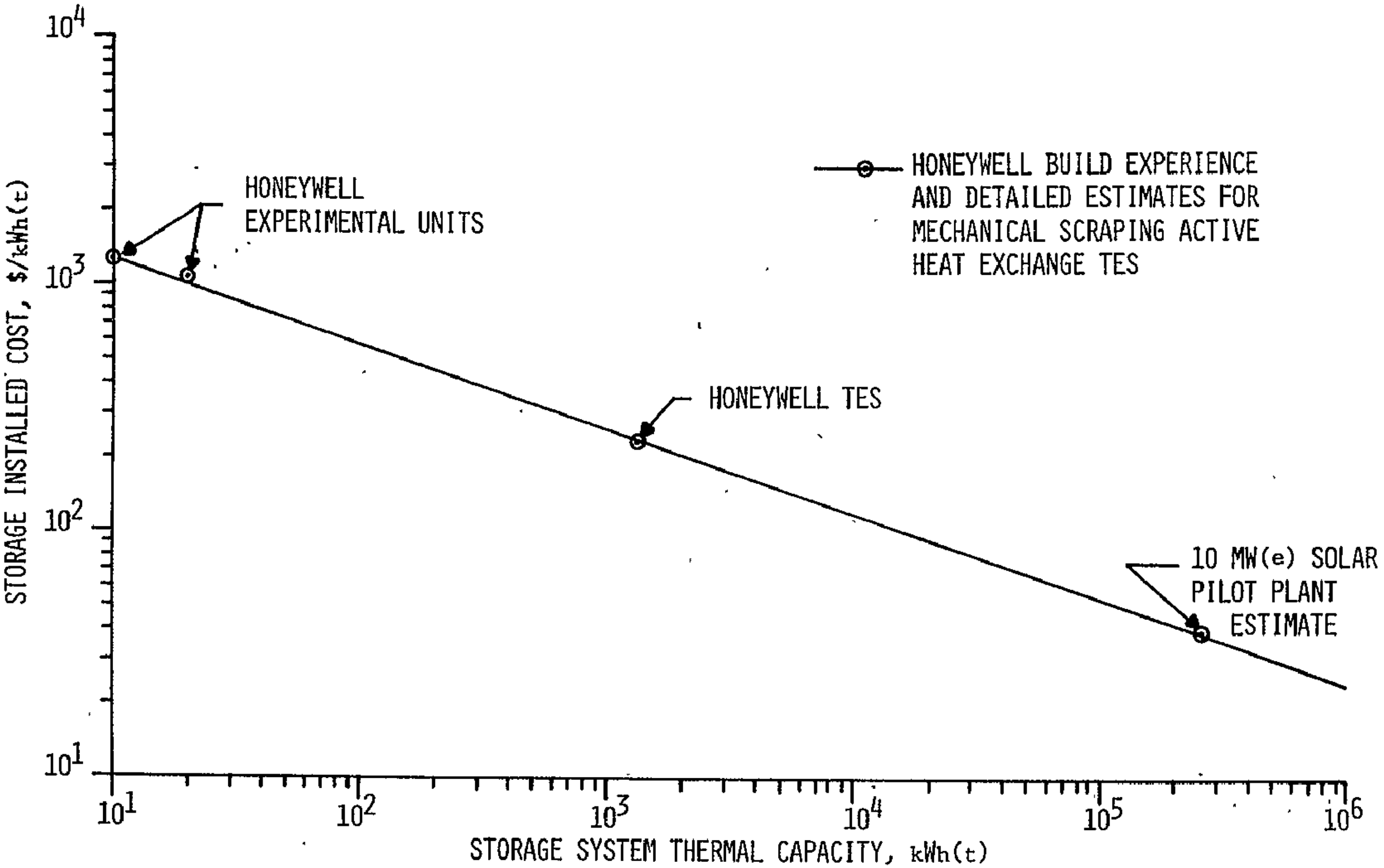


Figure 4-1. Latent Heat/Active Heat Exchange Storage Cost Trends

density salts will have smaller containment, smaller lengths of piping, reductions in valves, controls, instrumentation, salt handling equipment, foundation and site preparation (like emergency containment for salt in event of leakage, etc.). Therefore, the salt cost (in \$/kWh(t) or \$/10^6Btu), determined from the specific salt cost and energy density, should not be used as the sole indication of system cost for screening salts. This would be especially true with low capacity storage systems where the balance of plant cost rather than salt cost is significant, and where a high heat of fusion salt would be more economical. A parametric analysis of the effect of salt properties and cost on TES system cost is presented in Appendix A. From this analysis, a plot was obtained of salt cost versus salt heat of fusion using system costs as parameters. The curves shown in Figure 4-2 can be used to estimate TES system costs once specific salt cost and heat of fusion are known. The curves are used in the following section for screening salts.

4.2 SALT SCREENING

A systematic technical and economic evaluation was conducted for about 200 salt mixtures with melting temperatures between 250° - 400°C. Figure 4-3 shows a flow chart of the salt selection methodology. A set of salts suitable to thermal storage applications was identified from extensive lists of salts investigated by Honeywell. A partial list of salts and salt eutectics with melting temperatures between 250°C and 350°C is given in Appendix B, Tables B-1 and B-2. The salt selection was made after screening on the basis of the criteria described below.

4.2.1 Nonavailability and Hazardous Properties

Salts of uncommon metals were eliminated because of high costs and nonavailability in large quantities. Table B-2 in Appendix B is a list of salts belonging to this category.

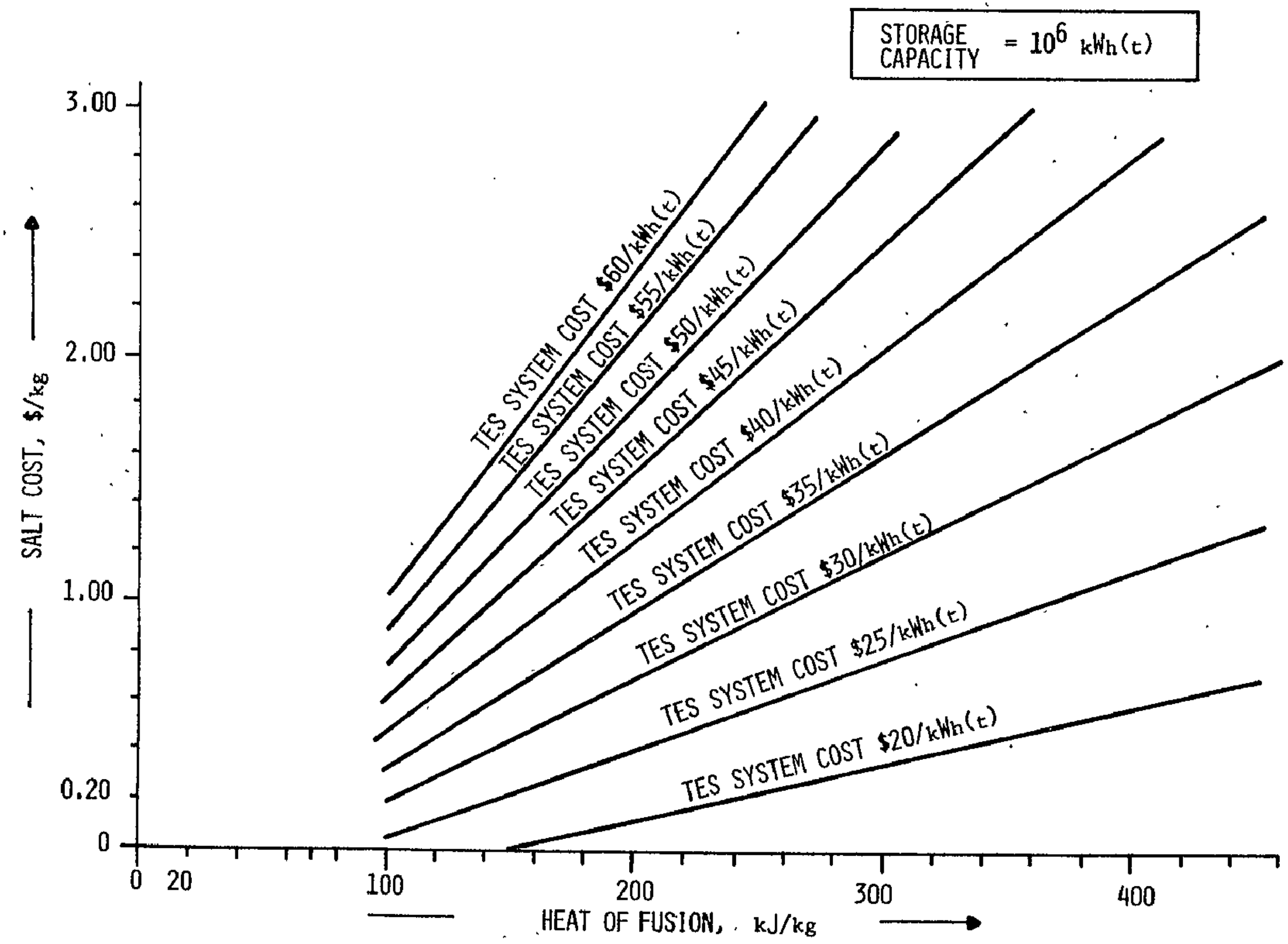


Figure 4-2. Phase Change TES System Cost Curve

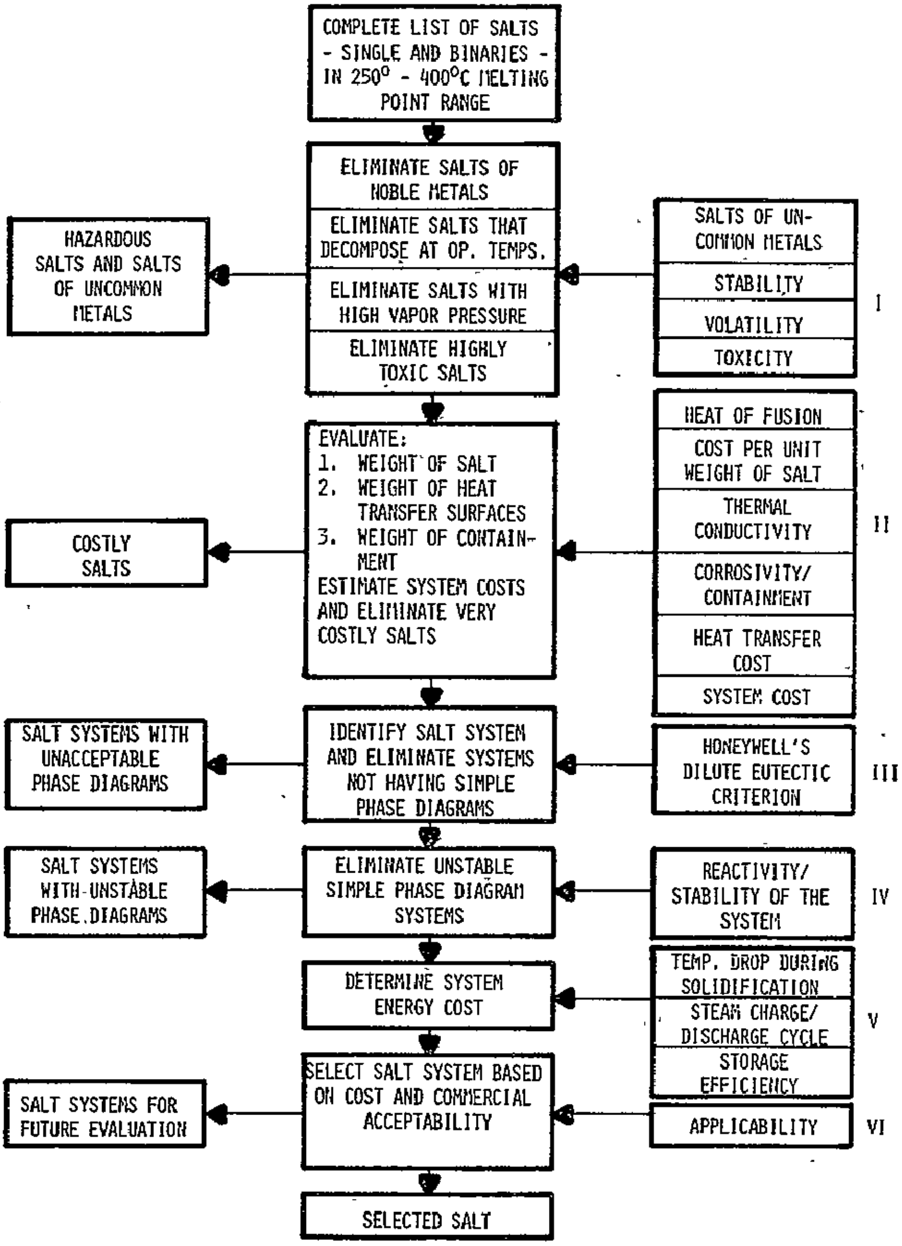


Figure 4-3. Salt Selection Methodology Flow Chart

Salts belonging to certain groups like amides, cyanides and chlorates were elminated because of their high toxicity and high volatility. Table 4-1 gives a brief evaluation of salts based on types. Salts and salt mixtures of chlorides, nitrates, nitrites, hydroxides, carbonates and sulfates remain for further consideration. A list of single salts with melting points between 250°C and 400°C and their evaluation based on hazardous properties is given in Appendix B (Table B-3).

Table 4-2 lists seven single salts and 45 binary and ternary eutectic salts together with their salt costs and heat of fusion, which were selected for further screening.

4.2.2 Salt Thermal Properties and System Costs

Important salt properties are salt energy density, thermal conductivity, and corrosivity. An earlier section explained the importance of salt energy density on system cost. Salt thermal conductivity affects the heat exchanger costs. In general, heat exchanger costs are inversely proportional to $\sqrt{h_f \cdot k_s \Delta T}$, where h_f is salt energy density, k_s is thermal conductivity, and ΔT is heat transfer temperature difference. Corrosion properties of salt affect the costs of containment, handling and heat exchangers. In the cost model in Appendix A, mild steel containment and the same thermal conductivity was assumed for all salts. Only the effect of energy density on system cost was determined. Corrections to system costs that would account for corrosion and thermal conductivity were made for only the selected salts after final screening.

The salt costs and heats of fusion given in Table 4-2 for the seven single salts and 45 eutectics are plotted on Figure 4-4, the system cost plot obtained from the cost model (Figure 4-1). The numbers on the graph refer to those in Table 4-2. TES system installed costs increase as you go from the lower right to the upper left corner of this figure.

Table 4-1. Major Component Phase Change Materials

CLASS	EXAMPLE	EVALUATION
ACETATES	$KCOOCH_3$	HEALTH HAZARD
FORMATES	NaOOCH	HEALTH HAZARD
AMIDES	KNH_2	DISASTER HAZARD
THIOCYANATES, CYANIDES	NaCNS	HEALTH AND DISASTER HAZARD
PERCHLORATES	$LiClO_4$	UNSTABLE, HEALTH AND DISASTER
CHLORATES	$NaClO_3$	HEALTH AND DISASTER HAZARD
CHLORIDES	NaCl $FeCl_3$ $(ZnCl_2)$	CONDITIONALLY ACCEPTABLE
HYDRIDES OXIDES SULFIDES CARBONATES SULFATES SILICATES, METASILICATES BORATES PHOSPHATES CHROMATES	GENERALLY OUTSIDE OF TEMPERATURE RANGE - CARBONATES AND SULFATES ACCEPTABLE FOR SUPERHEATER MEDIA	
HYDROXIDES	NaOH	ACCEPTABLE - WHEN USED BELOW 370°C AND WITH PROPER DESIGN, OPERATING AND HANDLING PROCEDURES.
NITRITES	$NaNO_2$	ACCEPTABLE - WHEN USED BELOW 316°C AND WITH PROPER DESIGN, OPERATING AND HANDLING PROCEDURES.
NITRATES	$NaNO_3$	ACCEPTABLE - WHEN USED BELOW 370°C AND WITH PROPER DESIGN, OPERATING AND HANDLING PROCEDURES.

SALT (A-B-C)	T_f °C	MOLE % (A-B)	WT % (A-B)	DENSITY AT M. Pt. kg/m^3	H_f kJ/kg	H_f MJ/m^3	$/kg	$/kWh(t)
1. $LiNO_3$	254	-	-	1776	372 (344)**	663	3.51	33.90
2. $NaNO_2$	282	-	-	1808	212	383	0.53	9.00
3. $ZnCl_2$	283	-	-	2384	150	354	3.06	74.12
4. $NaNO_3$	310	-	-	1920	174	335	0.18	3.65
5. NaOH	318	-	-	1776	158	281	0.33	7.50
6. NaOH	318 *** (299)***	-	-	1776	316	563	0.33	3.75
7. KNO_3	337	-	-	1872	116	218	0.33	10.25
8. KOH	360	-	-	1728	167	290	0.55	11.85
9. $NaNO_3$-NaOH	246 (250)***	70	83	1926	182 (167)**	352 (317)	0.19	3.80
10. $LiNO_3$-Li_2SO_4	250	98	97	1797	190	342	2.76	52.20
11. $LiNO_3$-Li_2CO_3	250	98	95	1784	192	342	2.73	51.30
12. $Ba(NO)_2$-$LiNO_3$	252	2.8	10	1901	181	387	2.51	49.90
13. NaBr-NaOH	260	22.3	42.5	2018	247	500	0.79	21.60
14. LiOH-LiCl	262	63	49	1725	423	730	2.95	25.20
15. Na_2CO_3-Na_2O-NaOH	263	6.5-7.4	15-10	1878	314	591	NA	-
16. $Ca(NO_3)_2$-LiCl	265	40.9	73	1866	177	330	1.06	21.50
17. $Ba(NO_2)_2$-KNO_2	265	95	98	3186	88	283	NA	-
18. LiBr-LiOH	275	55	81.6	2538	235	597	6.13	94.00
19. KCl-LiCl-LiOH	280	11.5-45	22.6-50	1710	364	624	3.65	36.05
20. $Ca(NO_3)_2$-NaCl-$NaNO_3$	280	5.8-7.9	16.3-5	2090	154	323	0.16	3.80
21. NaCl-$NaNO_2$	281	1.1	1	1813	202	367	0.43	7.65
22. NaCl-Na_2CO_3-NaOH	282	7.8-6.4	10-14.9	1876	316	594	0.26	2.90
23. KCl-LiCl-LiOH	283	1.5-36.5	3.6-49.1	1701	444	756	2.86	23.20
24. Na_2CO_3-NaOH	283	7.2	12	1872	340	636	0.29	3.10
25. $Ba(NO_3)_2$-$NaNO_2$	284	15.2	40.4	1904	154	489	0.27	24.70
26. KNO_3-$NaNO_2$	285	45.2	49.8	1851	152	281	0.41	9.75

* CHEMICAL MARKETING REPORTER (1975) PRICE LIST.

** EXPERIMENTAL VALUES.

*** TRANSITION TEMPERATURE.

Table 4-2. Properties of Selected TES Inorganic Salts

SALT (A-B-C)	T_f °C	MOLE % (A-B)	WT % (A-B)	DENSITY AT M. PT. kg/m^3	H_f, kJ/kg	H_f MJ/m^3	$/kg	$/kWh(t)
27. $NaCl-NaNO_3-Na_2SO_4$	287	8.4-86.3	5.7-85.5	1956	176	345	2.15	3.50
28. LiOH-LiCl	290	63	49	1664	432	719	2.96	24.70
29. $KNO_3-Ba(NO_3)_2$	290	87	72	2277	124	282	0.26	7.70
30. $NaCl-NaNO_3$	284	6.4	5	1906	171	327	2.15	3.35
31. LiOH-LiCl	297	50	36	1827	460	841	3.07	24.05
32. LiBr-KBr	310	68	60.8	2597	151	392	4.84	95.65
33. KOH-LiOH	314	60	77.8	1773	341	605	0.91	9.65
34. $KCl-KNO_3$	320	6	4.5	1890	150	284	0.37	9.00
35. $KNO_3-K_2CO_3$	320	98	97.3	1890	147	277	0.39	9.55
36. $KNO_3-K_2SO_4$	330	98	96.6	1880	149	281	0.39	9.40
37. $BaCl_2-KCl-LiCl$	337	6.4-39.4	20.2-44.8	2080	241	502	1.22	18.30
38. $KCl-LiCl-CaCl_2$	340	45-45	52.8-29.9	1763	262	462	0.98	13.50
39. $KBr-KCl-KNO_3$	342	10-10	4.7-7.3	1920	140	269	0.42	10.90
40. KCl-LiCl-NaCl	346	24-43	32.4-32.8	1720	281	483	1.15	14.70
41. LiCl-KCl	355	58	44	1704	282	481	1.41	17.95
42. KBr-KCl-LiCl-LiBr	357	21.3-37.7	34.4-38-20	1880	214	403	1.54	29.30
43. NaF-NaOH	360	10	10.5	1819	396	720	0.36	3.30
44. NaCl-NaOH	370	20	26.8	1744	370	645	0.28	2.70
45. $K_2CO_3-Li_2CO_3-LiOH$	422	16.4-26.4	40-35	1966	352	693	1.40	14.35
46. $FeCl_2-NaCl$	374	44	63	-	224	-	NA	-
47. $FeCl_2-KCl$	380	52.2	65	-	203	-	NA	-
48. KCl-LiCl-NaCl	384	30-15	41.2-42.7	1690	303	513	1.48	17.60
49. $K_2CO_3-Li_2CO_3-Na_2CO_3$	394	25-43.5	34.5-32.5	2085	252 (276)**	527 (581)**	0.73	10.45
50. $KCl-MgCl_2-NaCl$	396	22-51	20.4-60	1764	261	461	0.19	9.35
51. $BaCl_2-Ca(NO_3)_2$	402	41.7	47.6	2734	140	382	0.18	4.60
52. $Ba(NO_3)_2-NaCl$	408	62	88	2848	122	347	0.30	23.80

* CHEMICAL MARKETING REPORTER (1975) PRICE LIST.
** EXPERIMENTAL VALUES.
*** TRANSITION TEMPERATURE.

Table 4-2. Properties of Selected TES Inorganic Salts (Concluded)

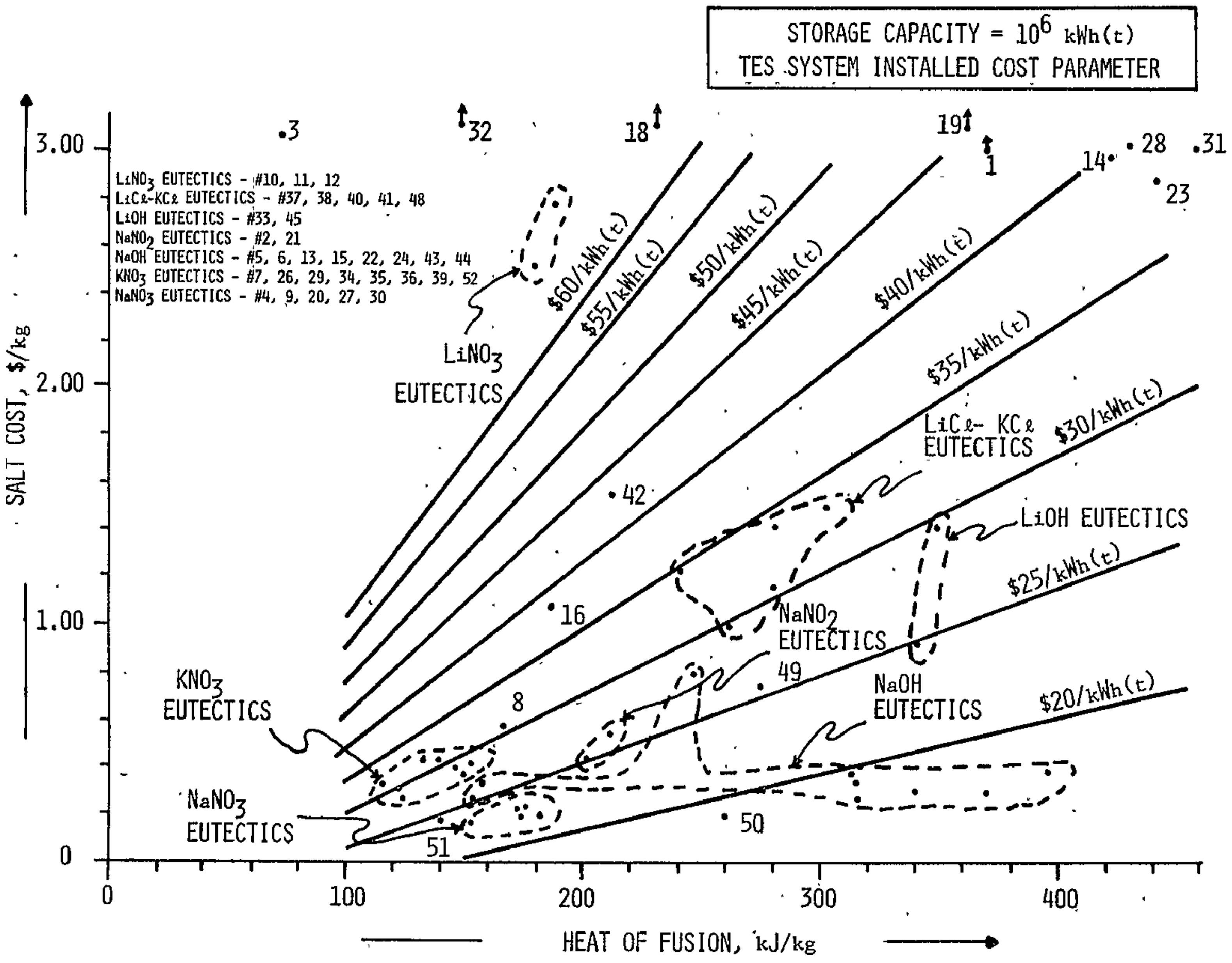


Figure 4-4. Salt Cost vs. Heat of Fusion-TES System Cost Parameter

Figure 4-4 shows that eutectics of NaOH and chlorides give system costs between 15 and 20 \$/kWh(t), except for salt 5, which is NaOH. Sodium hydroxide undergoes a crystalline transition at about 299°C with a heat of transition of 158 kJ/kg and melts at 318°C with a heat of fusion of 158 kJ/kg. Salt 5 utilizes only the heat of fusion of NaOH to store heat while salt 5 utilizes both heat of fusion and heat of transition. However, with salt 6 there is a larger temperature drop through storage in utilizing the heat of transition; therefore, it has lower system efficiency. The costs are subject to using mild steel containment, but are estimated to increase by 30 percent with stainless steel containment. $NaNO_3$, $NaNO_2$, eutectics of these salts, LiOH and carbonates give system costs between 20 and 30 \$/kWh(t). Note that salt cost for $NaNO_3$ is \$3.65/kWh(t), while salt costs for eutectics of LiOH (salt 33) and carbonate (salt 49) are \$9.65 and \$10.45 per kWh(t), respectively; however, they all have about the same system costs. The eutectics of KNO_3, LiOH-LiCl and LiCl-KCl give system costs between 25 and 35 \$/kWh(t). $LiNO_3$ gives system costs of 49 \$/kWh(t), and its eutectics give system costs of over 60 \$/kWh(t). $ZnCl_2$ (salt 3) gives very high system costs of about 75 \$/kWh(t).

Based on the evaluation described above, a clearer rating of salt cost is seen. Although a few salts ($LiNO_3$ and $ZnCl_2$, for example) demonstrated high system costs, none are eliminated at this stage of the screening, allowing all salts to remain under consideration until the end of the screening process when cost considerations are crucial. For now, the cost criteria merely undertone other considerations.

4.2.3 Dilute Eutectic Criterion

Through experimental and analytical work, Honeywell has demonstrated that solidification characteristics of the molten salt mixture are important selection criteria. A desirable mixture would solidify gradually over a wide temperature range. In such a case, the cooling fluid can be maintained at a lower temperature (just above the solidus line, as shown in Figure 2-3), allowing a large heat transfer ΔT. Meanwhile, the temperature drop that is required in the media for a given amount of solidification is small; this makes less heat loss in storage. These characteristics would also maintain a two-phase slush in the crystallizing material making heat transfer to the melt and pumping the material more efficient.

Such crystallization characteristics can be achieved by adding another component (salt or salt mixture), which, together with the primary salt, forms a simple eutectic system. A simple eutectic system is one that does not form any significant solid solutions between the single salt melting point and the eutectic point for the system. The minor component is added in small quantities (about one weight percent), hence the term dilute eutectic system.

It is desirable that the melting point drop during freezing (measured along the solubility curve) be small for a large amount of solidification. Honeywell has demonstrated that up to 60 percent solidification can be achieved at a constant heat rate with as much as 80 percent solidification at a much lower heat rate. To maintain a good heat transfer ΔT throughout crystallization, the melting point drop should be no greater than 5 C° to 6 C°. This would mean that the operating temperature for a salt would be between the melting point of the 99-1 mixture (close to the melting point of the major component) and the lowest melting temperature reached due to the drop of this temperature upon solidification. Approximately fifty experiments were conducted at Honeywell using a $NaNO_3$ - NaOH dilute eutectic, demonstrating this characteristic with reproducible results. The experiments involved mechanical scraping of freezing salts from the outer surface of a tube through which coolant is running.

The difference between the scrapability of a pure salt or eutectic salt and a salt mixed with a minor component has been observed in experiments. In the former case, the scrapers stalled immediately or needed a very high torque, while in the latter case, they ran very smoothly, demonstrating that scraping a slurry is easier than scraping a solid. However, in the latter case—when the tube surface temperature was dropped below the eutectic system's solidus temperature (or the eutectic temperature for the simple eutectic system)--the scrapers stalled immediately, suggesting the formation of a eutectic composition near the freezing interface. This situation must be accounted for in system designs.

The next step in salt screening was based on the dilute eutectic criterion; here, the purpose was to find simple eutectic phase diagrams for the 52 salts listed in Table 4-2. These 52 salts would be major components of the simple eutectic system, if such a system could be identified. The eutectic systems for the seven single salts are listed in Appendix B (Table B-4); complete phase diagrams for systems with more than two components were not available for the remaining 45 salts. However, most of these are eutectics of the seven single salts except for chlorides, carbonates and LiOH. Combinations of alkali chlorides with common ion tend to give continuous solid solutions provided the interionic distance is small enough. This indicates that it may be difficult to find a simple eutectic among these salts. From system cost, the systems of interest are the chloride eutectic of KCl-$MgCL_2$-$NaCl$ (Salt 50), the carbonate eutectic of K_2CO_3-$LiCO_3$-Na_2CO_3 (Salt 49) and the LiOH eutectics (Salt 33 and 45). For the former two, quaternary simple eutectic systems are not expected, but LiOH eutectics are promising. The other promising salts based on system cost are eutectics containing mainly $NaNO_3$, $NaNO_2$, NaOH and $LiNO_3$. The system costs of the eutectics of these salts are about the same as those of their single salts. Therefore, the seven single salts were further evaluated.

Table 4-3 gives the system costs of the seven salts. (Notice that the information contained in this table is a subset of that in Table 4-2, reprinted here for convenience.) The $ZnCl_2$ system was eliminated because of very high system cost. The melting point of $LiNO_3$ is 254°C and is too close to the limit of the range of interest. For other salts, the steam charge and discharge cycles are listed in the comments column. The charge cycle refers to steam conditions of a standard steam turbine cycle required for charging storage. The heat

Table 4-3. Selected Major Components-System Cost

SALT #	MAJOR COMPONENT (99 wt%)	MELTING POINT (°C)	HEAT OF FUSION (kJ/kg)	SALT COST ($/kg)	TES SYSTEM COST ($/kWh(t))	COMMENTS
1	$LiNO_3$	254	372	3.51 (2.51)	49 39	MELTING POINT TOO CLOSE TO LIMIT OF RANGE OF INTEREST-ELIMINATE
2	$NaNO_2$	282	212	0.53	26	FITS 8.6 MPa CHARGE/4.1 MPa DISCHARGE (1250/600 PSI)
3	$ZnCl_2$	283	150	3.06	75	VERY HIGH SYSTEM COST - ELIMINATE
4	$NaNO_3$	310	174	0.17	22	FITS 12.4 MPa CHARGE AND 6.9 MPa DISCHARGE CYCLE (1800/1000 PSI)
5	NaOH	318	158	0.33	26	FITS 16.5 MPa CHARGE/12.4 MPa DISCHARGE CYCLE (2400/1800 PSI)
6	NaOH	318	158	0.33	19	IF SYSTEM COULD BE DESIGNED TO UTILIZE THE HEAT OF TRANSITION
7	KNO_3	337	116	0.33	30	FITS 22 MPa CHARGE/--DISCHARGE CYCLE (3200 PSI)
8	KOH	360	167	0.55	29	FITS SUPERCRITICAL CYCLE

charged is the heat of condensation of steam. The condensation temperature is assumed to be about 18 to 20 C° over the salt temperature in determining charge condition. Similarly, discharge cycle refers to the steam conditions of a standard steam turbine cycle obtained when storage is discharged. The heat transferred from storage is used to vaporize water. A ΔT of about 18 to 20 C° is allowed for heat transfer in determining the standard discharge cycle.

4.2.4 Final Media Selection

The list of salts selected at this step was reduced to the eutectic systems of $NaNO_3$, $NaNO_2$, and NaOH. Table 4-4 lists eutectic systems of these salts. In selecting the minor component, several factors must be considered:

- Reactivity
- Supercooling
- Temperature drop
- Stability
- Safety
- Cost and availability.

The minor component should not react with the major component. In the NaOH - Na_2CO_3 system, Na_2CO_3 reacts with moisture to give off CO_2 and NaOH absorbs moisture. Supercooling is a common phenomena, and it is a serious problem with phase change materials in passive systems. The amount of supercooling is generally less for large samples. The $NaNO_3$ - $Ca(NO_3)_2$ system supercools and the solid form is glassy. The freezing temperature of the eutectic system (generally) decreases with solidification. The freezing temperature drop for a large amount of solidification should be as small as possible for efficient operation. Table 4-4 lists the calculated temperature drop for the eutectic systems. The system should be stable. $NaNO_2$ decomposes at temperatures greater than 450°C. Furthermore, the system should maintain thermal and physical properties over the life of the storage system. The component should be proven

Table 4-4. Salt System Selection

Major Component (Melting point)	Minor Component (1wt%)	Eutectic Melting Point (°C)	Temperature drop for 60% Solidification (°C)	Comments	Selected System	Recommended System
$NaNO_3$ (310°C)	NaOH	243	6	Has performed very well	$NaNO_3$(99wt%) + NaOH(1wt%)	$NaNO_3$(99wt%) + NaOH(1wt%) we have all the data available on this sytem and will be an excellent candidate for heat exchanger evaluation.
	$Ca(NO_3)_2$	232	2	supercools; forms vitreous solid		
	KOH	222	10	Has a larger temp drop and is no better than NaOH.KOH is more corrosive.		
	NH_4NO_3	121	4	Hazardous minor component.		
	$TlNO_3$	162	1	Very costly minor component.		
	$LiNO_3$	196	4	$LiNO_3$ is hygroscopic; could be an alternate candidate.		
$NaNO_2$ (282°C)	NaOH	232	7	A possible candidate for lower cycle selection	$NaNO_2$(99wt%) + NaOH(1wt%)	The $NaNO_2$ system will require salt characterization studies and is therefore not recommended for application at this time.
NaOH (318°C)	Na_2CO_3	283	2	Reacts to give CO_2	NaOH(99wt%) + $NaNO_3$(1wt%)	NaOH system will need a corrosion inhibitor*. It's selection is therefore conditional.
	Na_2SO_4	293	3	Eutectic temp too close		
	NaBr	265	2	Possible candidates. $NaNO_3$ & $NaNO_2$ are believed to have a passivating effect for corrosion.		
	NaI	215	2			
	$NaNO_3$	258	3			
	$NaNO_2$	238	4			

*Comstock and Wescott have a patented corrosion inhibitor for this system.

safe. NH_4NO_3 is a hazardous salt, and $TlNO_3$ is very toxic and should be avoided even in minute quantities. Cost of the minor component is generally unimportant. However, 1 weight percent of $TlNO_3$ added to $NaNO_3$ increases the salt mixture cost by about twofold.

Table 4-4 also lists the reasons in the 'comments' column, for selecting the candidate salt media listed in the column 'selected system'. The recommended salt system is 99 weight percent $NaNO_3$ with 1 weight percent NaOH. The recommended system, besides meeting all the criteria discussed, has performed well with current state-of-the-art active heat exchange devices. Most of the data required for advanced active heat exchange design and evaluation is available for this media.

SECTION 5.0
COMPARATIVE EVALUATION OF HEAT EXCHANGER CONCEPTS

5.1 HEAT EXCHANGER EVALUATION CRITERIA

To get an idea of the total system cost implications of the basic concepts chosen in Section 3.0, it was necessary to make a preliminary system layout and estimate costs of all major components for each of the systems. The following conditions provided the basis for all cost estimates:

- Storage medium has the properties of $NaNO_3$ plus 1% NaOH.
- The latent heat storage module will supply saturated steam at 6.5 MPa/281°C (950 psi/538°F).
- The heat rate would be 1000 MW(t) (3.41×10^9 Btu/hr) for six hours.
- All systems would be charged by steam condensing coils in the storage tanks (except in the tube-intensive system where the same tubes perform both charge and discharge functions).

The performance and costs of the eight heat exchanger concepts are compared in Section 5.2. The comparison criteria were broken into five major groups.

1. Performance parameters are those heat transfer-related quantities necessary to size the various systems and which indicate the extent of possible system size reductions attainable if the heat transfer coefficient is improved. With water vaporizing inside of a 1-inch O.D., 13-gauge carbon steel tube, the overall heat transfer coefficient will be less than 6000 W/m^2-K due to thermal resistance of the tube wall and the water film coefficient. Salt film coefficients and any fouling resistance will further reduce this value.

2. Operational criteria are those parameters of control and maintenance significance that may influence the overall complexity of the systems. Some of the critical control items are discussed, along with the numbers of individual units that may contribute to maintenance and/or control complexity.

3. Subjective evaluation criteria are parameters that are strictly engineering judgment. It would be difficult to place a dollar figure on these quantities, but they must be considered in the selection and overall evaluation of the system.

4. Materials required are weight estimates of major components of the thermal storage system. These estimates were made by calculating sizes and weights of the necessary fluid handling and storage components while considering the various code requirements and good engineering practices in designing systems.

5. System costs were broken down into costs of each of the major components and finally into capacity and rate-related costs. The final bottomline figure is the estimated cost for the total system capable of providing 1000 MW(t) for a six-hour period. These cost estimates were based upon data obtained by quotations developed under the Honeywell Solar Pilot Plant program and scaled using appropriate scaling laws for each of the components. For the costs, estimated accuracy is on the order of ± 10 to 20 percent. The passive tube-intensive system was chosen as a reference to which cost comparisons could be made.

5.2 PERFORMANCE AND COST EVALUATION OF SYSTEMS

The following paragraphs discuss each of the concepts chosen in Section 3.2. Table 5.1 outlines their performance based on the criteria described in 5.1. Notice that for most systems the balance of plant cost, which includes all auxiliary components, is a large percentage of the total system cost.

			1	2	3	4
CRITERIA		UNITS	INTERNAL SURFACE SCRAPER	EXTERNAL SURFACE SCRAPER	SHELL AND TUBE FLOW-BY	JET IMPINGEMENT
PERFORMANCE	HEAT TRANSFER COEFF.	W.m^{-2} K^{-1}	2271	2868	2260	2084
	TEMPERATURE DROP	K	18	18	18	18
	HEAT TRANSFER RATE	W.m^{-2}	40878	51624	40680	37512
	AUXILIARY POWER	kW(e) x 10^{-3}	25.2	25.2	8.4	9.0
	PERCENT OUTPUT (a)		8.4	8.4	2.8	3.0
OPERATION	CONTROL REQUIREMENTS		FREEZE-UP	FREEZE-UP	TEMP. BAL.	TEMP. BAL
	MAINTENANCE	TYPE	SHARPENING	WEAR	MINIMUM	MINIMUM
		FREQUENCY	3 MON.	3 MON.	INFREQUENT	INFREQUENT
	SYSTEM SIZE	m	0.25m x 6.1m	35m x 2.4m	1.5m x 12.2m	3m x 3m x 5.5m
		# OF UNITS	5300	54	10	10
SUBJECTIVE EVALUATION PARAMETERS	SCALABILITY		BAD	BAD	GOOD	GOOD
	TECHNOLOGICAL DEV.		GOOD	PHOTOTYPE	GOOD	CONCEPT
	COMPATIBILITY WITH STEAM CYCLE		FAIR	GOOD	GOOD	GOOD
	INSTITUTIONAL BARRIERS		NONE	NONE	NONE	NONE
	SAFETY		TUBE ABRASION	TUBE ABRASION	TUBE EROSION	TUBE EROSION
MATERIALS REQUIRED	HEAT EXCHANGERS					
	SURFACES	kq x 10^{-6}	—	1.40	0.42	0.83
	CONTAINMENT	"	—	NONE	0.09	0.05
	MANIFOLDING	"	0.27	0.27	0.20	0.20
	TANKAGE	"	3.7	7.6	3.7	3.7
	STORAGE MEDIA	"	166	166	166	166
COSTS	HEAT EXCHANGERS	\$/kWh(t)	27.50	3.13	1.52	1.90
	MANIFOLDS	"	0.33	0.33	0.25	0.25
	TANKAGE	"	2.14	4.20	2.14	2.14
	MEDIA @ 0.1 \$/LB	"	6.10	6.10	6.10	6.10
	BALANCE OF PLANT	"	10.8	10.8	10.8	10.8
	RATE RELATED COST	\$/kW	201	54.9	44.7	47.0
	CAPACITY RELATED COST	\$/kWh(t)	13.4	15.5	13.4	15.4
	SYSTEM COST	\$/kWh(t)	46.9	24.6	20.9	21.2
	SYSTEM TOTAL COST	\$ x 10^{-6}	281	147	125	127
	RELATIVE COST		1.72	0.90	0.77	0.78
	REL. COST LESS BALANCE OF PLANT		2.2	0.84	0.62	0.63

Table 5-1. Performance and Cost Evaluation of Candidate Heat Exchanger Concepts

CRITERIA		5	6	7	8	9
		SELF PRESSURIZING REFLUX BOILER	CONTINUOUS SALT FLOW (c) REFLUX BOILER	OPEN SYSTEM REFLUX BOILER	TUMBLING ABRASIVE	PASSIVE TUBE INTENSIVE
PERFORMANCE	HEAT TRANSFER COEFF.	4656	--	--	568	55
	TEMPERATURE DROP	15	15	4	18	18
	HEAT TRANSFER RATE	69840	69840	--	10224	990
	AUXILIARY POWER	9.0	9.0	9.0	9.0	1.5
	PERCENT OUTPUT (a)	3.0	3.0	3.0	3.0	0.5
OPERATION	CONTROL REQUIREMENTS	SLURRY CONV.	SLURRY CONC.	SLURRY CONC.	MINIMAL	MINIMAL
	MAINTENANCE	VALVE SEATS INFREQUENT	MINIMUM INFREQUENT	VALVE SEATS INFREQUENT	TUBE WEAR INFREQUENT	NONE INFREQUENT
	SYSTEM SIZE	2.1m x 12.2m 24	2.1m x 12.2m 8	2.1m x 12.2m 16	1.8m x 12.2m 117	35m x 12.2m 6
SUBJECTIVE EVALUATION PARAMETERS	SCALABILITY	GOOD	GOOD	GOOD	GOOD	GOOD
	TECHNOLOGICAL DEV.	CONCEPT	CONCEPT	CONCEPT	CONCEPT	SMALL SCALE
	COMPATIBILITY WITH STEAM CYCLE	GOOD	GOOD	GOOD	GOOD	GOOD
	INSTITUTIONAL BARRIERS	PR. VESSEL CODE	PV. VESSEL CODE	PR. VESSEL CODE	NONE	NONE
	SAFETY	ABMA CODE	ABMA CODE	ABMA CODE	TUBE EROSION	NONE
MATERIALS REQUIRED	HEAT EXCHANGERS					
	SURFACES	0.29	0.29	0	2.70	16.5
	CONTAINMENT	1.11	0.65	0.93	1.25	NONE
	MANIFOLDING	0.09	0.09	0.09	0.27	1.12
	TANKAGE	3.7	3.7	3.7	3.7	3.1
	STORAGE MEDIA	166	166	166	166	125
COSTS	HEAT EXCHANGERS	2.58	1.84	1.92	3.60	8.63
	MANIFOLDS	0.11	0.11	0.11	0.33	1.38
	TANKAGE	2.14	2.14	2.14	2.14	1.78
	MEDIA @ 0.1 $/LB	6.10	6.10	6.10	6.10	4.58
	BALANCE OF PLANT	10.8	10.8	10.8	10.8	10.8
	RATE RELATED COST	50.2	45.5	46.0	57.7	94.1
	CAPACITY RELATED COST	13.4	13.4	13.4	13.4	11.5
	SYSTEM COST	21.7	20.9	20.5(b)	23.0	27.2
	SYSTEM TOTAL COST	130	126	123(b)	138	163
	RELATIVE COST	0.80	0.77	0.75	0.85	1.00
	REL. COST LESS BALANCE OF PLANT	0.66	0.62	0.59	0.74	1.00

FOOTNOTE: (a) PERCENTAGE OF THERMAL OUTPUT USED TO GENERATE ELECTRICITY TO DRIVE AUXILIARIES

(b) SYSTEM COSTS ADJUSTED FOR HIGHER EFFICIENCY ATTAINABLE AT HIGHER TEMPERATURE.

(c) AT THIS LEVEL OF AN ESTIMATION, THE CONTINUOUS SALT FLOW REFLUX BOILER WITH AND WITHOUT HYDRAULIC HEAD RECOVERY ARE REPRESENTED BY THE SAME NUMBERS.

(d) ALL ESTIMATES IN THIS TABLE HAVE BEEN SIZED TO A 1000 MW$_r$, 6 HR. STORAGE UNIT OPERATING WITH 1000 PSI SATURATED STEAM.

Table 5-1. Performance and Cost Evaluation of Candidate Heat Exchanger Concepts (Concluded)

5.2.1 Internal Surface Scraper

The internal surface scraper was envisioned as either an Armstrong or Votator commercially available scraped surface heat exchanger. This device has a long record of successful commercial utilization and does not need major design changes to be adapted to thermal storage applications. The device can be disassembled readily to service the scraper blades.

The system layout assumes that the heat exchangers would be centrally located between the storage tanks and that the salt would be pumped to the exchangers and pumped back to storage. Here, the salt slurry would separate and the rich liquid would be recycled back through the exchanger. Based on previous experimental work, a seventy-five percent heat recovery should be attainable by this method of media handling.

The heat transfer coefficient was estimated as 2271 W/m^2-K based on Votator literature data. For a 1000 MW(t) heat rate and 18 C° heat transfer ΔT, the heat transfer surface required is $2.44 \times 10^4 m^2$. The largest commonly manufactured Votator unit made was listed as 4.65 m^2 (50 sq. ft.) of surface, 0.25 m (10 inch) diameter by 6.1 m (20 ft.) in length. Therefore, this requires about 5300 units.

A disadvantage in the utilization of these units is that the heat transfer surface area per unit weight and volume is relatively small. A second deficiency of these units is that high pressure steam must be contained in a large diameter annulus; this requires very thick-walled tubular construction and may require exotic expansion joints to accommodate differential expansion between inner and outer shells. This potential problem could be overcome with a shell and made from membrane wall structure formed into a cylinder, but this would require further development and would not overcome the low surface-to-volume ratio or improve the heat transfer coefficient.

The system is basically not scalable since larger single units decrease the surface-to-volume ratio; hence, large systems must contain large numbers of individual units manifolded together. Maintenance on large numbers of active scraper systems is potentially a major operational problem.

The cost estimate for this system of exchangers is based upon cost estimates for large number of systems from Votator, Division of Chemtron. It is estimated to cost $4305/m^2 surface.

The relatively high cost of individual units and the large number of them places this system at a price disadvantage compared with other systems.

5.2.2 External Surface Scraper

The heat exchanger system modeled in this concept was basically the external tube scraper designed by Honeywell under the Solar Pilot Plant program[15]. The scraper modules are located in the top of the storage tanks, with a large tank top surface area required by the slow solid salt settling rate. Improvement in the overall heat transfer rate compared with the internal scraper is obtained by the more favorable geometry and the thinner tube walls. Scraping power requirements were assumed to be similar.

The heat transfer coefficient for this concept is derived from the energy conservation equation, written as (see Figure 5-1),

$$dq = U_o \cdot dA_o \cdot \Delta T = \rho_s H_{f_s} \cdot \frac{dx_s}{dt} \tag{1}$$

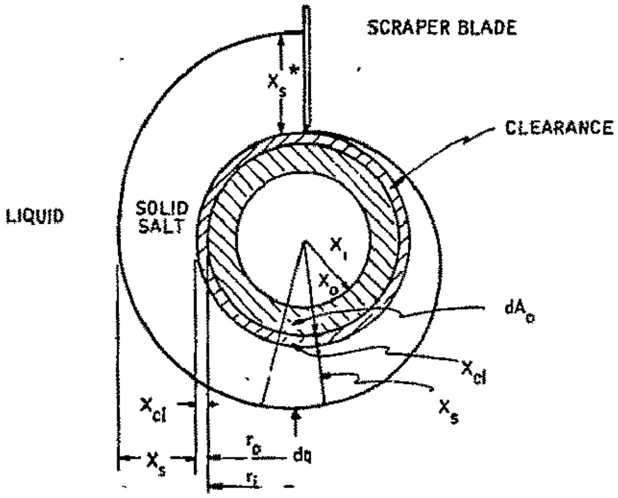


Figure 5-1. External Surface Scraper

where

$$\frac{1}{U_o} = \frac{r_o}{r_i h_i} + \frac{r_o \ln\left(\frac{ro}{ri}\right)}{k_t} + r_o \ln\frac{\left(\frac{r_o + X_{cl}}{ro}\right)}{k_s} + r_o \ln\frac{\left(\frac{r_o + X_{cl} + X_s}{r_o + X_{cl}}\right)}{k_s}$$

$$\begin{pmatrix}\text{overall}\\\text{resistance}\end{pmatrix} = \begin{pmatrix}\text{Inside}\\\text{Resistance}\end{pmatrix} + \begin{pmatrix}\text{Tube wall}\\\text{Resistance}\end{pmatrix} + \underbrace{(\text{clearance}) + \begin{pmatrix}\text{outside}\\\text{salt film}\end{pmatrix}}_{\text{outside resistance}}$$

h_i = Inside coefficient, W/m^2-K°

k_t = Tube material thermal conductivity = 13.3 W/m-K° (25 Btu/hr-ft-F°)

k_s = Salt thermal conductivity = 0.16 W/m-K° (0.3 Btu/hr-ft-F°)

ΔT = $T_{sat'd} - T_{salt}$ = overall temperature difference = K°

U_o = Overall coefficient, W/m^2-K°

ρ_s = Salt density, kg/m^3

H_{f_s} = Salt heat of fusion, kJ/kg

X_{C_L} = clearance between scraper blade and tube, m

X_s = Salt thickness outside of clearance, m

For,

$$\frac{x}{r_o} << 1$$

$$\ln\left(\frac{r_o + X}{r_o}\right) = \ln\left(1 + \frac{X}{r_o}\right) \simeq \frac{X}{r_o}$$

$$U_o = \frac{1}{\frac{ro}{r_i h_i} + \frac{r_o \ln\left(\frac{r_o}{r_i}\right)}{k_t} + \frac{X_{cl}}{k_s} + \frac{X_s}{k_s}}$$

Substituting U_o in Equation (1) and integrating, we get.

$$X_s\ (t) = k_s \left(-B + \sqrt{B^2 + \frac{2\ \Delta\ T\ t}{\rho_s H_{f_s} K_s}} \right) \tag{2}$$

where,

$$B = \frac{r_o}{r_i h_i} + \frac{r_o \ln \frac{ro}{ri}}{k_t} + \frac{X_{cl}}{k_s}$$

B has the units of reciprocal heat transfer coefficient.

Let $h_{i,eff} = \frac{1}{B}$

Defining a dimensionless variable,

$$\theta = \frac{h_{i,eff}^{2}\ \Delta T \cdot t}{\rho_s H_{f_s} k_s}$$

$$B_i = \frac{h_{i,eff} X_s}{k_s}$$

Equation can be written in dimensionless form as,

$$Bi = -1 + \sqrt{1 + 2\theta} \tag{3}$$

The overall coefficient, U_o

$$U_o(t) = \frac{1}{B + \frac{X_s}{k_s}} = h_{eff}\ \frac{1}{1 + Bi} \tag{4}$$

$$U_{o,\ avg} = \frac{\int_{o}^{t^*} U_o(t)\ dt}{\int_{o}^{t^*} dt} \tag{5}$$

$$t^* = \frac{1}{60N} (\text{hrs})$$

N = Scraping speed in (rpm)

Substituting and integrating, we get

$$U_{o,\ avg} = h_{eff} \frac{Bi}{\theta} \tag{6}$$

For a 120 rpm scraper speed, for example, with 18 C° ΔT and 7.62×10^{-6}m (3 mil) scraper clearance, an overall coefficient of 2867 W/m^2-K was obtained. The results of the model correlated well with the experimental data in the Solar Pilot Plant program. The heat transfer surface required for 1000 MW(t) heat rate is $1.94 \times 10^4 m^2$.

The solid salt scraped from heat exchanger tubes has to settle to the bottom of the tank. Due to the slow solid settling rate a large tank top area is required. It was determined from the experiment that a heat rate of 20,500 W/m^2 of tank surface can be obtained. Therefore, the design required about 54 tanks, each 35m in diameter by 2.4m in height.

Cost estimates for the scraper units were based on fabrication cost of the modules made under the Solar Pilot Plant program, design changes to reduce the total weight, and an 85 percent learning curve for the increased quantity production. No salt manifolding was required, but tank costs increased due to the unfavorable surface-to-volume ratio required by having the exchanger in the tank. The total system cost estimate ranks this system close to the passive system, but maintenance and auxiliary power requirements were not included in the costs.

Scalability is poor because of the limited numbers of units that can be powered by a common drive and because the surface-to-volume ratio decreases as pipe size is increased. Heat transfer and high pressures tend to make 1-inch diameter tubing nearly optimal for the system.

5.2.3 Shell and Tube Flowby

This system was modeled assuming a shell and tube exchanger could be designed to function with a latent heat storage medium. Remarks in Section 3.0 indicate that with the proper combinations of salt, tube coating or plating, flow velocities and temperature control, this system may function with minimal fouling (see Figure 5-2).

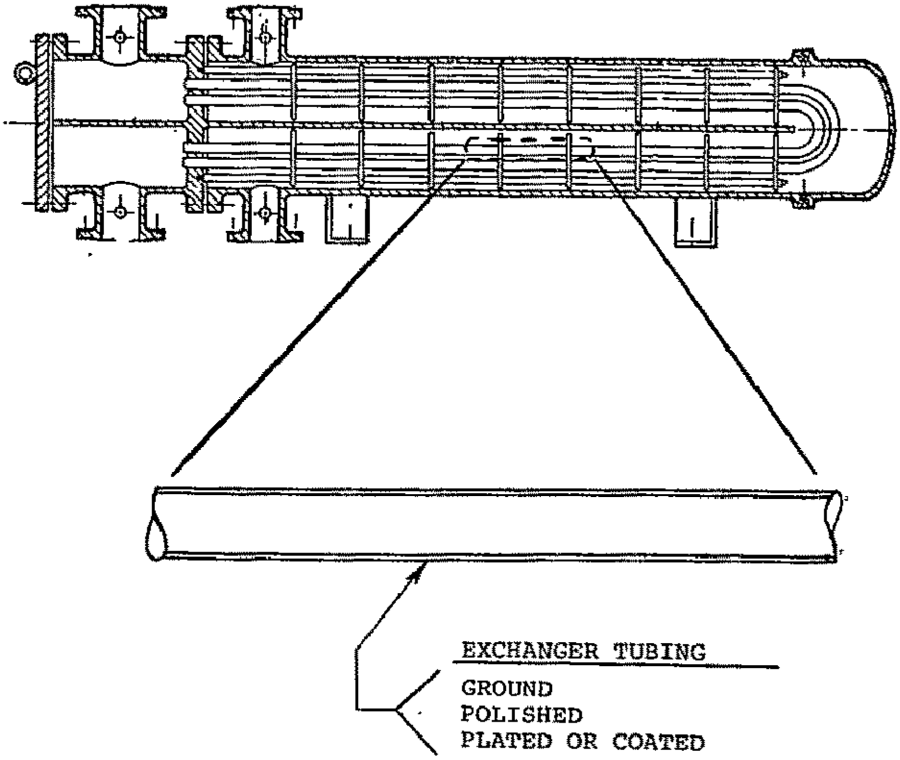


Figure 5-2. Shell and Tube Exchanger with Deposit Resistant Tubes

The heat transfer coefficient for a shell and coated tube exchanger was estimated to be 2260 W/m^2-K. The shell side or salt side coefficient can be obtained by DeVore's method[16]. A shell side coefficient of 4383 W/m^2-K was used based on the manufacturer's[17] design coefficient for 'Hitec storage' in a solar pilot plant. The design used a 0.6 m/s salt velocity. For a 1000 MW(t) heat rate, $2.46 \times 10^4 m^2$ heat transfer surface is required.

Pumping power for the salt and for the water, assuming that a recirculating boiler concept is utilized, accounted for only a small percentage of the total power output. Besides initial cost, the main advantages of this system over scraped surface exchangers are that shell and tube exchanger technology is very well developed, and that a few large exchangers can provide sufficient heat transfer area. Scalability is good, with presently manufactured shell and tube exchangers having surface areas from less that 0.1 m^2 to over 500 m^2 in one shell. Maintenance should be minimal, requiring only an occasional inspection for tube erosion.

In estimating the price of the exchangers, the estimate for the tube bundles was doubled to allow for grinding, polishing, and plating as necessary. A highly polished nickel plating on all tubes was assumed to be required. The exchanger accounts for only a small fraction of the total cost of the system. The balance of the plant is the largest single item and includes instrumentation, steam control valves, water treatment, preheaters, foundations, etc.

5.2.4 Jet Impingement

The jet impingement concept is one where high velocity jets of salt would be directed toward the heat exchange surface to aid in removing the solids build-up. This would be an option if the shell and tube flowby concept has marginal performance, or if flow velocities high enough to wipe the salt from the complete circumference of the tubes cannot be maintained.

The heat exchange surfaces are assumed to be formed from membrane wall material and are polished and coated to decrease salt adhesion. Membrane walls are a common heat transfer surface used in fossil fired boilers. The idea here is to apply developed, commercially available equipment and processes to salt storage. The salt pumping power requirements are not significantly different from a shell and tube design since only two meters of head are required to obtain salt velocities greater than 5 m/s.

The heat transfer coefficient is lower due to both the buildup of layers of solids on the surface and the reduced conductance of the membrane walls as opposed to single tubes. For a membrane wall with a tube size of 0.025 m OD x 0.019 m ID (1" OD x 0.75" ID), a spacing of two diameters and 70 percent fin efficiency, an overall coefficient was assumed to be 2975 W/m^2-K. For 1000 MW(t) a 2.67 x $10^4 m^2$ of heat transfer surface was required. The quantity of metal in the heat exchangers is increased due to both the lower transfer coefficient and the increased weight of the membrane wall structure. In this case, the area per unit volume of exchanger is less than that of a shell and tube unit, requiring a much larger exchanger volume. These factors all lead to slightly higher system costs.

5.2.5 Reflux Boiler Heat Exchanger

The reflux boiler heat exchanger concept utilizes water as an intermediate fluid to transfer latent heat from the molten salt to a conventional heat exchanger where the heat is imparted to the treated power plant water. Direct contact heat exchange between the water and salt provides good heat transfer and prevents fouling of heat transfer surfaces by solid salt deposits. Also, since the thermal energy does the salt pumping, this system offers the possibility of using pure eutectic materials to minimize temperature degradation during discharge of storage. The disadvantages of the system are that all of the condensers and refluxing boilers require large expensive high pressure shells. Pressure cycling of the relux boilers may pose a fatigue problem in thick-walled pressure vessels.

For reflux boilers, there are two transfer coefficients. One is for direct contact of salt and water in the refluxing boiler and the other for condensation of steam on boiler tubes. For direct contact a temperature drop of 3 C° was assumed. Therefore, if 18 C° are allowed overall, a 15 C° Δ T is available for steam condensation. The condensation coefficient was assumed to be 11,356 W/m^2-K, which gives an overall coefficient of 4656 W/m^2-K. A heat transfer surface of $1.19 \times 10^4 m^2$ is required for a heat transfer rate of 1000 MW(t).

The size of the refluxing boiler is based on steam velocity at the salt surface and the residence time of the salt. The required salt rate, assuming 60 percent solidification per cycle, is 5m^3/s for 1000 MW(t) heat rate. The steam rate, calculated using steam properties, is 15.7m^3/s. For 0.07 m/s (1/4 ft/s) steam velocity, the salt surface area requires is 24 m^2. For a horizontal cylindrical tank,

$$A = L \times D \times N$$

$$V = \frac{N}{2} \; \frac{\pi D^2}{2} \; \frac{D}{2} + \frac{L}{2}$$

$$W = \pi D \, (L + D) \, \frac{t}{12} + \rho \times N$$

where,

A = surface area
L = length of tank
D = diameter of tank
N = number of tanks
V = volume of salt in tank (1/2 filled)
W = weight of steel per tank
t = tank thickness = $PD/2S$
ρ = density of steel

Eight cylindrical tanks 2.3 m diameter by 12.2 m long give the required area with the salt residence time of 38 seconds per cycle. Twice the number of tanks are required if one set is filling while the other set is discharging. The total weight of steel required for the 16 tanks was estimated at about 1×10^6 kg.

Self-Pressurizing System--Figure 5-3 is a schematic of a self-pressurizing reflux boiler heat transfer system. Liquid salt is allowed to flow into the reflux boiler because of head differences. After closing the supply valve, water injected into the molten salt flashes to steam quickly. This raises the system above the condensing pressure and opens the steam valve. Condensate from the shell and tube exchanger is continuously pumped through the salt until 50 to 60 percent of the latent heat is removed. Slurry density can be measured ultrasonically or be more easily calculated based upon salt volume and the amount of condensate injected into the salt. At completion of the discharge, the steam valve and condensate return valve are closed to isolate the reflux boiler from the condenser. The pressure balancing valve is opened to relieve excess pressure, and the vented steam is used for feedwater heating at other points in the plant. When the pressure is sufficiently reduced, the salt return valve can be opened and the remaining pressure can be used to push the slurry back to storage for settling and further separation. Recharging the reflux boiler with salt is then started by closing the return valve, venting the remaining pressure and opening the salt supply valve.

All valves in the steam and salt handling system are pressure compensated large bore pintle valves to minimize the external forces necessary for actuation and to facilitate short cycle times. Several reflux boilers may be coupled in parallel to one or more condensers to provide a continuous flow of steam to the condensers. In the design of the reflux boiler, it is advantageous to have a large salt surface area to minimize steam velocities leaving the surface and to reduce carryover. It is also necessary to minimize the ullage space to reduce

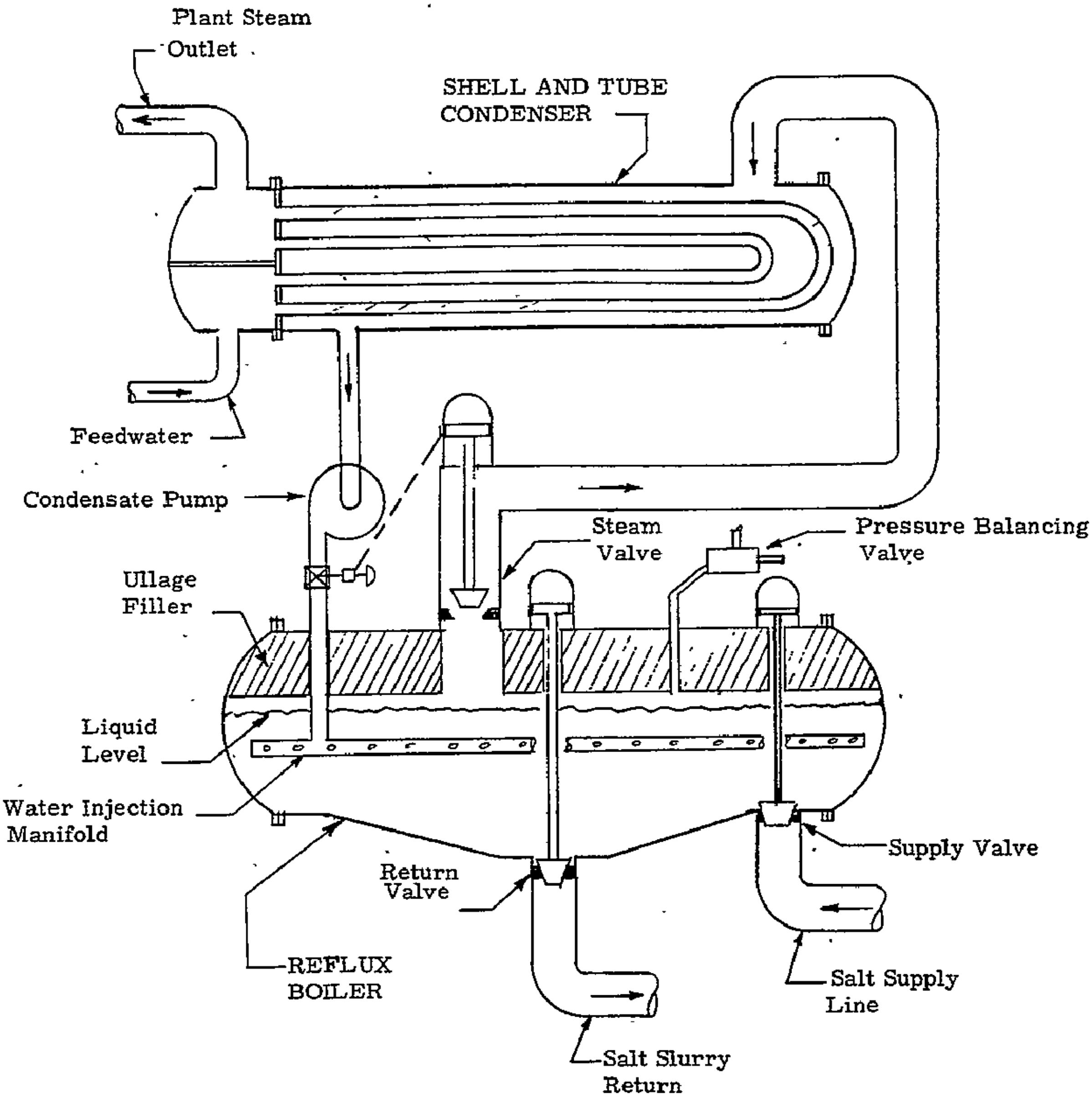


Figure 5-3. Self-Pressurizing Reflux Boiler

the amount of steam blown down at the end of each discharge cycle. To accomplish these goals within a pressure vessel, it is necessary to include an incompressible filler in the ulllage space to minimize the free ullage volume. With the free ullage volume equal to 20 percent of the salt volume, assuming 60 percent salt solidification, more than 8 percent of the extracted energy would be blown down at the end of every cycle. With the free ullage space equal to 8 percent of the salt volume, less than 3 percent of the latent heat would be blown down. These low ratios would improve if the system temperature was lowered from the assumed 303°C saturation conditions.

Continuous Salt Flow Reflux Boiler--The reflux boiler can be used more effectively by operating on a continuous basis if a high pressure source of salt is available. This has the advantages of reducing the number of reflux boilers required, reducing the high pressure steam and salt valving requirements and eliminating the flow surges in the salt supply and return lines. Figure 5-4 illustrates a system where the salt is pumped up to the working pressure, the latent heat is extracted and the salt slurry is throttled back down to ambient pressure through an orifice and control valve. Assuming that a saturation temperature of 303°C must be reached, that 60 percent of the salt is solidified, and that the combined pump plus motor efficiency is 60 percent, then approximately 7.5 percent of the thermal output must be put back into the system as electric power to drive the pump. If the power plant efficiency is assumed to be 30 percent, the net decrease in electric power output is 25 percent. One characteristic of steam is that the pressure increases very rapidly with increasing temperature. For the pumped salt system, the pump work increases linearly with system pressure, but electric power generation efficiency increases with temperature. Therefore, this system would work much more efficiently at lower pressures and temperatures and would become extremely inefficient at temperatures above 300°C.

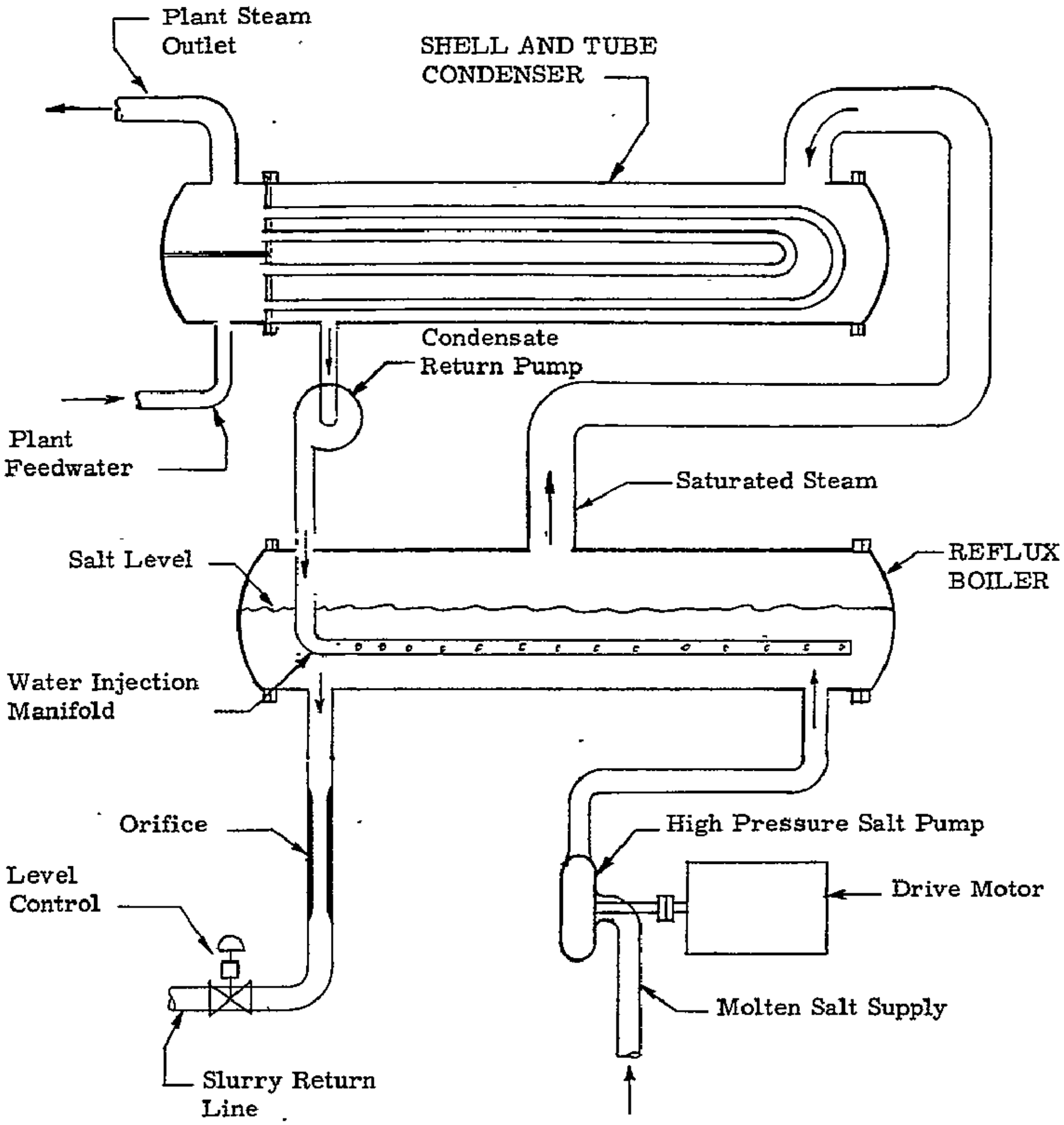


Figure 5-4. Continuous Salt Flow Reflux Boiler

To decrease the amount of pump work required to operate the continuous salt flow reflux boiler, a turbine may be used to recover the hydraulic head in the discharge slurry stream. The turbine is a pump run in reverse which can be directly coupled to the high pressure pump. A system of this type is shown in Figure 5-5. Using the same pressures and slurry densities as in the previous systems and assuming an expander/turbine efficiency of 80 percent, the pumping power requirements can be cut to 4.1 percent of thermal output. Assuming an electric generation efficiency of 30 percent, the electric power required to drive the salt pumps is 14 percent of the total electric output.

Reflux Boiler, Open Cycle--A basic assumption previously made was that steam passed through the turbine must be treated to the exacting standards of power plant feedwater; this need not always be true. Since heat from storage will generally be needed during peak plant hours (when all turbines may be operating at fullest capacity), separate turbines may be necessary to handle the discharge steam from the storage system. If a larger thermal storage system has a turbine dedicated solely to it, the water treatment standards may not be as exacting. Salt carryover might be sufficiently minimized by good steam separators and by acceptably clean and noncorrosive water obtained directly from the reflux boilers. This would eliminate approximately one-third of the high pressure shells required and all of the condensing tube surfaces plus their associated temperature and pressure losses. Assuming the temperature could be increased by approximately 15 C° by going to the open cycle reflux boiler, the saturation pressure could be increased from 6.55 to 8.27 MPa (950 to 1200 psia) with an accompanying increase in thermal plant efficiency of approximately 3 percent.

The reduced cost of the heat exchangers and the slight improvement in cycle efficiency appear to make this system the most economical to build and operate.

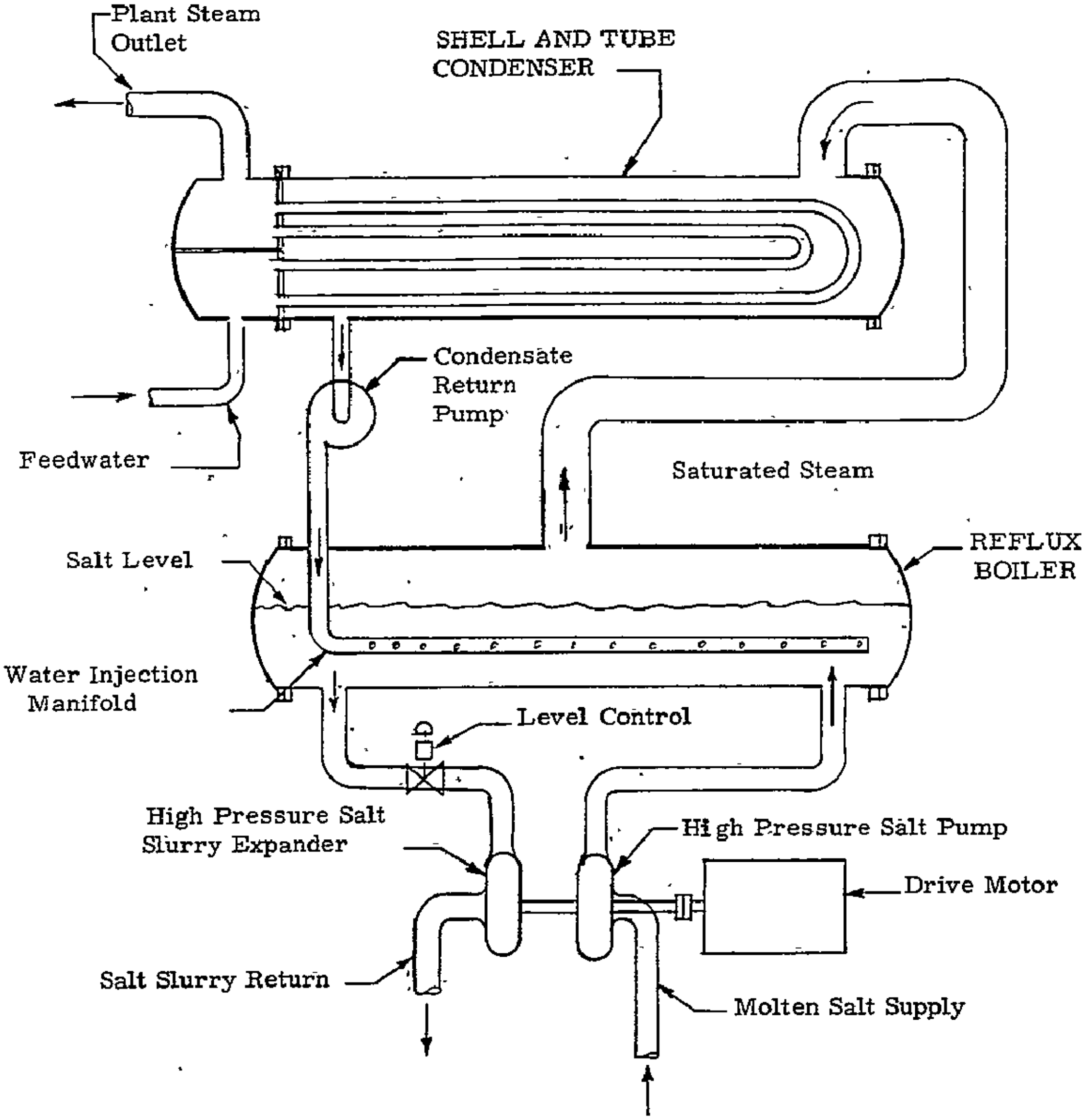


Figure 5-5. Continuous Salt Flow Reflux Boiler with Hydraulic Head Recovery

5.2.6 Tumbling Abrasive

This system consists of a U-tube heat exchanger tube bundle, around which is placed a drum carrying abrasives to the top of the bundle. As the drum is rotated, the abrasives rain down over the tubes and remove the salt from the tubes by impact and abrasion. The abrasive material probably would be steel shot. Shot size and rate of transport would be proportional to the strength of the salt-to-tube bond and the heat flux. This system would require greater tube spacing than that of standard shell and tube exchangers to permit free passage of the shot and would have a lower heat transfer coefficient due to salt buildup on the lower surfaces of tubes where the shot would not be effective in removing the deposits.

Higher exchanger costs, lower heat transfer rates and possible rapid erosion of the exchanger tubes makes this type of system less attractive than the shell and tube flowby or jet impingement systems.

5.2.7 Passive System (Reference System)

The modeled passive system assumed that enough 3/4-inch OD tubes would be placed into a storage tank to provide 1000 MW(t) of energy for six hours, at the end of which time 100 percent of the salt would be converted to a solid. Calculations showed that the required tube spacing was on the order of 5.7 cm (2-1/2 inches). This requires a very large investment in tubes and creates a large manifolding and pressure balancing problem. These costs are compensated by the ability of the system to recover 100 percent of the latent heat, thus reducing both tankage and media requirements. Further savings are accrued by having the same in-tank exchanger perform both charging and discharging functions.

Disadvantages of the passive system include the tremendous manifolding problem from the number of pressure tight tube-to-tube welds required and from flow balancing. Flow velocities through the tubing would be less than 0.3 m/s thus having very low pressure drops. Orifices would be required in most lines to provide both pressure differences and reasonably high velocities in the main steam lines. These problems, plus difficulties with large variations in heat rate, have not been considered in system prices.

The equations for sizing the passive tube-intensive system are derived from the heat rate and heat storage equations, given by

$$Q = \rho h_f \, \pi \, x_s \, (2r_o + x_s) \, L \tag{7}$$

$$\dot{q} = \frac{2 \, \rho \, k_s L \cdot \Delta T}{\ln \dfrac{(ro + X_s)}{ro}} \tag{8}$$

where,

Q = heat stored

$\dot{q}$ = heat rate

ρ = solid salt density

h_f = salt heat of fusion

X_s = salt thickness around the tube

r_o = outside tube radius

L = total tube length

k_s = salt thermal conductivity

$\Delta T = T_{salt} - T_{steam}$

Solving the equation and eliminating X_s we get

$$\ln\left(1 + \frac{Q}{L \cdot \rho h_f \cdot \pi r_o^{\,2}}\right) = \frac{4\pi k_s \cdot \Delta T \cdot L}{\dot{q}} \; . \tag{9}$$

Equation (9) is solved for L, assuming that the heat rate at the end of the discharge cycle is the design heat rate (C = 1000 MW(t)) and heat stored is the product of storage time (6 hours) and heat rate. The tube thickness or gauge is determined from the working pressures.

5.3 RECOMMENDED CONCEPTS

The comparative analysis of active heat exchange systems indicate that the most economical systems are those that employ the most compact heat transfer surfaces. The compactness of the shell and coated tube heat exchanger and the high heat transfer rate associated with the direct contact reflux boiler concept are the two features that appear to be the most promising for large-scale implementation, i.e., 1000 MW(t) rate and 6-hour capacity. Two systems that embody these features are recommended for further study:

- a coated tube and shell flowby system, and
- a direct contact reflux boiler.

The coated tube and shell flowby system capitalizes on commercial availability of tube and shell heat exchangers and assumes successful development of a non-stick finish for the exchanger tubes. Studies and discussions with consultants have indicated that there is a good possibility of achieving major reductions in the adhesion strength of solid salts to the cool metal surfaces of the tubes. One technique suggested is polishing the heat transfer surfaces to minimize the mechanical bonding of the salt to the surface. Another technique involves the application of a thin coating of an amorphous material or a material with a crystalline structure different from, yet compatible with, the salt. This might reduce bonding strength on the microscopic scale.

Currently, the possibility of a bright nickel plating on heat exchanger tubes is being investigated. The plating process and additives introduced into the plating material can have dramatic effects on the result. Thus, an intensive look into plating and metal finishing literature may yield information on the most effective means of obtaining clean, smooth nickel coatings. The most commonly added agents in nickel baths are those used for production of bright nickel deposits. Such brightening agents smooth surface imperfections on the exchanger tubes. Since imperfections are the points at which solid salt can adhere most readily, the smoothing introduced by brighteners may inhibit adhesion. Any such plating material must, of course, be chemically compatible with the salt media. One crucial consideration is how the salt crystal growth will affect the wear of surface finish.

The second system recommended for further study is the direct contact reflux boiler. Although two heat exchange processes are required here (salt to water/steam and condensing steam on tubes), the individual thermal resistances are so low that their sum is less than the thermal resistance of most liquid-to-pipe-to-pipe-to-liquid exchange processes. Consequently, a high overall heat transfer coefficient can be continuously maintained. Furthermore, the system can be designed to operate without salt transfer pumps. This is accomplished by gravity filling the refluxing boiler and subsequently expelling the slurry with residual steam pressure.

Improved thermal efficiency through elimination of the heat exchangers can be achieved in a system where the heat transfer medium is the working fluid. The lifetime of this type of system is directly related to the content of salt remaining in the working fluid as it enters the turbine. The salt content can be minimized by good separator design.

5.4 RECOMMENDED EXPERIMENTS

The first recommended experimental module would test a series of flowby heat exchange processes where molten salt is pumped over specifically prepared heat exchanger tube surfaces. The purpose of the test would be to determine the effects of various surface finishes and coatings, flow velocities, and temperature conditions on solid salt buildup on heat exchanger tubes. It is expected that a small, easily-modified apparatus would be built to provide rapid qualitative assessment of these parameters and to provide heat transfer data. Should bulk flow of salt parallel or perpendicular to the tubes prove inadequate, jet impingement of the flow would be a third alternative.

The second recommended experimental module would test a scale model of the refluxing boiler. A small high pressure apparatus would be built to measure the heat transfer rates attainable, the proper point of injection of water into the salt, the dynamics of the vapor-salt heat transfer interface with special emphasis in the amount of salt carryover onto the condensing surfaces. Salt carryover could be measured by removing and analyzing small samples of the condensate. Another phenomenon of interest is the formation of solids in the melt as the heat is extracted. How well the solids settle, agglomerate and the ultimate slurry density attainable are important experimentally-determined factors. Water carryover with the discharged salt and possible chemical decomposition are other facets of the total system that would be reviewed to determine salt and heat transfer fluid compatibility.

The remainder of the tasks are dedicated to designing, building, testing and evaluating the viability of these two concepts. This work will be documented in a final report to be completed about midyear 1979.

APPENDIX A

TES COST EVALUATION

THERMAL ENERGY STORAGE SYSTEM COST EVALUATIONS

Thermal energy storage (TES) costs given in this document are for the state-of-the-art (SOA) heat of fusion storage systems. The heat of fusion TES system is now in a developmental stage. With future development, an improvement in cost and cost prediction is expected. Therefore, the costs cited here should not be compared with the costs of a well-developed technology, such as sensible heat storage. Figures A-1 and A-2 depict qualitatively the correlation between SOA, cost and time. Curves (a) and (a') in these figures are for a typical sensible heat storage system. Curve (a) shows that the sensible heat TES system is essentially mature and little further development can be expected. Correspondingly, the cost reduction potential is low, as shown by curve (a'). Curves (b) and (b') are for the latent heat storage system. The technology or SOA advancement for latent heat TES is in its infancy and considerable improvement can be expected with continued research and development. Correspondingly, the cost reduction potential is high for the latent heat system. This fact provides the impetus for continued research and development.

From the above, it is clear that care should be taken to incorporate the SOA technology into the comparative system economics. A successful completion of this active heat exchange experimental program should provide sufficient design information to refine the costs given in this document.

TES systems include the storage medium, the containment for the medium, heat exchangers, circulation equipment for working fluid and storage medium, instrumentation and control for the storage medium handling and other equipment. Storage system costs will include those of all the above components as well as foundation and site preparation costs. The TES system integrated with a solar-thermal electrical generating plant could require a dual injection turbine if

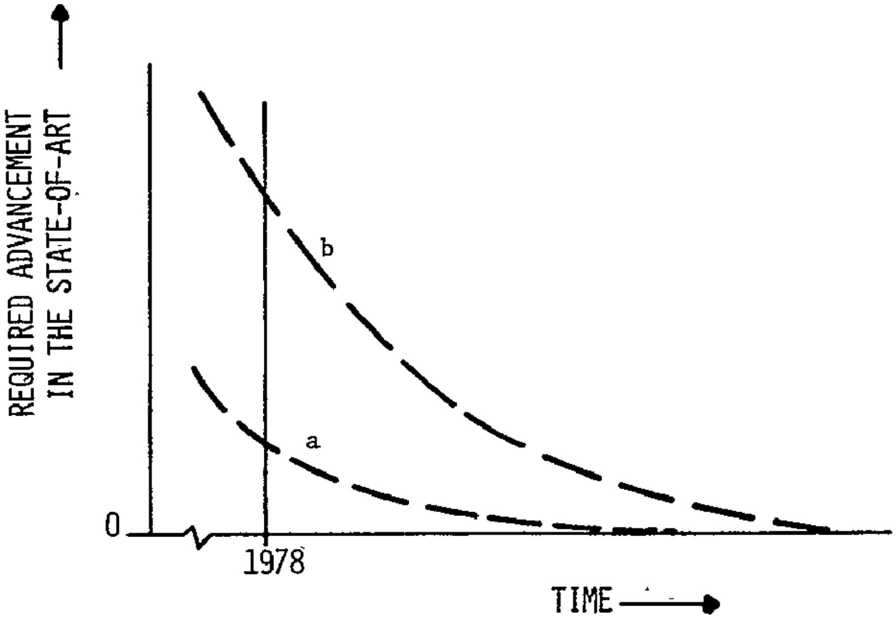


Figure A-1. Correlation of Technological Advancement with Time

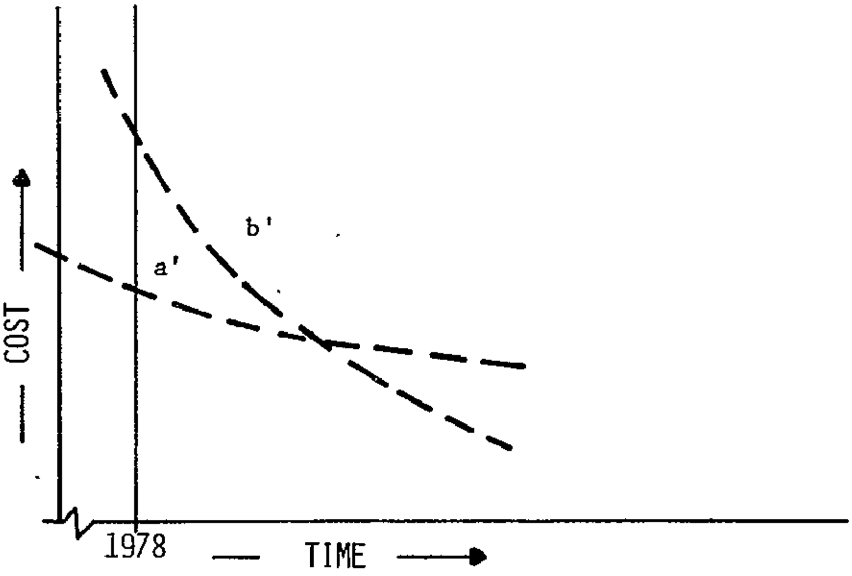


Figure A-2. Correlation of System Cost with Time there is a large temperature/pressure mismatch between direct solar-generated steam and storage-generated steam. Therefore, there will be another Δ- cost for the turbine added to TES costs.

The TES system capital costs may best be classified as rate-related and capacity-related costs. This helps in identifying storage systems in terms of duration of storage. For example, a system with high rate-related cost and low capacity cost would become economical for longer storage hours. The rate-related costs include those of heat exchanger circulation equipment, instrumentation and control, and Δ- turbine costs, if any. The capacity costs include those of storage medium containment, support equipment, foundation and site preparation. Part of the site preparation costs, like heat exchanger foundation, etc., may be assigned to rate-related costs. However, a major portion is capacity-related costs, which include storage building, lighting, dikes, emergency containment structure, safety protection equipment, etc. In addition to rate and capacity costs, there are recurring operating and maintenance costs. The recurring costs were only qualitatively assessed for the various concepts.

For estimating costs of storage systems, methods are required to scale up or down a set of estimates to a different design size. Methods generally used are based on expressing component costs as a percentage of major subsystem or total cost and using the same percentage for all design sizes. Some authors use costs expressed in \$/kg (\$/lb) of storage medium or \$/kWh of storage capacity.

A six-tenth factor, which is an empirical relationship between cost and size of the facility, is used for order-of-magnitude or study estimates[18]. According to this relationship, as facility size increases, its cost increases thus:

$$\frac{\text{cost}_1}{\text{cost}_2} = \left(\frac{\text{size}_1}{\text{size}_2}\right)^n \quad \text{or} \quad \frac{\text{cost}_1/\text{size}_1}{\text{cost}_2/\text{size}_2} = \left(\frac{\text{size}_1}{\text{size}_2}\right)^{n-1}$$

where n = 0.6. An exponent of 0.7 is often applicable and others may occur under various circumstances.

For the present study, an equation of the type described above was used for scaling costs of some components of the TES system. The exponent was determined by plotting actual acrued costs for the 10 kWh(t) and 1330 kWh(t) experimental TES units built by Honeywell and detailed cost estimates for a 42 MWh(t) pilot scale TES unit. The detailed cost estimates were developed under the Honeywell Pilot Plant Solar Central Receiver Program. The TES system for these units was a latent heat storage system using a $NaNO_3$-NaOH mixture and scraped surface heat exchanger for vaporizer. Figure A-3 shows storage installed costs per unit capacity versus storage capacity on a logarithmic plot based on these actual acrued costs. The slope of the curve, which is the exponent (n-1) in the equation above, is determined to be -0.34. This exponent is used for scaling of costs other than salt and tankage. Separate equations are developed for tankage cost (which is a function of salt energy density) and for salt cost (which is a function of salt heat of fusion and specific salt cost).

A cost model is developed to estimate TES installed cost for a six-hour storage unit as functions of storage capacity, salt cost, and salt heat of fusion and using the scaling law described above. The costs scaled were based on the pilot plant cost estimates.

The cost model establishes a relationship between specific salt cost, heat of fusion, and TES system cost. Results of the model were used for salt screening based on system cost. In evaluating heat exchanger concepts, costs were expressed as rate-related and capacity-related costs for a fixed storage time and heat rate. A simple sensitivity analysis, presented later in this section, shows the influence of storage time and pressure on system costs with different heat exchanger concepts.

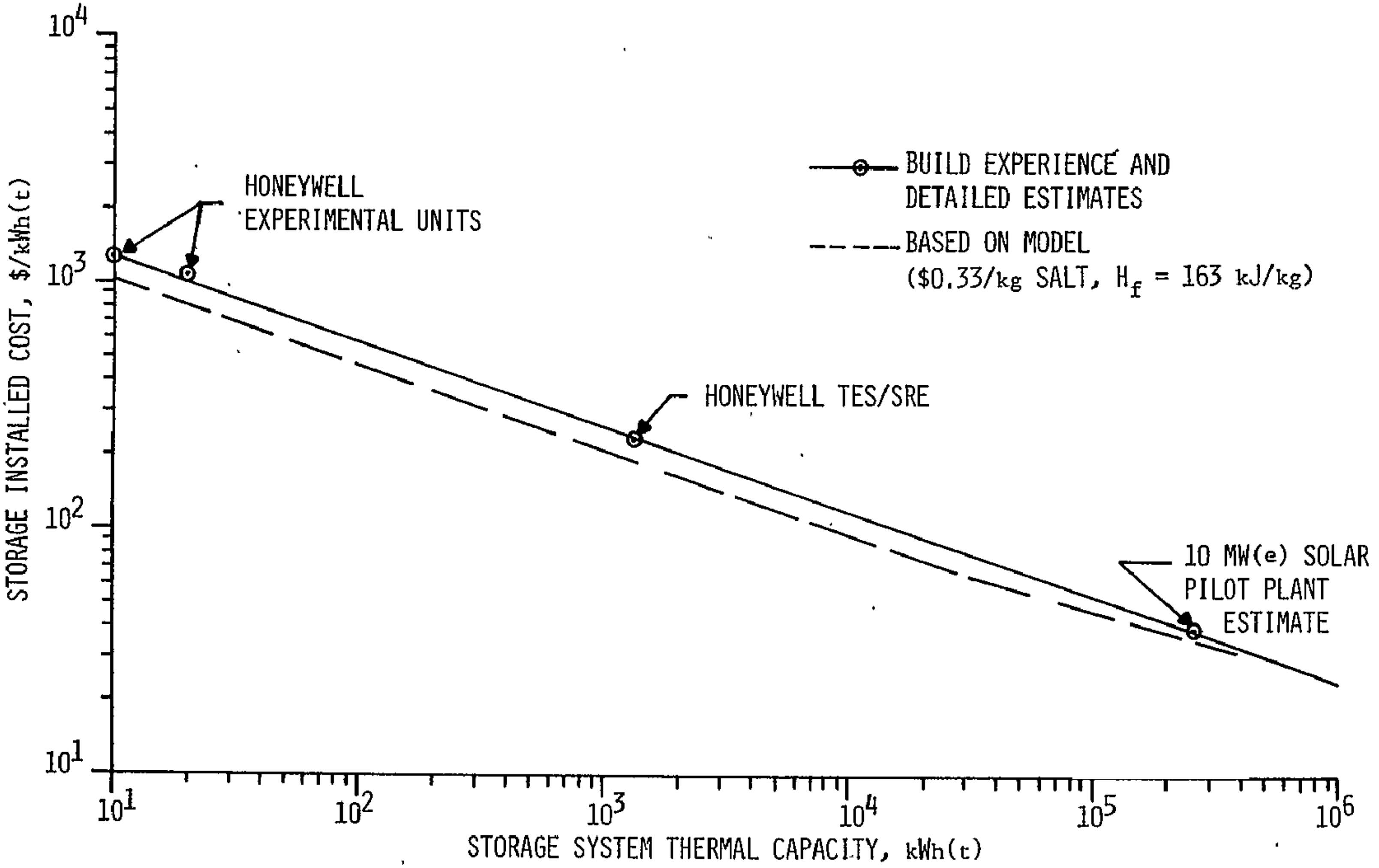


Figure A-3. TES System Installed Costs

Cost Model Development

The total system installed costs are given by:

TES System Cost = Tankage Cost + Salt Cost + Foundation and Site Preparation Cost + Salt Support Equip. Cost + Rate Related Costs

The rate-related costs include heat exchanger, circulation equipment for steam and salt, and instrumentation and control. The salt support equipment cost and rate-related costs are lumped as other costs, and a 0.34 exponent is used for scaling to other design sizes. The tankage cost is a function of capacity, salt energy density and tankage material. A mild steel containment is assumed for all salts. Corrections for other containments are made later for selected salts not compatible with mild steel. The tankage costs, C_t, is typically given by:

$$C_t(\$) = kW^a$$

where,

W = weight of tankage material (kg),
k = tank cost constant = 47,
a = tank cost exponent = 0.8.

The weight (W) for mild steel is (based on estimates of Brown Tank Co., Minneapolis):

$$W = 2.61 \times 10^4 D\ (H + 0.8D)\ (t + x)\ [\mathrm{kg}]$$

where

D = tank diameter (m),

H = tank height (m),
t = average shell thickness (m),
x = thickness allowance for corrosion, supports, etc. $\cong 5.1 \times 10^{-3}$ m (0.2 in.)

The thickness (t) is estimated from,

$$t = 2.45 \frac{\rho H D}{S E}$$

where ρ is salt density, S is allowable stress (1.79×10^{8} N/m^2 or 26,000 psi), E is the joint efficiency factor (0.8). For an H/D ratio of β, the tank diameter is

$$D = \left(\frac{4V}{\pi\beta}\right)^{1/3} = \left(\frac{4}{\pi\beta} \cdot \frac{3600\ Q}{N\rho H_f}\right)^{1/3}$$

where

Q = total storage capacity (kWh(t)),
N = number of tanks,
ρ = salt density = 1.92×10^{3} kg/m^3 (120 lb/ft^3)
H_f = salt heat of fusion kJ/kg.

Defining

$$R = Q/10^{6} \text{ and}$$

$$F = \left(\frac{R}{N\rho H_f}\right)^{2/3}$$

the tank cost equation in \$/kWh(t) becomes

$$C_t\ (\$/\text{kWh(t)}) = 163.8\ \frac{N}{R}\ [F(43.8\rho F + 5.1)]^{0.8}$$

The salt cost is given by

$$C_s\ (\$/\text{kWh(t)}) = \frac{\hat{C}_s}{H_f} \cdot 3600$$

where

$\hat{C}_s$ = salt cost in \$/kg,
H_f = salt heat of fusion in kJ/kg.

The foundation and site preparation costs are estimated from

$$C_F(\$/\text{kWh(t)}) = \frac{730}{H_f} \cdot (R)^{-0.34}$$

The other costs are estimated from

$$C_o\ (\$/\text{kWh(t)}) = 11.85\ R^{-0.34}$$

The total TES cost is given by

$$\text{TES cost}\ (\$/\text{kWh(t)}) = C_t + C_s + C_F + C_o$$

A typical breakdown of other costs for 10^6 kWh(t) capacity (R=1) is as follows:

Salt Support Equipment	= 1.10 \$/kWh(t)
Instrumentation and control	= 0.67 \$/kWh(t)
Circulation equipment (piping, valves, etc.)	= 4.52 \$/kWh(t)
Heat exchangers and manifolds	= 3.66 \$/kWh(t)
Insulation cost	= 2.20 \$/kWh(t)

Results

The parametric analysis of TES system costs with storage capacity, salt cost and salt heat of fusion as parameters is presented in Figures A-4 through A-7. Figure A-4 shows storage installed costs in \$/kWh(t) versus storage capacity with salt cost as parameter for a salt having heat of fusion of 150 kJ/kg (65 Btu/lb). Notice that, at low storage capacities (<10 MWh), the effect of salt cost on total cost is minimal. The hardware cost controls the TES cost at low capacities. At high capacity, the salt cost becomes significant. For example, in Figure A-4, for a storage capacity of 1000 MWh(t) and salt costs of \$2/kg and \$0.30/kg, the TES system costs are \$66/kWh(t) and \$27/kWh(t), respectively. But for a storage capacity of 1 MWh(t) and salt costs of \$2/kg and \$.30/kg, the TES system costs are \$240/kWh(t) and \$200/kWh(t). The effect of salt heat of fusion and salt cost on storage system costs is shown in Figure A-8. The storage capacity was fixed at 1000 MWh(t). The plot shows that with a \$0.10/kg and 190 kJ/kg (\$1.89/kWh(t)) salt, the system cost will be \$20/kWh(t). The same system cost of \$20/kWh(t) will be obtained with a \$0.50/kg and 225 kJ/kg (\$8.00/kWh(t)) salt. Therefore, eliminating salts based solely on \$kWh(t), salt cost is not a good criterion. Figure A-9 is a plot of system cost versus salt cost for a 175 and 250 kJ/kg salt energy density with storage capacity as parameter. To obtain storage system costs of less than \$20/kWh(t), the storage capacities with any salt cost should be greater than 1000 MWh(t) with the present hardware costs. The plot of salt cost versus salt heat of fusion with storage system costs as parameter is a useful plot for evaluating salts based on system cost criterion.

COST EVALUATION OF HEAT EXCHANGER CONCEPTS

To take into account the total system cost implications of the basic heat exchange concepts, a preliminary system design and cost estimate was made based on the weights of the materials. Each of the systems was designed around the conditions stated in Subsection 5.1.

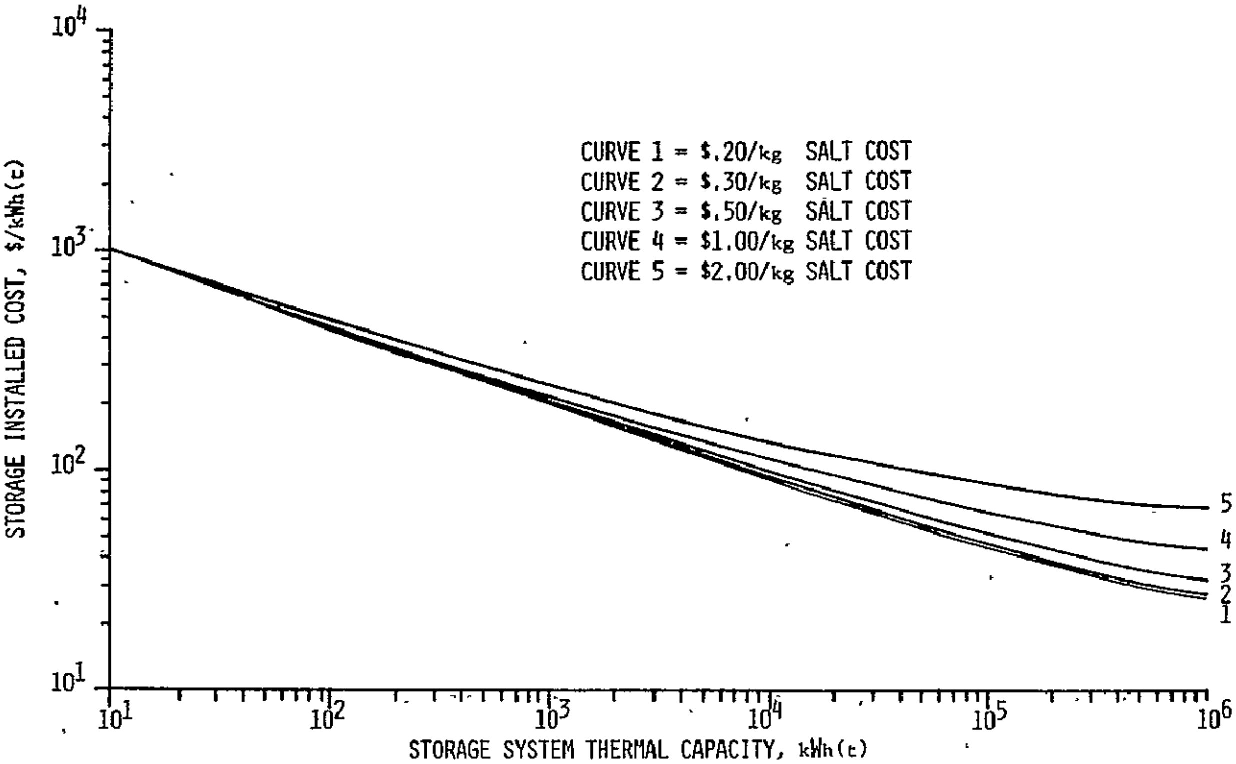


Figure A-4. TES Installed Costs vs. Capacity (ΔH_f = 150 kJ/kg)

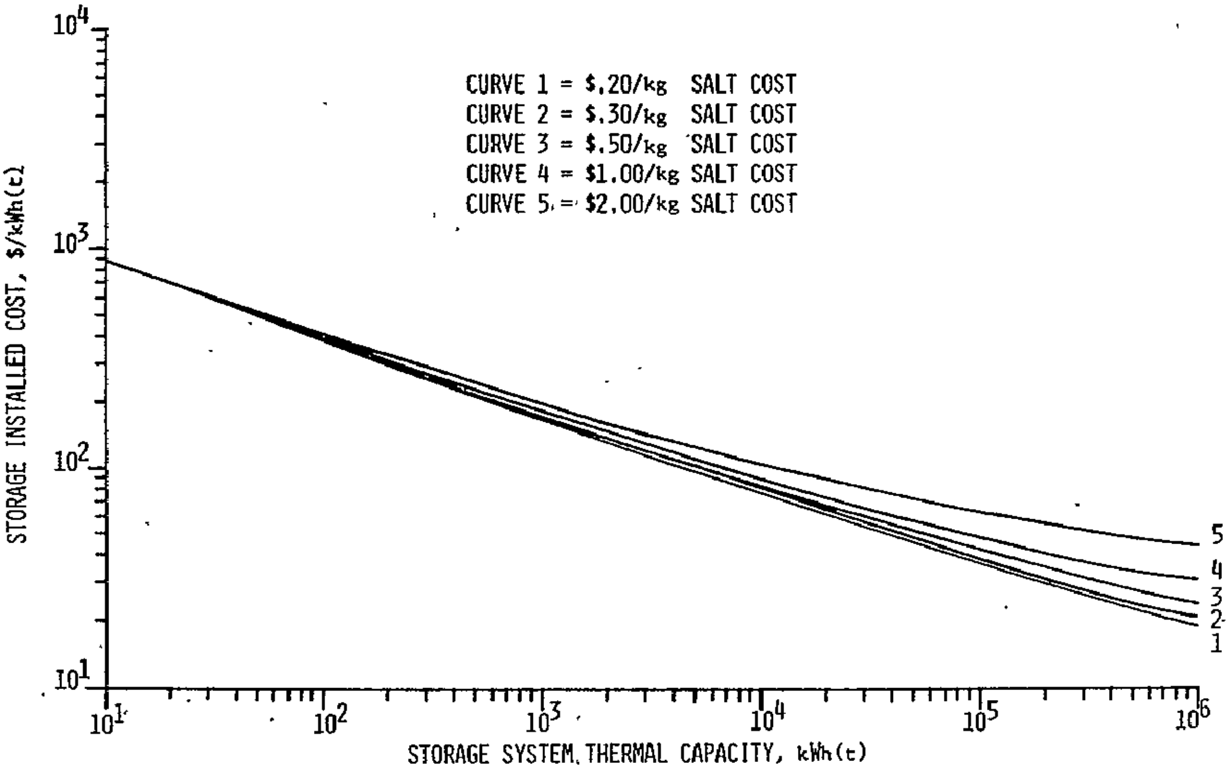


Figure A-5. TES Installed Costs vs. Capacity (ΔH_f = 250 kJ/kg)

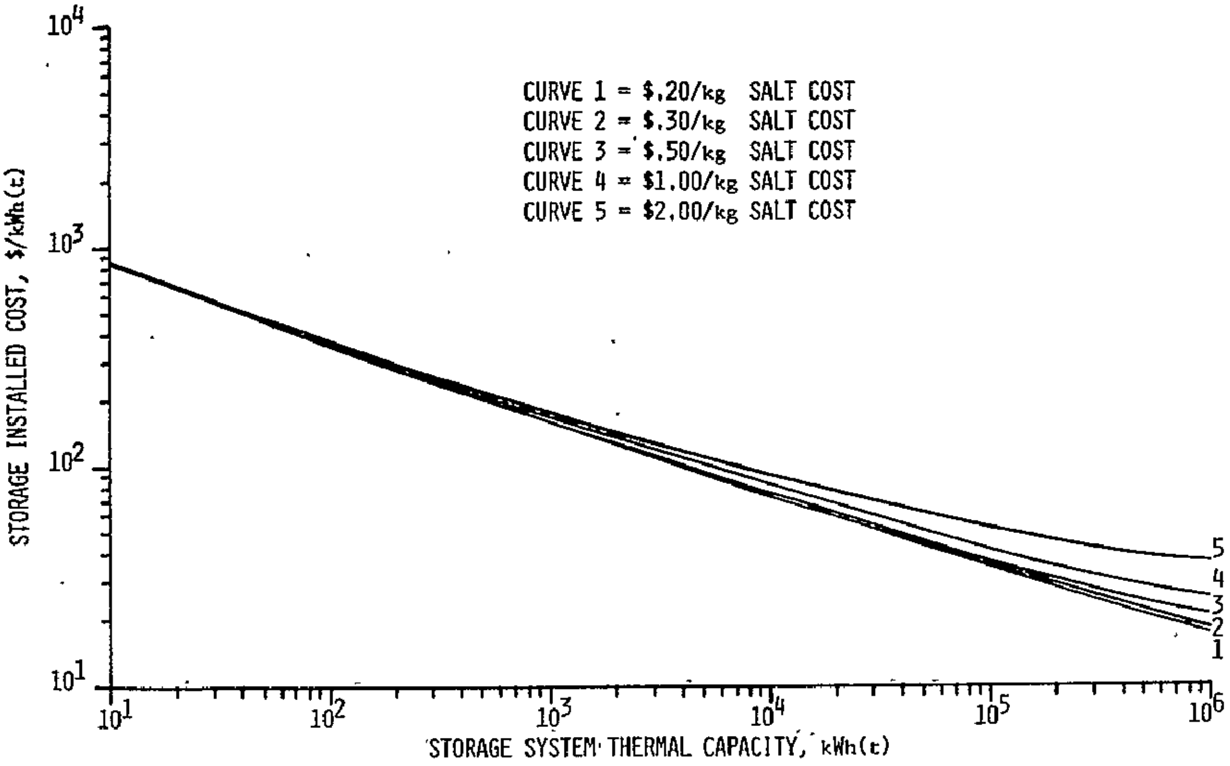


Figure A-6. TES Installed Costs vs. Capacity (ΔH_f = 350 kJ/kg)

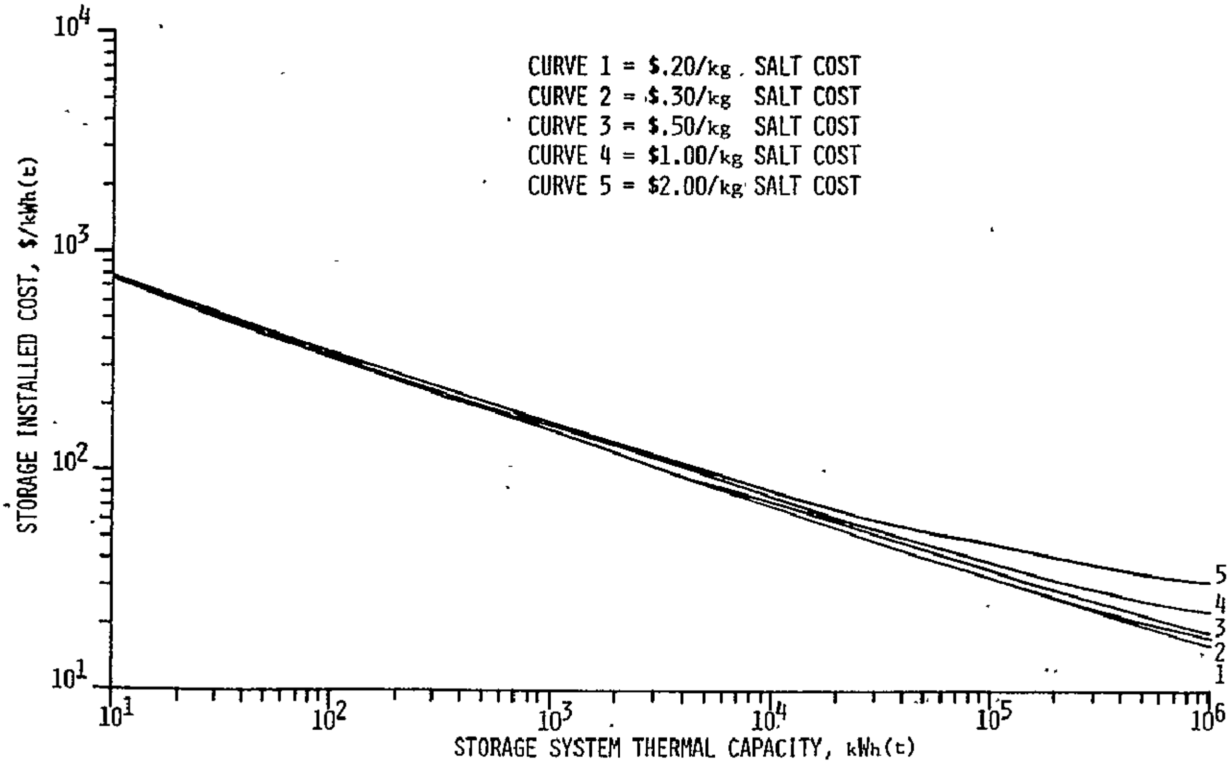


Figure A-7. TES Installed Costs vs. Capacity (ΔH_f = 450 kJ/kg)

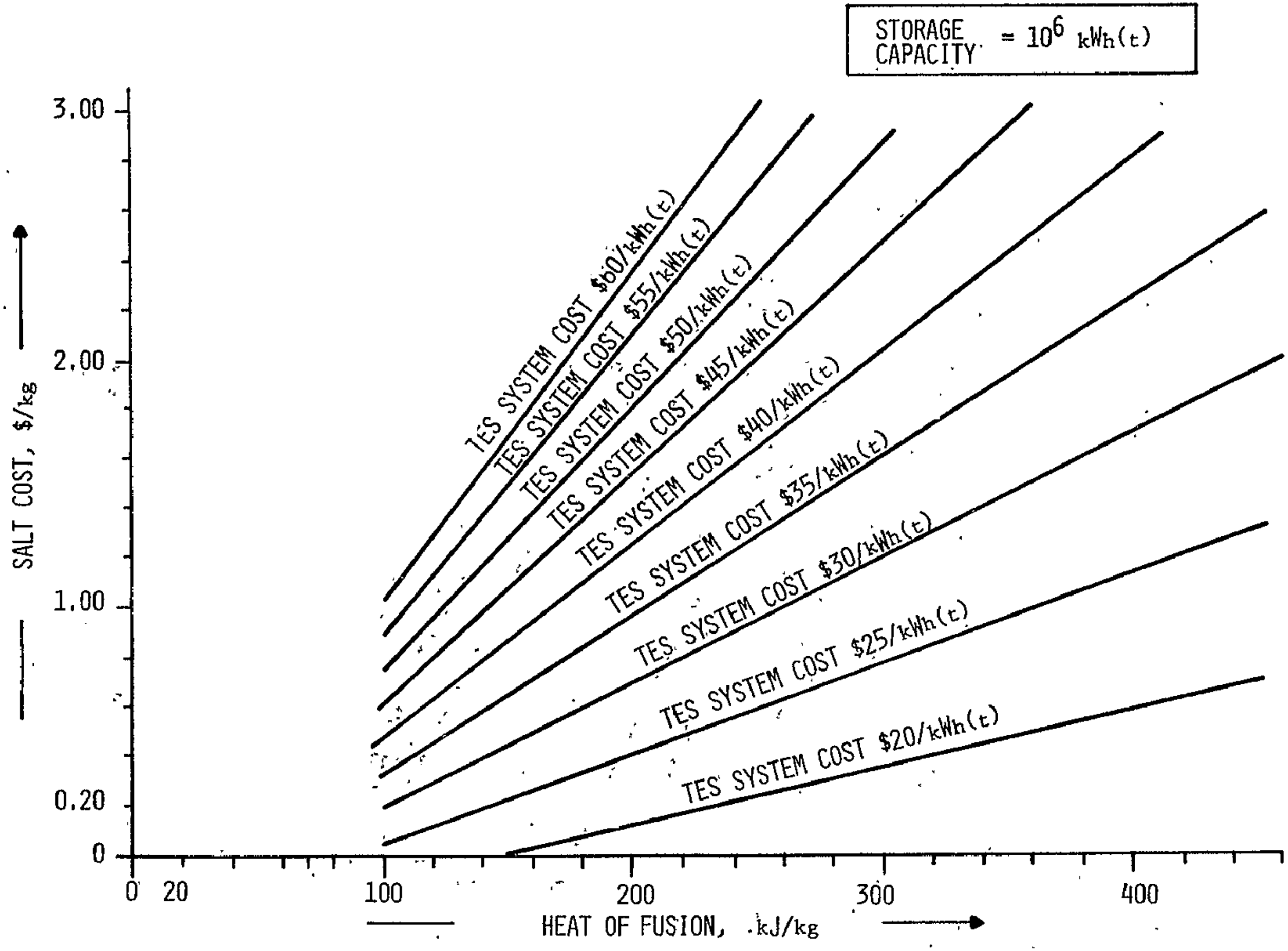


Figure A-8. Phase Change TES System Cost Curve

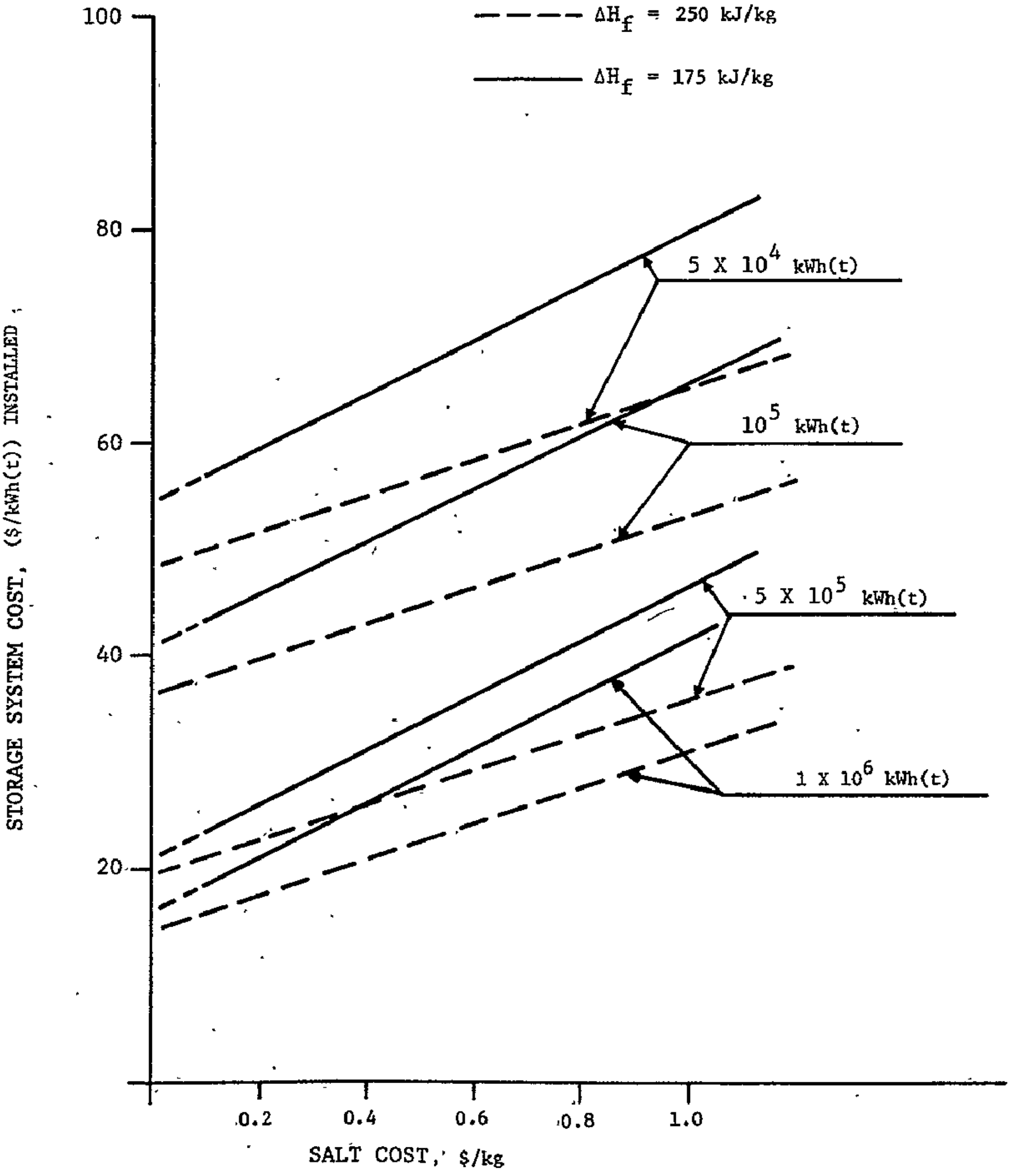


Figure A-9. TES System Cost versus Salt Cost

The costs are expressed as capacity and rate-related costs. The capacity-related costs for all active systems are essentially the same, except for the external scraper concept where the number of tanks is determined by the experimentally obtained value of tank top heat rate. A 75 percent utilization factor was used for all active systems, and a 100 percent factor was used for passive systems. The heat exchanger and manifolding costs are determined from the weight of steel used for manifolds. The following installed costs were used:

Tube	= \$2.09/kg
Tube (nickel coated)	= \$4.41/kg (typical cost)
Tube assembly (includes heaters, etc.)	= \$4.60/kg
Membrane wall	= 4.52/kg (typical weight 1.5 kg/m
Headers and manifolding	= \$7.38/kg
External scraper	= \$517/m^2 (from 85 percent learning curve)
Internal scraper	= \$4305/m^2 (Votator quotation)
Salt	= \$0.22/kg
Tankage (35.7 m x 12.2 m)	= \$1.75 x 10^6 (Brown Tank Co. est.)

The cost of the steam condensation system was estimated at \$1.10/kWh(t). The heat transfer coefficient for transferring heat from condensing steam inside tubes to the melting salt outside the tubes is about 511 W/m^2-°K. This was based on our experimental and analytical studies on the Solar Pilot Plant program. For a charge rate of 1000 MW(t) and a 19 C° temperature drop, 1.27 x 10^7 m^2 of heat transfer surface is required. The 1-inch O.D. tube (1.04 kg/m) has a surface of 0.08 m^2/m, and at \$4.60/kg for tube assembly, the cost of the condenser is \$60.5/m^2. The total cost for the condenser system is \$6.6 x 10^6 or \$1.1/kWh(t) stored.

The cost of vaporization systems for different heat exchanger costs was based on the weights of heat exchangers (see Section 5.0) and the costs indicated above.

COST SENSITIVIY ANALYSIS

The heat exchanger concepts were evaluated for the particular set of conditions of steam discharge at 6.5 MPa/281°C, 1000 MW(t) heat rate, and a storage time of six hours. A cost sensitivity analysis was performed to determine the effects of storage time, heat rate and steam conditions on the selection of heat exchanger concepts.

As storage capacity decreases, the salt cost in \$/kWh remains essentially constant, while tankage and other capacity-related costs will increase according to the scaling laws previously discussed. The rate-related costs are not affected. The system cost in \$/kWh will go up as storage time decreases because:

$$\text{TES Cost} = \text{Capacity cost} + \frac{1}{t} \cdot \text{Rate cost.}$$

Figure A-10 shows heat exchanger cost versus storage time for a given heat rate. The storage time does not affect the heat exchanger costs for active heat exchanger concepts. However, for passive tube intensive systems (current), heat exchanger costs in \$/kWh decrease with time of heat extraction. This is because, in a passive system, decreasing the extraction time results in a decrease in salt buildup on tubes and an increase in effective heat transfer coefficient. The dotted curves show the effect of tube gauge or decrease in pressure on the cost of the tube-intensive (passive) concept. Figure A-11 shows the partial TES cost in \$/kWh(t) as a function of storage time. With

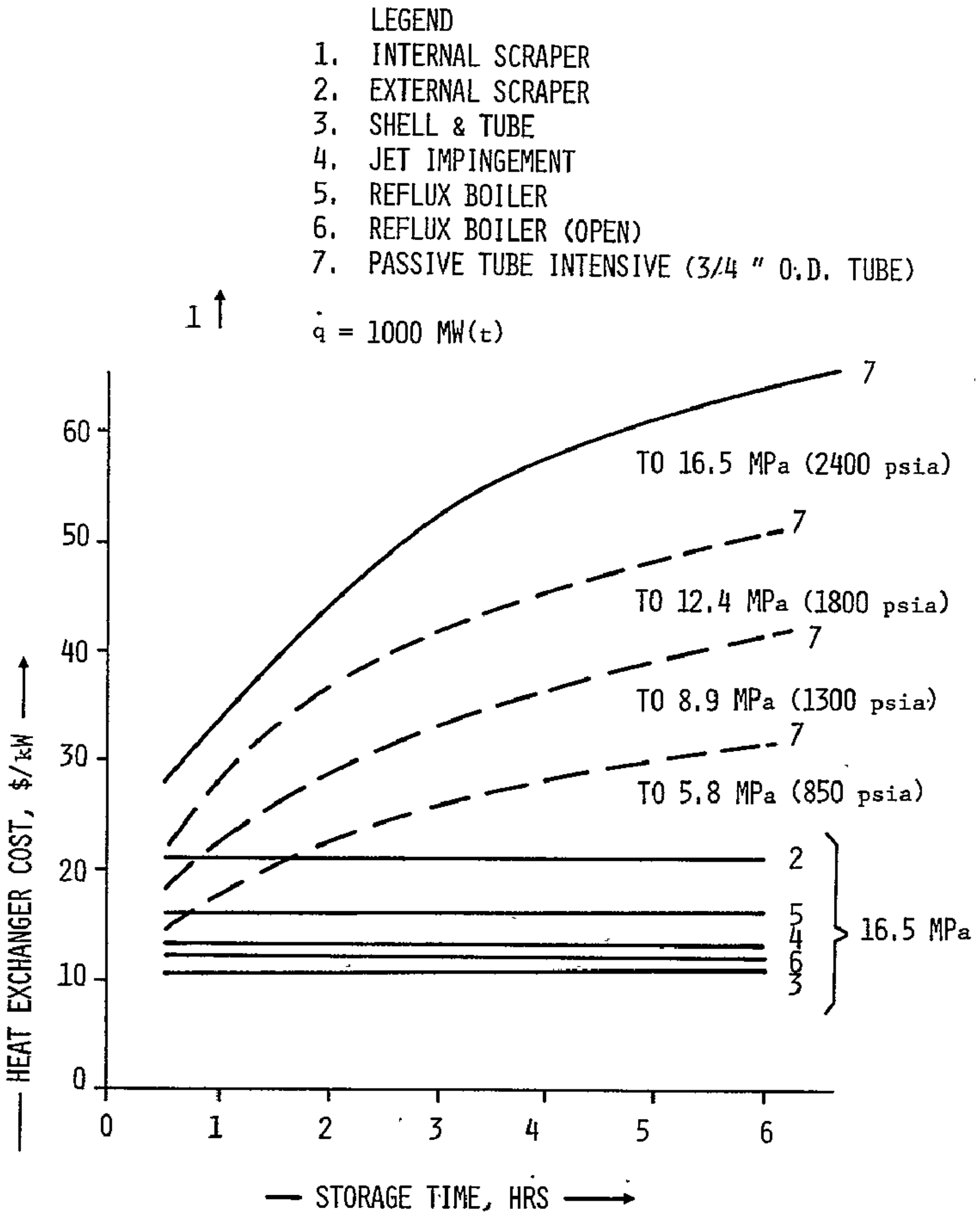


Figure A-10. Rate-Related Cost (Heat Exchanger) versus Storage Time and System Pressure

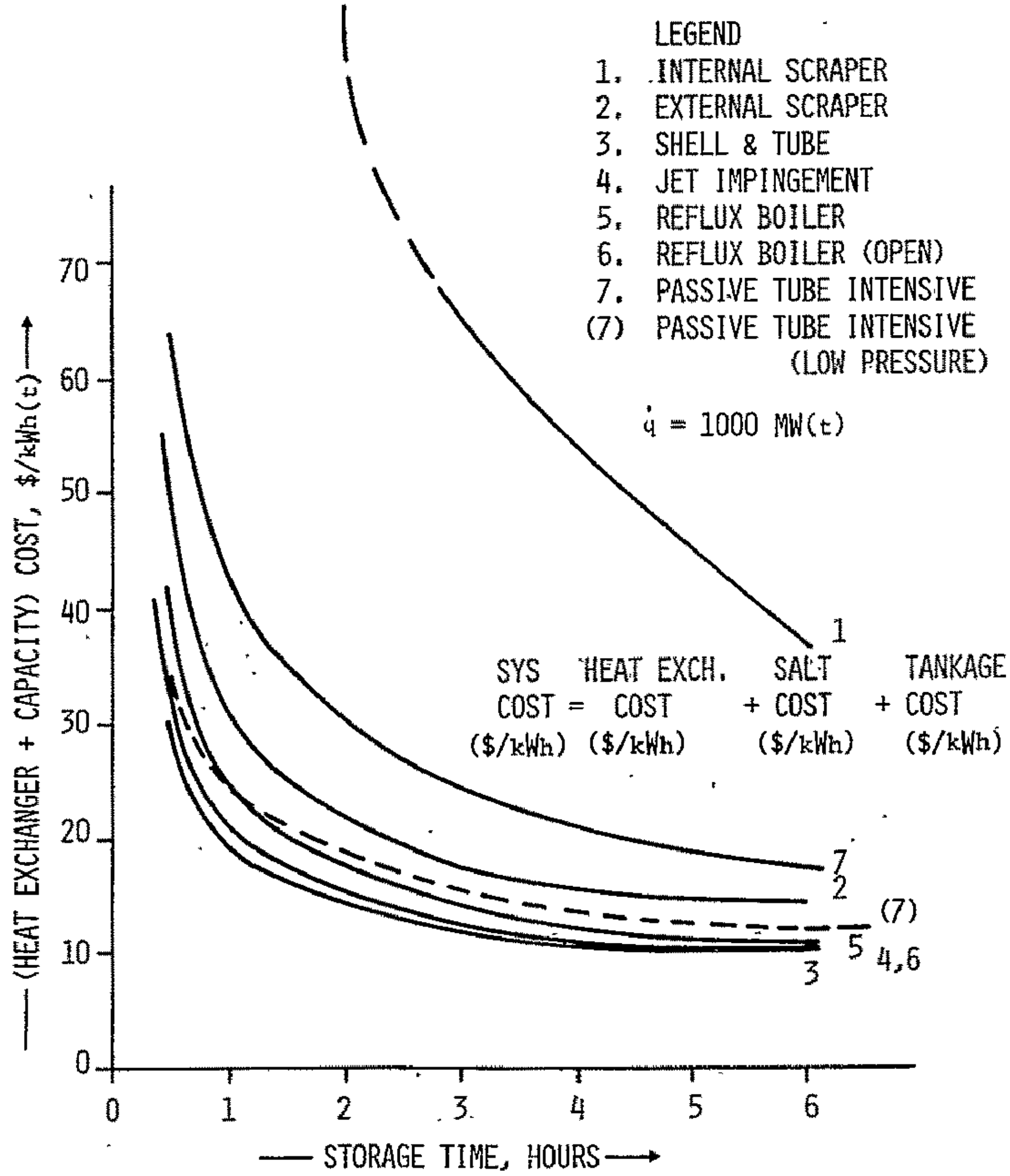


Figure A-11. Total Cost versus Storage Time increase in storage time for a given heat rate, the capital cost in \$/kWh(t) decreases with time for all concepts because of increased utilization of the rate-related equipment. The dotted curve in Figure A-11 is for the low pressure tube-intensive system. Therefore, the tube-intensive system becomes more attractive at low pressures and temperatures. Decreasing the heat rate for the same storage time will only have a scaling effect on both capacity and rate-related costs.

TABLE B-1. MIXTURES OF THE MORE COMMON SALTS

System No.	Mixture	Eutectic	
	A B	Composition (mol % of A)	mpt. (°C)
1	$CdCl_2$-$ZnCl_2$	1LT	262 APP
2	LiCl-LiOH	37	262
3	CsCl-$ZnCl_2$	42.5	263
4	CuCl-$FeCl_3$	39.6	263
5	Na_2CO_3-Na_2O-NaOH	6.5-7.4-86.1	263
6	KI-NaCNS	17.9	263.6
7	AgBr-KI	80.3	264
8	AgCl-AgI	53.5	264
9	$HgCl_2$-NaCl	86	264
10	KI-LiCl-LiI	Work in progress	264 APP
11	$Ca(NO_3)_2$-LiCl	40.85	265
12	KI-LiBr-LiI	Work in progress	265
13	$MnCl_2$-$ZnCl_2$	2	266
14	$CdCl_2$-NH_4Cl	53	267
15	KNO_3-$Sr(NO_3)_2$	63.1	267
16	KNO_3-$Sr(NO_3)_2$	71.9	267
17	LiCl-NH_4Cl	50	267
18	CsCl-$ZnCl_2$	20.1	268
19	LiCl-LiOH	42	268
20	KCl-$PbCl_2$-PbI_2	31.2-27.8-40.9	270
21	NaCl-$ZnCl_2$	42	270
22	$MgCl_2$-$ZnCl_2$	1	271
23	KNO_3-$Sr(NO_3)_2$	85.6	271.7
24	$CsNO_3$-$Sr(NO_3)_2$	76.9	272
25	LiCl-LiOH	34.5	274
26	$NaNO_3$-$Pb(NO_3)_2$	84.5	274.2
27	$CsNO_3$-$Sr(NO_3)_2$	75	275
28	KNO_3-$Sr(NO_3)_2$	85	275
29	LiBr-LiOH	55	275
30	AgBr-$PbBr_2$	54	276
31	AgBr-$PbBr_2$	Composition not reported	276
32	$CdCl_2$-CdI_2-PbI_2	33-13-54	276
33	$CdBr_2$-KBr-$PbBr_2$	24-52-24	277
34	KCl-LiCl-$PbCrO_4$	36.3-50-13.6	277
35	$HgCl_2$-LiCl	98.4	278
36	KBr-LiBr-$PbBr_2$	43-40.7-16.3	278
37	KCl-KI-PbI_2	4.8-33.2-61.9	278
38	NaCl-$NaNO_3$-Na_2SO_4	8.4-86.3-5.3	278
39	$Ba(NO_3)_2$-NaCl-$NaNO_3$	5.8-7.9-86.2	280
40	$CdBr_2$-KBr-$PbBr_2$	17-11-72	280
41	$CdBr_2$-NaBr-$PbBr_2$	13-25-62	280
42	CuCl-$PbCl_2$	59.1	260

APP = Approximate

APPENDIX B

TES SALTS

TABLE B-1. MIXTURES OF THE MORE COMMON SALTS (CONTINUED)

System No.	Mixture A B	Eutectic Composition (mol % of A)	 mpt ($^\circ$C)
43	$KCl-LiCl-LiOH$	11.5-45.0-43.5	280
44	$NaOH-Na_2S$	95.7	280
45	$NaCl-NaNO_2$	1.1	281
46	$KI-LiCl-LiF$	Work in progress	281 APP
47	$HgCl_2-PbCl_2$	100 NEAR	281 NEAR
48	$KBr-LiBr-PbBr_2$	43.6-30.8-25.6	282
49	$NaCl-Na_2CO_3-NaOH$	7.8-6.4-85.8	282
50	$PbBr_2-ZnBr_2$	60	282
51	$CuCl-ZnCl_2$	12	283
52	$KCl-LiCl-LiOH$	1.5-36.5-62.0	283
53	Na_2CO_3-NaOH	7.2	283±1
54	$CuCl-CuI$	57	284
55	$KBr-NaCNS$	9.1	284.6
56	$AgBr-KBr$	68	285
57	$CdI_2-NaCl-NaI$	36.2-36.2-27.5	285
58	KNO_3-NaNO_2	45.5	285
59	$LiCl-Li_2SO_4-ZnCl_2$	23-0.44-76.5	285
60	$AgBr-KBr$	69	286
61	$AgCl-CdCl_2-PbCl_2$	39.7-23.7-36.6	286
62	$LiBr-NaCNS$	8.7	286.8
63	$Ba(NO_3)_2-KNO_3$	12.7	287
64	$Ba(NO_3)_2-KNO_3$	12.4	287
65	$Ba(NO_3)_2-KNO_3$	12.5	287
66	$Ba(NO_3)_2-KNO_3$	13.3	287
67	$NaCNS-NaI$	83.7	287.5
68	$KBr-LiBr-PbBr_2$	15-18.3-66.6	289
69	$AgBr-KBr$	51	290
70	$AgCl-Ag_2SO_4-Li_2SO_4$	Not reported	290
71	$NaCl-Na_2CO_3-NaOH$	6-6.6-87.3	291
72	$CdBr_2-KBr-NaBr$	35-52-13	292
73	$Li_2SO_4-ZnCl_2-ZnSO_4$	0.7-90.3-9.0	293
74	$NaCl-Na_2SO_4-NaCNS$	4.2-1.0-94.8	293
75	$NaOH-Na_2SO_4$	95.3	293
76	$NaNO_3-Sr(NO_3)_2$	93.6	293.4
77	$CsCl-NaCNS$	5.3	293.6
78	$Ba(NO_3)_2-NaNO_3$	6.4	294
79	$LiCl-NaCNS$	6	294
80	$LiCl-ZnCl_2$	23	294
81	$KCl-NaCNS$	5.2	294.1
82	$NaNO_3-Sr(NO_3)_2$	93	294.9
83	$Ba(NO_3)_2-NaNO_3$	5.8	295
84	$CdCl_2-PbCl_2-PbI_2$	31.5-37-31.5	295
85	$KCl-ZnSO_4$	66.6	295

TABLE B-1. MIXTURES OF THE MORE COMMON SALTS (CONTINUED)

System No.	Mixture A B	Eutectic Composition (mol % of A)	Eutectic mpt. (°C)
86	$KF-NaF-KNO_3$	7-2.5-90.5	295
87	$K_2S_2O_7-V_2O_5$	92	295
88	$NaI-PbBr_2$	22.2	295
89	$NaI-NaNO_3$	14	296
90	NaBr-NaCNS	9.4	296.1
91	$CdBr_2-KBr$	36	297
92	$CdBr_2-KBr-PbBr_2$	38-31-31	297
93	CsCl-LiCl-LiF	38-59.5-2.5	297
94	$NaCl-NaNO_3$	6.5	297
95	$FeCl_2-FeCl_3$	13.5	297.5
96	$Ba(NO_3)_2-NaNO_3$	6.4	298
97	$CdCl_2-CdF_2-NaF$	46.3-9.3-44.4	298
98	$CdCl_2-TlCl$	29.5	298
99	$CsCl-LiCl-SrCl_2$	39.8-58.2-2.0	298
100	$KBr-PbI_2$	47.3	298
101	$KCl-KClO_3-KNO_3$	6.9-18.6-74.5	298
102	$KF-KNO_3$	9	298
103	$NaCl-NaNO_3$	5	298
104	$CdCl_2-NaF$	55 APP	298±5
105	$CdBr_2-KBr$	37	299
106	$CdBr_2-KBr$	37	300
107	$CdCl_2-ZnCl_2$	8	300
108	KBr-KOH	25	300
109	$NaNO_3-Na_2SO_4$	95.5	300
110	$ZnCl_2-ZnSO_4$	90	300
111	NaCl-NaCNS	6	300.3
112	NaCl-NaCNS	4.8	302
113	$KBr-K_2CrO_4-LiBr$	15.3-8.9-75.8	303
114	$AgCl-Ag_2SO_4$	69.3	304
115	$CdBr_2-KBr$	38	304
116	$CdSO_4-TlCl-Tl_2SO_4$	19.7-72.6-7.6	304
117	$KBr-NaBr-PbBr_2$	7.9-16.7-75.4	304
118	$NaBF_4-NaF$	92	384
119	$NaF-NaNO_3$	3.5	304
120	$CdBr_2-KBr$	37	305
121	$CuCl_2-FeCl_2$	48.5	305
122	AgCl-KCl	70	306
123	CsCl-LiCl	40.5	306
124	$KBr-PbI_2$	27.6	306
125	$PbCl_2-PbI_2$	24	306
126	LiF-NaCNS	0.6	306.5
127	$CsCl-PbI_2$	23.2	307
128	$KBr-LiCl-PbBr_2$	13.7-14.6-71.7	308
129	$KI-PbBr_2$	44.9	309

TABLE B-1. MIXTURES OF THE MORE COMMON SALTS (CONCLUDED)

System No.	Mixture A B	Eutectic	
		Composition (mol % of A)	mpt (°C)
130	K_2CO_3-KOH-LiOH	3.1-30.9-66	309
131	AgCl-$PbCl_2$	Composition not reported	310
132	KBr-KCl-LiBr-LiCl	28.5-9.5-46.5-15.5	310
133	KBr-KCl-LiBr-LiCl-NaBr-NaCl	29.7-5.2-49.3-8.7-5.9-1	310
134	KCl-K_2CrO_4-KNO_3	2.7-1-96.3	310
135	Li_2SO_4-$ZnCl_2$	1	310
136	AgCl-$PbCl_2$	61.5	311.5
137	$CoCl_2$-$ZnCl_2$	7.3	311-313
138	AgCl-$PbCl_2$	60.02	314
139	CsCl-LiCl	42.5	314
140	CuCl-NaCl	74	314
141	CuCl-NaCl	75	314
142	CuCl-NaCl	73	314
143	KBr-KCl-LiBr-LiCl	21.3-37.7-34.8-6.1	314
144	KBr-LiCl-$PbBr_2$	42.6-24.33.3	314
145	AgCl-KCl-KNO_3	0.39-5.61-94.0	315
146	$Cs_2Cr_2O_7$-$Na_2Cr_2O_7$	21	315
147	$SnCl_2$-TlCl	24	315
148	AgBr-KCl	76	315
149	$CdSO_4$-TlCl	52.7	316
150	CuCl-NaCl	75	316
151	KBr-LiCl-$PbBr_2$	45.4-31.9-22.7	316
152	AgCl-KCl	70	318
153	CsCl-$PbBr_2$	12.2	318
154	Li_2CrO_4-LiOH	29	318
155	AgCl-KCl	70	319
156	$Ca(NO_3)_2$-K_2CrO_4-KNO_3	0.13-0.7-99.18	319
157	$BaCl_2$-KCl-LiCl	6.38-39.36-54.26	320
158	$BaCl_2$-KCl-LiCl	5.43-40.92-53.65	320
159	$CaCl_2$-$LiNO_3$	40.3	320
160	$CdCl_2$-KCl-$PbCl_2$	43-22-34.8 APP	320
161	$CdCl_2$-KCl-$PbCl_2$	42.5-19-38.5	320
162	$CuCl_2$-KCl	38	320
163	KBr-KNO_3	9.5	320
164	KCl-KNO_3	6	320
165	KCl-LiBr-NaBr	38-55-7	320
166	KCl-LiCl-$PbCl_2$	39.2-33.6-27.1	320
167	KI-$PbBr_2$	13.1	320
168	AgCl-KBr	75	320
169	$CdCl_2$-LiCl-$PbCl_2$	31.4-18.2-50.5	321
170	KCl-LiCl-$PbCl_2$	43.2-42.6-14.2	321
171	KI-PbI_2	31.9	321

TABLE B-2. ADDITIONAL MIXTURES

System No.	Mixture	Eutectic	
	A B	Composition (mol % of A)	mpt. (°C)
1	$CsBr-LiBr$	37.5	262
2	$Ba(NO_2)_2-TlNO_2$	97	263
3	$HgCl_2-InCl_3$	98	265
4	$KCl-LiCl-RbCl$	Work in progress	265 APP
5	$Ba(NO_2)_2-KNO_2$	93.2	266
6	$AlBr_3-RbBr$	48	267
7	$Ca(NO_3)_2-CsNO_2$	63.5	267
8	$KBr-LiBr-RbBr$	9-57-34	268
9	$Ca(ClO_4)_2-NaClO_4$	55	270
10	$CdCl_2-TlI$	27.0	270
11	$NaCl-TaCl_4$	55	270
12	$NaBeF_3-NaPO_3$	60	270 APP
13	$InCl_3-NaCl$	49	272
14	$CsCl-TaCl_3$	54	273
15	$LiBr-RbBr$	55	273
16	$CsCl-WCl_5$	2 APP	275
17	$InCl_3-ZnCl_2$	4	276
18	$TaCl_5-TlCl$	36	276
19	$RbCl-ZnCl_2$	37	277
20	$CsI-PbCl_2-PbI_2$	23.8-28.6-47.6	278
21	$KF-SnF_2$	45	278
22	$NaCNS-RbI$	88.5	279.2
23	$KF-SnF_2$	56	280
24	$NaNO_3-TlCl$	91	281
25	$CsCl-NbCl_4$	43 APP	282
26	$CdBr_2-NaBr-TlBr$	25-2.5-72.5	284
27	$CsNO_2-Sr(NO_2)_2$	40 APP	284
28	$RbCl-TaCl_4$	53 APP	284 APP
29	$NaCNS-RbBr$	91.3	284.9
30	$CdCl_2-CsCl-TlBr$	26.6-7.6-65.8	285
31	$CsNO_3-RbNO_3$	14	285
32	$CsCl-ZrCl_4$	32.8	286
33	$CsBr-NaCNS$	7.9	286.3
34	$CdBr_2-TlCl$	23.8	288
35	$CsBr-NaBr-PbBr_2$	7.9-15.8-76.2	289
36	$Ca(NO_2)_2-RbNO_2$	56.2	290
37	$CdCl_2-CdSO_4-TlCl$	16-7.4-76.5	290
38	$CdCl_2-CsCl-TlCl$	21.2-3.6-75.1	290
39	$CdCl_2-NaCl-TlCl$	22-4-74	290
40	$CdCl_2-TlCl$	22.7	290
41	$GaCl_3-TlCl$	32	290
42	$KCl-NbCl_5-ZrCl_4$	51-47-2	290

TABLE B-2. ADDITIONAL MIXTURES
(CONTINUED)

System No.	Mixture A B	Eutectic	
		Composition (mol % of A)	mpt. (^{0}C)
43	$CsNO_3$-$RbNO_3$	15 APP	290 APP
44	KNO_3-$RbNO_3$	30	30
45	$BeCl_2$-$PbCl_2$	53	292
46	$CdBr_2$-CsCl-TlBr	27.4-10.2-62.4	292
47	Cs_2CO_3-CsOH	10.3	292
48	InCl -TlCl	50	292
49	NaCNS-RbCl	94.4	293.4
50	$CdBr_2$-KBr-TlBr	28.2-24.3-47.4	295
51	$CdBr_2$-$PbBr_2$-TlBr	16-29.9-54	295
52	$CdCl_2$-TlBr	25.8	296
53	$CdBr_2$-$PbBr_2$-TlBr	17.6-72.8-9.5	298
54	KCl-$NbCl_4$	40 APP	298
55	$BeCl_2$-LiCl	56	300
56	$CdCl_2$-TlCl	27	300
57	CdI_2-TlCl	33.3	300
58	$FeCl_3$-$ZrCl_4$	85.18	300
59	$KBeF_3$-KPO_3	80 APP	300
60	KCl-UCl_4	57	300
61	RbCl-$TaCl_3$	55 GT	300
62	Rb_2SO_4-$RbNO_3$	1.5	300
63	$KBeF_3$-KPO_3	80	300 AP
64	$CdCl_2$-CdF_2-NaF	49.4-3.8-46.7	301
65	$CdBr_2$-$PbBr_2$-TlBr	27.4-43.6-29	302
66	CsCl-$HfCl_4$	34.9	302
67	$CdBr_2$-$PbBr_2$-TlBr	20.3-19.6-60.1	303
68	$Na_2Cr_2O_7$- $Rb_2Cr_2O_7$	78	69
69	KF-SnF_2	77	305
70	KNO_3-TlCl	88.9	305.5
71	$BeCl_2$-BeF_2	27.5	306
72	KOH-RbOH	65.6	306
73	CsBr-KBr-$PbBr_2$	11-4.6-84.3	307
74	KBF_3OH-KBF_4	91.5	307
75	NaI-PbI_2-TlI	9.1-65.3-25.6	307
76	CdBr -CsBr-TlBr	31.6-9.2-59.2	308
77	KF-SnF_2	92	309
78	NaBr-$PbBr_2$-TlBr	14-80-6	309
79	$Ba(ClO_4)_2$-$NaClO_4$	43	310
80	$BeCl_2$-TlCl	55	310
81	$CdBr_2$-TlBr	25	310
82	$BeCl_2$-LiCl	51 APP	310 APP
83	NaCl-$ZrCl_4$	35.4	311
84	$CsAlCl_4$-CsCl- Cs_2NbOCl_5	75-10-15	312
85	CsCl-$LiBO_2$-LiCl	43.5-0.5-56	312

TABLE B-2. ADDITIONAL MIXTURES (CONCLUDED)

System No.	Mixture	Eutectic	
	A B	Composition (mol % of A)	mpt. (°C)
86	$CsI-PbCl_2-PbI_2$	18.2-61.4-20.4	312
87	$FeCl_3-InCl_3$	3	312
88	$Ba(ClO_4)_2-NaClO_4$	40	313
89	$CdBr_2-TlBr$	25	313
90	$Ba(ClO_4)_2-Ca(ClO_4)_2$	43	314
91	$KNO_3-K_2WO_4$	94.2	314
92	$NaCl-NaOH$	6.3	314
93	$NaCl-ZrCl_4$	37.6	314
94	$CdBr_2-CsI$	45.5	315
95	$AlCl_3-RbCl$	46 APP	315 APP
96	$CdBr_2-CsCl-TlBr$	21.9-32.9-45.1	316
97	$InCl_3-KCl$	47.5	316
98	$InCl_3-NaCl$	78	316
99	$TlCl-TlI$	52.5	316
100	$Na_2Cr_2O_7-Rb_2-Cr_2O_7$	25	317
101	$LiCl-RbCl$	58.3	318
102	$BeF_2-NaF-ThF_4$	43-55-2	320
103	$Ca(NO_2)_2-CsNO_3$	84	320
104	$CdBr_2-CsBr_2-NaBr$	53.8-20-26.1	320
105	$CdBr_2-RbBr$	40	320
106	$CsAlCl_4-Cs_2NbOCl_5$	79.5	320

TABLE B-3. SINGLE SALTS MELTING BETWEEN 250 AND 400° C

	MELTING POINT °C	COMMENTS	ACCEPTABLE?*
Chlorides			
$ZnCl_2$	283	Fumes hazardous; caustic.	yes
$FeCl_3$	300	d 319° C: produces highly toxic HCl fumes; reacts with H_2O to produce corrosive & toxic fumes.	no
Oxides			
SeO_2	330	Sublimes at 322° C; Se is close to As in toxicity.	no
Sulfides			
P_4S_7	307	Sulfides are highly toxic.	no
P_4S_{10}	283		no
Nitrates			
$LiNO_3$	254	Both nitrates and nitrites are dangerous due to fire and explosion hazards. They are powerful oxidizing agents.	yes
$NaNO_3$	310		"
KNO_3	337		"
$RbNO_3$	316		"
Nitrites			
$NaNO_2$	271		yes

*Salts marked "YES" are acceptable for commercial thermal storage application with proper design.

TABLE B-3. SINGLE SALTS MELTING BETWEEN 250 AND 400° C (CONCLUDED)

Chlorates			
$NaClO_3$	255	Fire hazards; may form explosive mixtures. Health hazards.	no
$Ca(ClO_3)_2$	340		no
Hydroxides			
NaOH	318	Caustic; highly corrosive. Rapidly reacts with H_2O or CO_2 to produce caustic solution and heat.	yes
KOH	360		"
RbOH	301		"
CsOh	272		"
Chromates			
$Na_2Cr_2O_7$	356	Highly toxic and corrosive.	no
Amines			
KNH_2	330	Toxicity comparable to ammonia; reacts with oxidizing materials. Disaster hazard.	no
$CsNH_2$	262		no
Formates			
NaOOCH	300	When heated, emits acrid fumes which may be health hazard.	no
CsOOCH	295		no
Acetates			
$LiCH_3CO_2$	280	When heated, emits acrid fumes which may be health hazard.	no
KCH_3CO_2	295		no

TABLE B-4. BINARY SYSTEMS OF SALTS

MAJOR COMPONENT (MELTING POINT)	MINOR COMPONENT	EUTECTIC MELTING POINT °C	COMMENT* (REF.)	ACCEPTABLE PHASE DIAGRAM
$ZnCl_2$ (283°C)	$CdCl_2$	262	2(a)	No
	$CdCl_2$	300	1	No
	CsCl	263	2(a)	No
	CsCl	268	3(a)	Yes
	$MnCl_2$	266	2(a)	No
	NaCl	270	2	No
	$MgCl_2$	271	2(a)	No
	CnCl	283	1	No
	LiCl	294	1	No
	Zn_2SO_4	300	1	No
	Li_2SO_4	310	1	No
	$COCl_2$	311	1	No
	AgCl	248	3(a)	Yes
	$CaCl_2$	270	2(a)	No
	KCl	262	3(a)	yes
	RbCl	277	1	No
	TlCl	210	2(a)	No
$LiNO_3$ (254°C)	$CaCl_2$	320	1	No
	$Ba(NO_3)_2$	250	1	No
	$Ca(NO_3)_2$	234	3(a)	yes
	Li_2SO_4	250	1	No
	$NaNO_3$	196	3(b)	Yes
	KNO_3	120	3(b)	Yes
$NaNO_3$ (310°C)	NI	296	2	No
	NaCl	296	2	No
	NaCl	298	2	No
	Na_2SO_4	300	2(a)	No
	NaF	304	1	No
	$Sr(NO_3)_2$	293	3(b)	Yes
	$Sr(NO_3)_2$	295	2(b)	No
	$Ba(NO_3)_2$	295	2	No

Salts marked "YES" are acceptable from the standpoint of phase diagram relationships.

*See end of table.

TABLE B-4. BINARY SYSTEMS OF SALTS (CONTINUED)

MAJOR COMPONENT (MELTING POINT)	MINOR COMPONENT	EUTECTIC MELTING POINT °C	COMMENT (REF.)	ACCEPTABLE PHASE DIAGRAM
	$Ba(NO_3)_2$	298	2	No
	NaOH	243	3(a)	yes
	$Ca(NO_3)_2$	232	3(a)	yes
	KNO_3	222	2(a)	No
	KOH	222	3(a)	Yes
	NH_4NO_3	121	3(a)	Yes
	$TlNO_3$	162	3(a)	Yes
	$NaNO_2$	226	2(a)	No
	Na_2CO_3	300	2(a)	No
	$LiNO_3$	196	3(b)	Yes
$NaNO_2$ (282°C)	NaCl	281	1	No
	KNO_3	285	1	No
	NaOH	232	3(a)	Yes
	$Ca(NO_3)_2$	172	3(a)	Yes
	KNO_2	230	2(a)	No
	KNO_3	150	2(a)	No
	KOH	212	3(a)	Yes
KNO_3 (337°C)	KF	298	3(b)	Yes
	KBr	320	2(b)	No
	KCl	320	3(b)	Yes
	$Sr(NO_3)_2$	267	2(b)	No
	$Sr(NO_3)_2$	275	3(b)	Yes
	$Ba(NO_3)_2$	287	3(a)	Yes
	$Ca(NO_3)_2$	174	3(a)	Yes
	$NaNO_3$	222	2(a)	No
	$AgNO_3$	130	3(a)	Yes
	K_2CO_3	330	1	No
	KNO_2	320	2(a)	No
	KOH	214	2(a)	No
	K_2SO_4	330	1	No

TABLE B-4. BINARY SYSTEMS OF SALTS (CONCLUDED)

MAJOR COMPONENT (MELTING POINT)	MINOR COMPONENT	EUTECTIC MELTING POINT °C	COMMENT (REF.)	ACCEPTABLE PHASE DIAGRAM
	$NaNO_2$	150	2(a)	No
	$NaNO_3$	222	2(a)	No
	NaOH	270	2(a)	No
	$TlNO_3$	182	2(a)	No
	$LiNO_3$	120	3(b)	Yes
KOH (360°C)	KB4	300	2(a)	No
	K_2CrO_4	361	1	No
	KI	250	3(a)	Yes
	$NaNO_2$	236	3(a)	Yes
	$NaNO_3$	196	3(a)	Yes
	NaOH	170	2(a)	No
	LiOH	220	2(b)	No
NaOH (318°C)	Na_2S	280	2	No
	Na_2CO_3	283	3(b)	Yes
	Na_2SO_4	293	3(b)	Yes
	KNO_2	300	3(a)	Yes
	KNO_3	270	2(a)	No
	KOH	170	2(a)	No
	LiOH	210	2(a)	No
	NaBr	265	3(a)	Yes
	NaCl	350	2(a)	No
	NaI	215	3(a)	Yes

Comment Code:
1) Eutectic m.pt. greater than or too close to that of major component.
2) Forms solid solutions; does not meet dilute eutectic criterion or phase diagram not known.
3) Simple eutectic system - meets dilute eutectic criterion.

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1 Report No NASA CR 159479	2 Government Accession No.	3 Recipient's Catalog No.

4 Title and Subtitle

Active Heat Exchange System Development for
Latent Heat Thermal Energy Storage

5 Report Date
February 1979

6. Performing Organization Code

7 Author(s)

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8 Performing Organization Report No.
HI 78336

10. Work Unit No.

9. Performing Organization Name and Address

Honeywell Inc.
Energy Resources Center
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Minneapolis MN 55413

11. Contract or Grant No.
DEN 3-38

13. Type of Report and Period Covered
Contractor Report

12 Sponsoring Agency Name and Address

U.S. Department of Energy
Division of Energy Storage
Washington, D.C. 20545

14 Sponsoring Agency ~~Code~~ Report No.
DOE/NASA/0038-79/1

15. Supplementary Notes

Topical Report. Prepared under Interagency Agreement EC-77-A-31-1034. Project Manager, James E. Calogeras, Power Generation and Storage Division, NASA Lewis Research Center, Cleveland, Ohio 44135

16 Abstract

This topical report describes active heat exchange concepts for use with thermal energy storage systems in the temperature range of 250°C - 350°C, using the heat of fusion of molten salts for storing thermal energy. It identifies over 25 novel techniques for active heat exchange thermal energy storage systems. Salt mixtures that freeze and melt in appropriate ranges are identified and are evaluated for physico-chemical, economic, corrosive and safety characteristics. Eight active heat exchange concepts for heat transfer during solidification are conceived and conceptually designed for use with selected storage media. The concepts are analyzed for their scalability, maintenance, safety, technological development and costs.

A model for estimating and scaling storage system costs is developed and is used for economic evaluation of salt mixtures and heat exchange concepts for a large scale application. The importance of comparing salts and heat exchange concepts on a total system cost basis, rather than the component cost basis alone, is pointed out. Comparison of these costs with current state-of-the-art systems should be avoided due to significant differences in developmental status. The heat exchange concepts were sized and compared for 6.5 MPa/281°C steam conditions and a 1000 MW(t) heat rate for six hours. A cost sensitivity analysis for other design conditions is also carried out.

The study resulted in the selection of a shell and coated-tube heat exchange concept and a direct contact-reflux boiler heat exchange concept. For the storage medium, a dilute eutectic mixture of 99 wt% $NaNO_3$ and 1 wt% NaOH is selected for use in experimenting with the selected heat exchanger concepts in subsequent tasks.

17. Key Words (Suggested by Author(s)) Energy Storage Active Heat Exchange Crystallization Process	18. Distribution Statement Unclassified - unlimited STAR Category 44 DOE Category UC-94a

19 Security Classif. (of this report) Unclassified	20 Security Classif (of this page) Unclassified	21. No of Pages 122	22. Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22161

U.S. GPO 1979-658-699